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PURIFICATION OF POLONIUM BY THE GLASS WOOL ADSORPTION OF COLLOIDAL POLONIUM HYDROXIDE

by

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ABSTRACT

The adsorption of colloidal polonium hydroxide on glass wool in solutions having a pH of about 4.2 has been demonstrated to be a fast and quantitative method for the purification of polonium. The method has worked well with both test and recovery solutions. The procedure consists of adjusting the pH of a solution of the polonium salt to 4.2 in the presence of glass wool, filtering and washing the glass wool, and leaching off the hydroxide in acid or base.

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INTRODUCTION

It has long been known that tracer polonium forms colloidal polonium hydroxide (or hydrated oxide) in aqueous solutions at pH's between 3 and 12.[1] We have recently developed a purification method based on this phenomenon to effect a rapid and efficient use of waste polonium solutions.

In this laboratory, a large fraction of the processes and operations involving polonium are based on the use of polonium metal as the starting material. As standard procedure, the polonium is obtained in metallic form by electrodeposition from 1.5 N nitric acid at a cathode potential of +0.3 volts relative to a saturated calomel electrode (+0.54 volts relative to the hydrogen electrode). Since only the most noble metals are cathodically deposited at this potential, the electroplating operation is quite effective in the purification of polonium. Furthermore, the electrodeposited polonium is frequently distilled prior to final usage and an additional purification thereby effected since only the Group IA, IIB, and VIA metals have vapor pressures higher than or comparable to that of polonium. At temperatures somewhat higher than polonium distillation temperatures, the Group IIA elements and Tl, Sb, Bi, and Pb are also distilled at appreciable rates. Because of these purifications a recovery process need only separate polonium from macro quantities of extraneous materials and yield polonium solutions suitable for electroplating.

An earlier method of polonium recovery was based on the separation of polonium from waste solutions through electrochemical exchange onto bismuth metal.[2] In this method, nitrate and ferric ions interfere with the bismuth "scrub" and must first be removed. This separation as well as the final separation of polonium and bismuth are tedious and time-consuming.

The present colloidal adsorption method rapidly and efficiently removes polonium from most waste solutions and the polonium is conveniently recovered in solutions suitable for the electroplating operation. In addition, it is believed that the method yields polonium solutions of high purity. This is to be expected from the application of known solubility products (discussed below). The absence of visible deposits on "assay" foils is supporting evidence.*

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[1] Haissinsky, M., Le Polonium, Hermann et Cie, Paris, 1937, Figures 4 and 5.

[2] Gutierrez, C. P., Treiman, M. W., and Bowman, M. G., LA-1404, 1952.

*Polonium solutions are assayed by evaporating aliquots onto metallic foils and measuring alpha emission from the foil in a methane proportional counter.

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COLLOIDAL ADSORPTION PROCEDURE

The colloidal adsorption method is based on the formation of colloidal polonium hydroxide between the pH's of 3 and 12, and on the ready adsorption of this colloid on clean Pyrex glass wool. About 1/2 gm of cleansed glass wool* is first added to 50 to 200 cc of an acidic solution of the polonium. The pH of the solution is then adjusted to about 4.2 with ammonium hydroxide. After standing for 15 min, the solution is filtered through a medium fritted Pyrex Buechner funnel. The glass wool remaining on the Buechner is then soaked for 5 min in 20 ml of acid or base. Concentrated nitric acid, concentrated hydrochloric acid, aqua regia, or 1.5$\underline{N}$ sodium hydroxide may be used for this leaching. The solution is then filtered from the glass wool, and the glass wool is treated with another leach of acid or alkali. This entire procedure is generally repeated on the leachings to obtain polonium of higher purity.

The neutralization to a final pH of 4.2 is based on two considerations. A pH of 4.2 is sufficiently high to produce a quantitative precipitation of polonium hydroxide from dilute solutions, and is sufficiently low to prevent precipitation of most other ions likely to be encountered in waste solutions. Table I lists the concentrations of some of these ions at pH's 4 and 5.

EXPERIMENTAL RESULTS

Actual waste solutions were employed in all but a few cases in this investigation. These solutions often contained appreciable concentrations of metallic ions such as mercuric, ferric, beryllium, nickel, and chromic, together with dissolved organic material (paper, grease, and solvents). Where a known amount of a given ion was added, or where the concentration of a particular ion was known to be high, it is indicated in the tables.

