NUMEC-NYO-9171

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QUARTERLY PROGRESS REPORT

The Decontamination and
Recovery of Precious Metals

Contract No. AT(30-1)-2528

Period from April 1, 1960
to July 1, 1960

NUCLEAR MATERIALS AND EQUIPMENT CORPORATION
Apollo, Pennsylvania

[redacted]

DISCLAIMER

Acknowledgment

The invaluable assistance of Mr. Leo Graup and Mr. Ira B. Whitney of the New York Operations Office, AEC is gratefully acknowledged.

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Introduction

This report is the first quarterly report under Contract AT(30-1)-2528 for the decontamination and recovery of precious metals from contaminated scrap. This program encompasses the recovery of gold, platinum, iridium, rhodium and palladium from scrap and contaminated laboratory ware, equipment, etc. which may be contaminated by alpha emitters (i.e., uranium, plutonium and possibly polonium or combinations of these), beta-gamma emitters such as fission products or all three sources of radiation. In addition the scrap can be chemically contaminated by base metals, graphite or other contaminants. Osmium, ruthenium or silver are not to be recovered.

Since the scrap can exist in such a great variety of forms such as platinum-rhodium laboratory crucibles, graphite crucibles containing platinum-base metal alloys derived from vacuum fusion baths, insulated thermocouple wires, reactor liners, porous platinum filters, alloys such as Baker alloy 413 (60 Au, 25 Pd, 15 Pt) it may be necessary to devise specific methods for a given type of scrap. Nevertheless the basic chemistry is the same and information and methods applicable to simple systems will apply directly to the more complicated ones. Accordingly the relatively simple systems would be investigated first and the more complicated ones later in the program.

An essential and major contribution to the success of the program is to devise or adapt accurate and precise analytical chemical techniques for scrap identification, process control, purity of the final products and accountability control. Accordingly, the emphasis on chemical analysis will be proportionally greater during the early stages of the program.

The residual activity level to be attained is presently stated as twice the standard deviation obtained in low background counters (alpha ~0.1 c/m, beta ~5 c/m) of virgin platinum.

28 C.

Program

At the outset of this investigation, a comprehensive program was developed and is presented below in outline form. There is no intention to investigate each item in detail but rather to select those items which will lead to an economically feasible process or processes which can recover the precious metals on a suitably large scale. If the first choice is not adequate then a more unique method will be investigated. Nevertheless, all the possibilities for solving the problems are listed and may prove of some benefit to others.

Program Outline for Contract AT(30-1)-2528

A. Literature Survey

B. Surface Decontamination

D.

1. Mixed acids - H_2SO_4-HF, HCl-HF, HNO_3-HF, HNO_3-H_2SO_4
2. Molten Salts (Fusion methods for removing surface contamination)
   a. NH_4HF_2
   b. $NaHSO_4$, $KHSO_4$
   c. $NaNO_2$
   d. Li_2SO_4
   e. Fluoborates
   f. NaH-NAOH
   g. Mixed nitrates (not preferred-possible explosive mixture)
   h. Perchlorates (not preferred-possible explosive mixture)
   i. Sulfamates
3. Chelating Agents
   a. EDTA
   b. Tartrates
   c. Citrates

4. Controlled solution methods

   a. removal of small amount of metal by initial treatment with aqua regia to remove most of the activity. Remove bulk of metal and redissolve.

C. Complete Solution

1. Aqua Regia

2. Chlorine plus NaCl

   a. $\sim 400^{\circ}$ non-molten NaCl
   b. $\sim 900^{\circ}$ molten NaCl
   c. Eutectic chloride salt mixtures for lower temperature operation

3. Pyrometallurgical methods

id.

   a. Solution in base metal such as Zn, Sn or Cu. Dissolve or distill base metal to render the precious metal in finely divided state for ease of solution.

   b. Slagging methods for decontamination.

4. Specialized techniques

   a. Solution of gold in bromine solutions
   b. Amalgamation methods
   c. Electrochemical solution methods

D. Separation Methods

1. Hydrolytic methods (Gilchrist-Wichers technique)

2. Solvent extraction especially for gold

3. Ion exchange

   a. Separation of elements
   b. Decontamination

4. Controlled electrolysis

5. Other chemical methods

   a. complexing techniques
   b. fractional crystallization
   c. organic precipitants
   d. homogeneous precipitation
   e. holdback carriers for decontamination
   f. carriers for distillation of Os and Ru
   g. getters, i.e., $Fe(OH)_3$, $Al(OH)_3$, etc.

