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Carolyn Johnson for the M.A. in Chemistry
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(Major Professor)

A method for recovering platinum from solutions by use of a mercury, mercurous chloride collector has been developed. The recovery of platinum from solutions containing as little as 0.00067 gm. in two liters averaged ninety one percent.

A mercury, mercuric amino nitrate collector was also applied to such solutions and has been found to be equally efficient in the recovery of platinum and more efficient in the recovery of silver.

Either type of collector could be used as a roughly quantitative method for the determination of small quantities of platinum from large volumes of solution.

A series of experiments were also carried out in order to devise some method for determining the weight of gold beads other than by direct weighing. Gooch and Morley's iodometric titration of auric chloride solutions was applied with modifications to gold beads. Accuracy within 0.2 mg. was obtained.

A method for detecting alkyl sulfides in the atmosphere was devised. The alkyl sulfide was adsorbed on activated charcoal. The charcoal with the adsorbed organic sulfide was then heated with metallic sodium; thus converting the alkyl sulfide to sodium sulfide which gives a characteristic pink to violet color with sodium nitroprusside.

THE DETERMINATION AND RECOVERY OF THE PLATINUM METALS FROM DILUTE SOLUTION

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CAROLYN ETMO JOHNSON

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APPROVED:

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Professor of Chemistry

In Charge of Major

Redacted for privacy

Head of Department of Chemistry

Redacted for privacy

Chairman of School Graduate Committee

Redacted for privacy

Chairman of State College Graduate Council

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PART I

THE DETERMINATION AND RECOVERY OF THE PLATINUM METALS FROM DILUTE SOLUTION

THE DETERMINATION AND RECOVERY OF THE PLATINUM METALS FROM DILUTE SOLUTION

Introduction

Because of the comparative rarity and the increasing demand for platinum, it is often considered economically feasible to recover minute quantities of this metal.

There has long been a need for a method of determining small amounts of platinum in solution. If some practical method could be devised it might be possible to enlarge upon such a method for an economical recovery of the metal.

Caldwell and McLeod (1) in their improvement of the method of Yasuda Mataichi (4) used a mercury, mercurous chloride collector to recover quantitatively minute amounts of gold from large volumes of solution. They also used a collector prepared by reacting ammonium hydroxide with mercurous nitrate, obtaining a mixture of finely divided mercury and mercury amino nitrate. Both methods were equally successful. Pierson (3) used mercurous chloride to determine colorimetrically minute amounts of the precipitate according to the metal brought down and to its concentration in the solution.

In the first procedure of Caldwell and McLeod the collector is prepared by adding mercuric chloride to a

gold and silver solution. This is followed by the addition of magnesium powder and hydrochloric acid. The molecular hydrogen which is produced by the action of magnesium on hydrochloric acid reduces the gold and silver to the metallic state and the mercuric chloride to a mixture of mercury and mercurous chloride. As this precipitate falls through the solution it collects the gold and silver by adsorption and also by amalgamation. After the residue is allowed to settle the greater part of the liquid is siphoned off and the residue is obtained by filtration of the remaining material. This residue is then mixed with granular lead and cupelled in an assay furnace to get a bead of gold and silver. The bead is then weighed and the gold and silver are separated by dissolving the silver in nitric acid. The residual gold is annealed and weighed and the weight of silver is obtained by difference.

The method using the mercury, mercuric amino nitrate as collector was essentially the same as the above method except the addition of magnesium, hydrochloric acid, and mercuric chloride was replaced by the addition of ammonium hydroxide and mercurous nitrate.

Since mercury will replace any of the metals below it in the electromotive series it was desirable to apply this method to large volumes of solution containing small

amounts of platinum.

Preliminary Experiments to Recover Platinum from Dilute Solutions.

Small particles of platinum, obtained from platinum wires, were weighed on an assay balance, placed in small porcelain crucibles and dissolved in aqua regia. Since platinum is very difficult to put into solution, prolonged heating was necessary. The resulting solutions of platinic chloride or chloroplatinic acid were then carefully transferred to two liter bottles and measured amounts of silver nitrate solution known to contain one milligram of silver per cc. was added. The resulting mixture was then made up to two liters by the addition of tap water. Collectors were prepared in each solution according to the method of Caldwell and McLeod (1). Runs were made using both the mercury, mercurous chloride collector and the mercury, mercuric amino nitrate collector in order to compare the efficiency of the two in collecting such small amounts of platinum from large volumes of solutions. After the precipitates had settled, most of the supernatant liquid was then decanted from each precipitate and each residue was obtained by filtration of the remaining liquid. After drying, the precipitates were mixed with granular lead on bone-ash cupels and cupellation was carried out in an

assay furnace. The resulting beads of silver and platinum were weighed, placed in small crucibles and the silver dissolved out with sulfuric acid; the resulting platinum was then weighed.