Table II contains the results of several tests of the colloidal adsorption procedure under different conditions. The first two experiments indicate the low adsorption which results when the glass wool is added after the colloid has been formed. The next six show the efficiency of colloid precipitation at various pH's and the effectiveness of various acid leachings. The last one demonstrates the ease of separation of polonium from mercuric ion. Within experimental error (5%), 100% recovery was effected in all but the first two cases.

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*Pyrex glass wool was selected as the adsorbent since virtually all colloidal polonium may be leached from it in a short time. Prior to use, the glass wool is washed with trichloroethylene, acetone, distilled water, concentrated nitric acid, and distilled water.

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TABLE I

Concentration of Ions According to Equilibrium Constants Compiled by Latimer[3]

Ion	Form of Soluble Ion	Concentration, Moles/Liter at pH 4	Concentration, Moles/Liter at pH 5
Ag^+	Ag^+	Solubility of Ag Salt	Solubility of Ag Salt
Hg^+	Hg_2^{++}	1.6×10^{-3}	1.6×10^{-5}
Be^{++}	Be_2O^{++}	.4	.04
Co^{++}	Co^{++}	Solubility of Co Salt	Solubility of Co Salt
Cu^{++}	Cu^{++}	Solubility of Cu Salt	.56
Hg^{++}	Hg^{++}	1.7×10^{-6}	1.7×10^{-8}
Hg^{++}	$HgCl_4^{=}$ (1 M Cl^-)	Solubility of Hg Salt	Solubility of Hg Salt
Ni^{++}	Ni^{++}	Solubility of Ni Salt	Solubility of Ni Salt
Pb^{++}	Pb^{++}	Solubility of Pb Salt	Solubility of Pb Salt
Mn^{++}	Mn^{++}	Solubility of Mn Salt	Solubility of Mn Salt
Al^{+++}	Al^{+++}	2×10^{-3}	2×10^{-6}
Al^{+++}	$Al(OH)^{++}$	2.7×10^{-5}	2.7×10^{-6}
Bi^{+++}	BiO^+	.01	1×10^{-3}
Bi^{+++}	$BiCl_4^-$ (1 M Cl^-)	8×10^{-9}	8×10^{-11}
Cr^{+++}	Cr^{+++}	.67	6.7×10^{-4}
Cr^{+++}	$Cr(OH)^{++}$	1	10^{-2}
Fe^{+++}	Fe^{+++}	4×10^{-8}	4×10^{-11}

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3. Latimer, W. M., Oxidation Potentials, Prentice-Hall, New York, 1938, p. 309-317.

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TABLE II

Tests of the Colloidal Adsorption Separation of Polonium

Solution No.	Millicuries in waste Solution	pH after Neutralization	Millicuries in Filtrate	Leaching Agent	Millicuries in 1st Leach	Millicuries in 2nd Leach	Other ions Present	Remarks
GW-1	600	6	230	aqua regia	180	90	Be^{++} Ni^{++}	Glass wool was added after the pH adjustment.
GW-2	52	4	30	"	14	6		
GW-3		5	0.3	"	77	0.1	"	
GW-4	200	6.8	0.5	"	170	60	Fe^{+++}	Fe^{+++} was not separated.
GW-5	230	4.22	2.2	conc. HCl	194	14		Third leach contained 1.7 millicuries.
GW-6	230	5.28	1.4	"	234	6		Third leach contained 0.8 millicuries.
GW-7	960	4.3	0.8	aqua regia	925	18		
GW-9	420	5	2	conc. HNO_3	408	1	Cl^-	$[Cl^-]$ = 1M.
GW-11	41	4.2	2	conc. HNO_3	38	1	Hg^{++}, Cl^-	$[Hg^{++}]$ = 0.05M, $[Cl^-]$ = 1M. The filtrate when made basic gave a white precipitate. The leach did not.

It is difficult to obtain accurate assays of waste polonium solutions because of the presence of extraneous salts and/or organic material. Therefore, four relatively pure polonium solutions were used to determine the quantity of polonium retained by the glass wool after the acid leaches, a quantity that must be estimated by difference. Within the accuracy of the method (1%), all losses including those on the glass wool averaged about 1.5%. The data obtained are shown in Table III. The three leaches indicated consisted of two of 1.5 M HNO_3 and one of conc. HNO_3, respectively. Table III also indicates the increased solubility of polonium hydroxide at lower pH's. At pH 3.1 the solubility of the hydroxide is sufficiently high to give low recovery yields.