E. Chemical Analysis

1. Identification

a. X-ray fluorescence
b. Spectroscopic methods

2. Assay

a. X-ray fluorescence
b. Wet chemical methods

1) Hydrolytic method
2) Electrochemical methods
3) Fire assay
4) Flame photometry

3. Purity of separated elements

a. spectrographic
b. X-ray fluorescence
c. Activation analyses
d. Conductivity (electrical) techniques

F. Activity measurements

1. Low level alpha counting
2. Low level beta-gamma counting
3. Scintillation crystal-multichannel analyses methods

A. Literature Survey

The detailed literature survey has essentially been completed. This phase of the work was greatly facilitated by a visit to Professor F. E. Beamish of the University of Toronto. Professor Beamish has just completed an exhaustive review of the methods of isolating and separating the platinum metals.

This review is entitled "A Critical Review of Methods of Isolating and Separating the Six Platinum Metals" and will be published in the near future in TALANTA. Professor Beamish very kindly loaned us the manuscript from which much useful information was extracted and made it possible to materially shorten the literature survey portion of the contract.

Detailed discussions were also held with Dr. Edward Wichers and Dr. Rayleigh Gilchrist of the National Bureau of Standards. These men gave very freely of their valuable time and much useful and pertinent information was obtained. This visit was especially valuable since it firmed up NUMEC's thinking on the various modes of attack on the problem and indicated which ideas should be initially pursued.

The results of NUMEC's literature survey in the areas of interest not covered in detail in Professor Beamish's review is included in this report as an appendix.

Experimental Results

The experimental results obtained during this first reporting period are necessarily rudimentary and incomplete. However a number of interesting avenues of investigation have been opened up which have promise of developing into usable commercially-oriented processes.

The material selected for this initial work is Baker Alloy 413 (60 Au, 25 Pd, 15 Pt). This alloy was selected for a number of reasons among which are: (1) there is a considerable quantity of this alloy which was used at Hanford and must be reclaimed, (2) the alloy contains gold besides the platinum metals and one of the main problems to be solved is the quantitative separation of gold from the platinum metals without loss, (3) the use to which it was put at Hanford would involve alpha, beta and gamma activities.

Accordingly, 5.23 oz. of Baker alloy 413 was purchased for the initial chemical and analytical investigations, since the scrap on hand is too highly contaminated to be used conveniently for the exploratory studies.

B. Surface Decontamination

1. Fused Salts

The use of fused salts for a preliminary surface decontamination treatment is an attractive consideration since the massive pieces of scrap can be conveniently handled in such a process. However to be effective the molten salt should not appreciably attack the metal itself.

The behavior of Baker alloy in contact with several fused salts was investigated. 1.0107 g. of alloy was immersed in 20 g. of molten ammonium bifluoride (NH_4HF_2) in an iron crucible for 6 hours at $\sim$200°C. Following this treatment 1.0110 g. of alloy was recovered intact thus indicating that the alloy is resistant to attack by this reagent. This is a very important observation since it has been shown by the Argonne National Laboratory that NH_4HF_2 is a very effective fusion medium for dissolving highly refractory PuO_2.

The effect of molten lithium sulfate (Li_2SO_4) was similarly checked. 1.0120 g. of alloy was immersed in molten Li_2SO_4 at 900°C in a vycor crucible for 5 hours. 1.0163 g. of alloy was recovered intact indicating no significant attack. Li_2SO_4 as a reagent is attractive since it melts at high temperatures without decomposition and may act as a solubilization agent in some cases.

An interesting observation incidental to the experiment is that the vycor crucible completely disintegrated when placed in boiling water. This treatment may thus prove effective in the removal of ceramic or silicious materials from the precious metals as in the case of insulation from thermocouple wires.

This type of experimentation will be extended to study the effects of virgo salt, sodium nitrite and potassium bisulfate on the alloy.

2. Solubilizing Effect of Single Acids and Other Solutions

Baker alloy exhibits a marked resistance to single acids. It is unaffected by 1:1 HNO_3 or 1:1 HCl. However it is general experience that these simple acids are ineffective in removing refractory radioactive oxide contaminants.

The alloy is not affected by 8 M sodium cyanide solution even after 4 hours of contact at the boiling point of the solution. However bromine water attacks the alloy and this process will be investigated as a possible method of selective gold extraction.