The results obtained were very promising. Although the percent recovery varied considerably, an average of 77% recovery was obtained in these first runs with both the mercury, mercurous chloride collector and the mercury, mercuric amino chloride collector. The latter collector seemed to be more efficient in the recovery of silver. The results obtained in this first set of experiments are shown in Table I.

Development of Method

The problem, therefore, was to see whether more consistent and better recovery could be accomplished. Since the results obtained by using the procedure outlined by Caldwell and McLeod (1) were so encouraging, it was thought that some slight changes in the procedure should increase the percentage recovery of platinum.

To make certain that the separation of silver from platinum was not involving some loss of platinum, test runs were made on this phase of the procedure. Several beads of weighed amounts of silver and platinum were made up by use of a blowpipe. The beads were then placed in

Table I

Hg, HgCl Method

Sample	Gm. Pt as H_2PtCl_6 added to 2 l. H_2O	Gm. Ag as $AgNO_3$ added	Gm. Pt recovered	Gm. Ag recovered	% recovery of Pt	% recovery of Ag
1.	0.00086	0.02000	0.00066	0.01540	77	77.0
2.	0.00141	0.030	0.00116	0.02381	82	79.3
3.	0.00093	0.030	0.00065	0.02381	70	79.3
4.	0.00146	0.030	0.00103	0.02999	71	99.9
5.	0.00075	0.030	0.00066	0.02540	88	83.4
			Hg $HgNH_2Cl$ Method			
1.	0.00398	0.040	0.00317	0.03421	79	85.5
2.	0.00080	0.020	0.00065	0.01905	81	95.0
3.	0.00123	0.020	0.00087	0.01960	70	95.0
4.	0.001139	0.020	0.00110	0.01803	85	90.0

small porcelain crucibles and slightly diluted sulfuric acid (9-1) was added. It is necessary to use sulfuric acid in separating platinum and silver as nitric acid will dissolve appreciable amounts of platinum. Highly concentrated sulfuric acid will also dissolve slight amounts of platinum. The crucibles containing the acid and the bead were heated until no further action between the residual mass and the acid occurred. (It is advisable to keep the temperature low enough to prevent the decomposition of sulfuric acid.) The resulting amorphous platinum was then carefully washed free of silver sulfate, dried on a hot plate and partly annealed by heating the crucible containing it to red heat. The platinum was then weighed on an assay balance.

Since the platinum recovered agreed within 0.02 milligrams of the amount originally in the platinum-silver bead, it was evident that this phase of the procedure was not the cause of the erratic results. (See Table II).

Cupellation losses are often encountered in any assay procedure. Consequently, it was thought advisable to refine this process as much as possible so as to eliminate losses which might occur in this step. To accomplish this the mercurial precipitate was subjected to a crucible fusion in order to have the metals intimately mixed with

Table II

Bead No.	Ag used	Mg. Pt. added	Mg. Pt recov.	% Pt rec.
1.	15.00	0.62	0.61	99
2.	15.00	0.65	0.65	100
3.	17.00	1.70	1.69	99
4.	16.00	1.21	1.19	99
5.	16.5	0.72	0.70	98

lead before the cupellation process.

Such a fusion is carried out by mixing the precipitate with sodium carbonate, litharge, silica, borax, and argols in a fire clay crucible and heating in an assay furnace. The argols and other reducing agents present in the mixture reduce the litharge to metallic lead. These minute particles of lead fall to the bottom and in doing so bring down all the noble metals. When the mixture is poured out into molds the lead button, containing the platinum and silver settles to the bottom and the other substances present form a glass-like slag on the top. This lead button is then cupelled and a bead of platinum and silver is left on the cupel as the lead in the form of lead oxide seeps into the cupel.

The recovery of platinum after this procedure more nearly approached the theoretical value.

It was found that if three separate collectors were allowed to settle through the solutions containing the platinum and silver, followed by the above assaying procedure, the percentage recovery was increased still more.

Suggested Procedure for Recovery of Platinum from Dilute Solutions.

The solutions containing minute quantities of platinum are placed in large bottles. (2-liter, 20-liter, or

40-liter bottles are suggested.) Silver is added in the form of silver nitrate until the amount of silver present in the solution is known to exceed ten times the amount of platinum present. If the volume of each platinum solution is about two liters the collectors are prepared as follows:

(a) To prepare the mercury, mercurous chloride collector 30cc. of 0.1M mercuric chloride is added followed by the addition of 3 gms. of magnesium and 40cc. of concentrated hydrochloric acid. The mercurial precipitate formed is allowed to settle for a period of about four hours and two more collectors are added in a similar manner.