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TABLE III

Colloidal Adsorption Method Applied to Pure Polonium Solutions

Solution No.	Millicuries in Original Solution	pH after Neutralization	Filtrate	Location of Polonium, Millicuries			
				1st Leach	2nd Leach	3rd Leach	Unaccounted for
GW-13	640	3.13	30	573	10	3	24
GW-14	573	4.16	13	523	29	2	6
GW-15	549	5.40	6	533	6	1	3
GW-16	533	3.12	68	457	4	2	2

The experimental results tabulated in Tables II and III indicate the value of the colloidal adsorption process for the purification of polonium solutions.

When the process was adapted for the routine recovery of polonium from waste solutions, the procedure described above was modified as follows:

1. After filtration, the glass wool (in all cases) was washed with nitric acid of the same pH as the filtrate. This wash was added to the filtrate.
2. Concentrated nitric acid was adopted as the leaching agent, and water washes were used after the leaching operation.

Table IV illustrates the use of this routine method in the purification of typical waste solutions.

In some cases, the routine procedure is modified when certain ions are present in the waste solutions. For example, in chloride solutions at pH 4, mercuric ions will remain in solution as the chloride complex while bismuth will precipitate as the oxychloride. On the other hand, in nitrate solution at pH 4, bismuth will remain in solution if the concentration is less than 0.01 M, while mercuric oxide will precipitate out. Thus a colloidal adsorption separation from nitrate solution followed by one from chloride solution, or the reverse procedure, will separate polonium from both bismuth and mercury. Another example is found in solution G-WS-N (Table IV) which contained tungstic acid. In this case, separation was poor at pH 4.2. However, an initial separation at pH 6 followed by one at pH 4.2 effected successful separation.

Occasional waste solutions are encountered from which it is difficult to achieve high polonium yields. Old solutions, containing silica, appear to give low yields, e.g., solutions G-WS-I and G-WS-J (Table IV). Usually, ferric hydroxide remains with the polonium and is later separated from polonium during the electroplating. However, in one case (G-WS-O, Table IV) colloidal ferric hydroxide, which was not adsorbed on the glass wool, appeared in the filtrate. Some polonium was carried by the ferric hydroxide and the result was a relatively low polonium recovery yield.

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TABLE IV

Separation of Polonium from Waste Solutions

Solution No.	Curies in Waste Solution	pH after Neutralization	Curies in Filtrate	Curies in Leachings	Remarks
GWS-A	20	4.2	0.92	19.8	Fe^{+++} was present.
GWS-B	20	4.5	0.006	21.4	
GWS-C	7	4.5	0.002	7.8	
GWS-D	22.3	5	0.044	22.1	
GWS-E	~40	4.5	0.020	42.2	
GWS-F	8.6	4.2	0.040	8.6	
GWS-G	~ 3	4.2	0.015	3.44	
GWS-H_1	~20	4.2	0.43	20.4	
GWS-H_2	~ 10	4.2	0.020	12.3	
GWS-I	.32	4.2	0.078	.148	Silica was present. Initial assay was obtained by the decay of an old assay. The solution was very old.
GWS-J	1.65	4.2	0.098	1.22	The initial assay was obtained by the decay of an old assay. The solution was very old.
GWS-L	4.61	4.2	0.0005	4.25	Fe^{+++} was present.
GWS-M	~15	4.2	0.28	14.8	
GWS-N	10.66	4.2	4.1	4.18	Tungstic acid was present. The solution and filtrate were yellow.
GWS-N'	4.1	4.2	2.4	- - -	Tungstic acid was present. GWS-N' was filtrate of GWS-N.
GWS-N"	2.4	6	0.38	3.79	Tungstic acid was present. GWS-N", filtrate of GWS-N', was filtered immediately after pH adjustment. The filtrate was colored.
GWS-N"'	10.5	4.2	0.30	10.6	GWS-N"' was combined leaches from GWS-N, N', and N".
GWS-O	~16	4.2	4.4	12.6	Fe^{+++} was present.
GWS-O'	12.6	4.2	0.06	12.6	GWS-O' was leach from GWS-O. Fe^{+++} was present.