(b) The mercury, mercuric amino chloride collector is prepared by adding 10cc. of 28% ammonium hydroxide and 15cc. of 10% mercurous nitrate. As in the case of the mercury, mercurous chloride collector the precipitate formed is allowed to settle and another collector is added. This whole procedure is repeated three times for best recovery.

After the third collector has been allowed to settle, all but 150cc. of the supernatant liquid is decanted off each precipitate and the precipitate itself obtained by filtering the remaining liquid. The residue is dried and mixed with 20 gms. of sodium carbonate, 20 gms. of silica, 25 gms. litharge, 3 gms. borax, and 2 gms. of argols in a fire clay crucible. After the mixture has been fused in

an assay furnace, the resulting lead buttons, which also contain the noble metals, are cupelled and silver and platinum beads are obtained. Each bead is then brushed free from any adhering bone-ash and weighed on an assay balance.

Separation of the silver from the platinum is carried out by treating each bead with sulfuric acid (9-1) in small porcelain crucibles. It is necessary to heat the crucibles containing the bead and acid until all action between the two has entirely ceased. The resulting amorphous platinum is then carefully washed free of silver sulfate, dried on a hot plate and partly annealed by heating the crucible up to red heat. The result is a greyish mass of platinum which is carefully transferred to the assay balance pan by use of a camel's hair brush and then weighed. The weight of the silver recovered is obtained by difference.

Discussion of Results

In examining the results of numerous runs (Table III) it was found that the platinum recovery averaged around 91%. Consequently, this method can be used to successfully recover minute amounts of platinum from solutions. Also, it can be used for a roughly quantitative method for determining the amount of platinum present.

In the recovery of platinum the mercury, mercurous chloride collector and the mercury, mercury amino nitrate collector are equally successful. The latter collector seems to be much more effective in the recovery of silver.

Solutions containing as little as 0.00059 gm. of platinum in two liters of solution were subjected to this method of recovery and, as seen in Table III, 0.00053 gm. was recovered. The loss of 0.00006 gram could easily be due to vaporization during cupellation, loss during parting, or some small error in technique.

Summary

1. A method for recovering platinum from solutions by use of mercury, mercurous chloride collector has been developed.

2. Mercury, mercuric amino nitrate collector has also been applied to such solutions and has been found to be equally efficient in the recovery of platinum and more efficient in the recovery of silver.

3. Either type of collector can be used as a roughly quantitative method for the determination of small quantities of platinum from large quantity of solution.

Table III

Hg, HgCl Method

Sample	Gm Pt as H_2PtCl_6 added to 2 l. H_2O	Gm Ag as $AgNO_3$ added	Gm Pt recovered	Gm Ag recovered	% recovery on Pt	% recovery of Ag
1.	0.00149	0.020	0.00130	0.014	87.2	70.0
2.	0.00150	0.025	0.00149	0.0173	99.5	69.9
3.	0.00064	0.025	0.00053	0.0173	82.8	69.9
4.	0.00214	0.025	0.00188	0.018	87.7	72.0
5.	0.00205	0.025	0.00205	0.020	100.0	80.0
6.	0.00209	0.025	0.00192	0.021	91.9	84.0
7.	0.00174	0.025	0.00164	0.020	94.2	80.0

Hg, $HgNH_2Cl$ Method

1.	0.00108	0.025	0.00092	0.024	85.0	96.0
2.	0.00059	0.025	0.00053	0.023	89.9	82.0
3.	0.00188	0.025	0.00169	0.024	89.9	96.0
4.	0.00269	0.050	0.00232	0.048	86.3	96.0
5.	0.00067	0.030	0.00065	0.255	97.0	85.0
6.	0.00262	0.030	0.00249	0.276	95.0	92.0
7.	0.00332	0.050	0.00284	0.471	85.6	94.0

PART II

A MICROTITRATION OF GOLD

A MICROTITRATION OF GOLD

Introduction

Gravimetric methods for the determination of minute quantities of gold require use of balances sensitive to 0.00001 gm. Since such balances are expensive and not usually found in the ordinary laboratory, a means of determining gold by some method other than that of direct weighing is often desirable.

Auric chloride liberates iodine from potassium iodide according to the reaction

$$AuCl_3 + 2KI \longrightarrow AuCl + 2KCl + I_2 .$$

Gooch and Morley (2) applied this reaction to the determination of the amount of gold in solutions of auric chloride. In their method of determination an excess of potassium iodide was added to an acidified sample of the auric chloride, a measured amount of standard sodium thiosulfate was then added, and the excess of the thiosulfate titrated with standard iodine solution, using starch as an indicator. By this method gold was successfully determined in solutions containing as little as 0.00087 gm.

The purpose of this study was to develop a modification of this iodometric titration of gold that could be applied to gold beads. If such an application was successful, assay procedures could be carried out without the use of an assay balance.

Preliminary Experiments

In order to check the procedure of Gooch and Morley and also to determine if an end point could be read satisfactorily in such dilute solutions, the following experiment was performed. Auric chloride was prepared by dissolving 50.52 mg. of pure metallic gold in aqua regia and taking the resulting solution to dryness in an evaporating dish at a temperature of 60° C. The residue was dissolved in water and the volume made up to 250 cc. After the solution of gold chloride was made, however, a small quantity of brown residue remained insoluble. This was thought to be gold which had been reduced to the metallic state during the above procedure. This residue was discarded; thus, the solution of gold chloride contained an unknown amount of gold.

It was still possible, however, to use this solution to check Gooch and Morley's procedure. This was done by taking measured volumes of the gold solution, acidifying with 0.3 cc. of concentrated hydrochloric acid and adding an excess of KI. The iodine liberated from the KI by the auric ion was then titrated with approximately 0.01 N sodium thiosulfate using freshly prepared potato starch as indicator. From the concentration of the gold solution, assuming that none of the gold had been reduced, the normability of the sodium thiosulfate was calculated.

Constant values for the normality of the sodium thiosulfate were obtained by using several different volumes of the auric chloride solution. These results served as a check on the work of Gooch and Morely and showed that a satisfactory endpoint could be read in such dilute solutions.

Standardization of Sodium Thiosulfate by Metallic Gold

Four gold beads of known weight were dissolved in aqua regia and taken to dryness in evaporating dishes at a temperature of 60° C. Care was taken that this temperature was not exceeded in order to prevent reduction of the gold from the trivalent to either the monovalent or metallic state. The resulting auric chloride was then dissolved in 10 cc. of water, the solution acidified with 0.3 cc. of concentrated hydrochloric acid, and 5 cc. of a 5% KI solution added. The liberated iodine was titrated with the sodium thiosulfate solution to be standardized. The starch used in this standardization procedure and in subsequent titrations was prepared by cooking a raw potato slowly for five minutes and filtering the resulting suspension.

The normalities of the thiosulfate calculated from the volumes required to react with the iodine liberated by known weights of gold are divergent. (See Table IV)

Table IV

Standardization of Sodium Thiosulfate by Gold

Bead No.	Gm. Au.	cc. $Na_2S_2O_3$	N. $Na_2S_2O_3$
1.	0.00257	2.50	0.0104
2.	0.00133	1.19	0.0113
3.	0.00183	1.60	0.0115
4.	0.00144	1.38	0.0108

Average Normality 0.0110

This is readily accounted for if the small volumes of solution and the small amounts of gold are considered. Since one drop of the sodium thiosulfate solution changes the burette reading 0.04 cc., an error of one drop in reading the end-point will make a large differende in the normality obtained.

Application of Method to Gold Beads of Unknown Weight

Several beads whose actual weights were withheld by a collaborator until after the experiment was finished were brought into solution as auric chloride by the same procedure as used for standardization. The solution was acidified with HCl, 5 cc. of 5% KI solution was added, and the liberated iodine titrated with the solution of sodium thiosulfate used previously. From the normality of the sodium thiosulfate, (obtained by averaging the normalities shown in Table IV), the weights of the beads were calculated.

In comparing the calculated weights of the beads with their actual weight, agreement within 0.2 mg. was found. See Table V. Therefore, it should be possible by this method to determine the weight of gold beads within 0.2 mg. of their actual value by the use of this procedure.

Further work in perfecting the technique of this titration might possibly increase the accuracy of the determination.

Table V

Sample	cc. $Na_2S_2O_3$ (.0110N)	Gm. Au found	*Gm. Au taken	Deviation (gm)
1.	2.50	0.00271	0.00286	-0.00014
2.	3.40	0.00369	0.00373	-0.00004
3.	1.39	0.00151	0.00142	+0.00009
4.	0.62	0.00068	0.00065	+0.00003
5.	0.73	0.00079	0.00078	+0.00001

* Wts. of beads were withheld until after titration was completed.

PART III

A QUALITATIVE DETECTION OF ALKYL SULFIDES IN THE ATMOSPHERE

A QUALITATIVE DETECTION OF ALKYL SULFIDES IN THE ATMOSPHERE

Introduction

This series of experiments was undertaken to devise, if possible, some method whereby organic sulfur compounds of the mercaptan or thioether type could be detected qualitatively in the atmosphere. If such a method could be devised it might be possible to determine quantitatively small amounts of mustard gas or other gases of similar nature.

Qualitative Detection

It has been known for some time that alkali sulfides can be detected qualitatively by the pink to violet color they form in the presence of sodium nitro-prusside. If sodium sulfide could be formed in some manner from the thioether or mercaptan a subsequent reaction with sodium nitroprusside should then furnish the desired method of colorimetric detection.

When small amounts of an alkyl sulfide are fused with metallic sodium a reaction takes place between the two and sodium sulfide is formed; thus the above reaction with sodium nitroprusside could be applied.

Diethyl sulfide was prepared by refluxing ethyl bromide with sodium sulfide at a temperature of 50° C.

for 48 hours. The thioether was then separated from other products of the reaction by fractional distillation. In order to see if the above method could be applied to a detection of this sulfide in the air, a quantity of air was first saturated with diethyl sulfide by bubbling the air through it. The air was then run through a glass 25 cm. long and containing 15 gms. of activated charcoal. That the charcoal had adsorbed all of the diethyl sulfide was indicated by absence of its characteristic odor in the exhaust air from the adsorption chamber.

The charcoal was then transferred to a pyrex test tube and mixed intimately with metallic sodium. After heating the mixture for ten minutes the resulting sodium sulfide was leached out with water. After removal of the charcoal by filtration, the addition of five drops of a 1% solution of the nitroprusside reagent gave the characteristic pink to violet color. This showed that this procedure could be used for at least qualitative detection of organic sulfides in the air.

It was further desired to determine if the color could be obtained in the presence of very minute amounts of sodium sulfide. One cubic centimeter of the diethyl sulfide used was dissolved in one hundred cubic centimeters of n. amyl alcohol and five hundred cubic centimeters of air was run through this resulting solution. After

subsequent treatment with sodium a deep pink color was obtained, thus showing that the method could be applied to very small amounts. In fact, if a colorimetric quantitative determination could be used it would be necessary to make a very dilute solution of the sodium sulfide before differences in color shades could be observed.

Quantitative Determination

Since the method described above was successful qualitatively it was thought that it might be applied as a quantitative determination.

Measured amounts of air were run through the amyl alcohol solution of the diethyl sulfide and then passed through the activated charcoal.

In order to get a quantitative yield of the sodium sulfide it was necessary to carry on the volatilization of the sodium in such a manner that no escape of the thioether would take place. Since this compound is quite volatile some had always escaped in the previous experiments. This took place even with light heating as was evidenced by the odor of the thioether issuing from the mouth of the test tube. In an attempt to overcome this difficulty a tube 25 cm long and closed at one end was used in place of a common test tube. A layer of sodium one centimeter thick was placed over the previously described mixture of

charcoal and sodium in order to catch the escaping ether. However, this was unsuccessful as some of the diethyl sulfide always escaped before a temperature sufficient to cause a reaction was reached.

Difficulties were also encountered in the attempt to use the sodium nitroprusside as a colorimetric reagent. It was found that the pink color thus obtained is very unstable and within two minutes completely changes to a murky blue. Prolonged boiling of the water used in making up standard solutions of sodium sulfide and the sodium nitroprusside increased the stability of the color to a slight extent. As yet no method of stabilizing the pink color has been developed.

The use of sodium nitroprusside as a colorimetric method for the determination of sulfide ion would also be limited because it can only be used within a comparatively limited range of sulfide concentrations. Above the limiting concentration the shade of color is too deep to ascertain slight changes. This might be overcome by making a definite dilution of the sulfide containing solution.

Summary

A method for qualitatively detecting the presence of alkyl sulfides in the atmosphere has been developed.

BIBLIOGRAPHY

1. Caldwell and McLeod. Determination of Gold and Silver. Ind. and Eng. Chem, Anal. Ed., 9, 530-532, 1937.

2. Gooch and Morley, Iodometric Titration of Gold. Am. Jour. Sci., 6, 261-266, 1899.

3. Pierson, Gordon G. The Use of Mercurous Chloride. Ind. and Eng. Chem., Anal. Ed., 11, 86-87, 1939.

4. Yasuda, M., Jour. Chem. Soc. Japan, 2, 321, 1927.