3. Controlled Solution Methods

A simple, and based on preliminary experiments, promising scheme for removing the major part of the surface activity is by controlled solution where the surface layer of an object is dissolved thus removing the contaminated layers and dissolving or dislodging the adherent oxides, etc. Admittedly the freshly exposed metal surface will be recontaminated by exposure to the solution but the level of contamination is greatly reduced. This may allow subsequent operations to take place in unshielded equipment in the case of penetrating radiation or in the case of alpha activity allow the subsequent operations to take place in simple hoods rather than completely closed dry boxes. Furthermore the decreased activity level also permits the use of techniques such as ion exchange, carrier techniques, etc. Some results obtained by these methods are presented below.

In order to obtain material for this test Lot No. 216 was opened. This lot contains 4 contaminated crucibles from Shippingport. The crucibles are contaminated with β-γ activity mostly Co-60. The crucible selected weighed 23.5 grars and had an initial activity

level of >250,000 counts per minute measured ~3 inches from a flow counter.

The crucible was treated in a controllable manner with aqua regia to remove the surface layer (1.1 g. Pt). After washing, the crucible counted only 100 counts per minute; a reduction of 2500X. By this treatment 95% of the platinum was recovered with practically no activity remaining. The removal of the very slight residual activity levels to the specification limits should easily be accomplished during the succeeding chemical operations. The solution containing the activity and the gram of platinum was used in the ion exchange and scavenging experiments reported below.

C. Complete Solution Methods

1. Aqua Regia

Aqua regia is the time honored and reliable method for dissolving the platinum metals and gold. For example Baker alloy dissolves very readily in aqua regia; 31.6 g. was easily dissolved in 120 ml of 4:1 HCl/HNO_3 in about 1 hour. There is, however, a major drawback in the use of aqua regia for a large scale reprocessing method. The nitric acid must be removed or destroyed before further chemical operations can be applied. The usual way to accomplish this is by repeated evaporations; this however is very expensive and time consuming and creates other major porblems in the excessive corrosion of equipment, fume ducts, etc.

If other means could be found to destroy the nitric acid a major accomplishment will have been attained since aqua regia is such an effective solvent. Experiments are underway at NUMEC utilizing the

reaction between nitrite and nitrate ions:

$$2H^+ + NO_2^- + NO_3^- \longrightarrow 2NO_2 + H_2O$$

On the laboratory scale this reaction goes very smoothly and is much less time consuming than the equivalent repeated evaporations.

In addition, in the presence of nitrite ions, gold is reduced to the metal:

$$Au^{+++} + 3NO_2^- \longrightarrow Au^0 + 3NO_2$$

Thus the gold is precipitated from solution in a readily filterable form.

A slight excess of solid sodium nitrite was added to a solution containing 2.8358 g of Baker alloy dissolved in 100 ml of aqua regia and subsequently diluted to 300 ml. After boiling for 4 hours, the evolution of brown NO_2 fumes had ceased and a clear solution of the Pt and Pd remained with the gold precipitated in a easily filterable form. The gold was recovered quantitatively. This method shows great promise and will be investigated in greater detail.

2. Chlorine-Sodium Chloride Reaction

The elimination of nitric acid completely in the dissolving of the platinum metals and gold would be very helpful in establishing simpler recovery processes. An old technique which will be investigated in detail is the reaction between the platinum metals in a sodium chloride bed and chlorine gas.

The advantages of this procedure in terms of a large scale system are:

1) All platinum metals including iridium and rhodium are dissolved.

2) No nitric acid is involved in the process.

3) Recent advances in salt bath techniques and in handling and availability of chlorine make this approach very favorable for large scale application.

4) At higher temperature, gold is removed by distillation in the chlorine gas stream.

5) A significant decontamination may result since refractory oxides may remain insoluble.

6) The equipment is simple and does not pose any major corrosion problem since the reaction can take place in glass lined vessels.

The only apparent major drawback is the resulting high ionic strength solutions which result when the soluble complex platinum metal chlorides and the excess sodium chloride are dissolved in water. Nevertheless, simple precipitation methods should suffice to provide for a quantitative separation prior to the purification and isolation steps.

There may be some advantage in carrying out the reaction in lower melting eutectic mixtures. This whole problem will be thoroughly investigated.

A variant of this reaction for the solution of the platinum metals in HCl under pressure in bombs is the well known Wichers method. Although very effective for analytical work, the use of pressure systems with the attendant hazards is to be avoided on the engineering scale.

Another variation was found in German patent 668,873(12-12-38) in which it was claimed that the platinum metals could be dissolved in boiling HCl when a stream of Cl_2 is bubbled through the refluxing solution. This scheme was tried with Baker alloy with a notable lack of success. 5.46 g. of alloy was refluxed with boiling concentrated HCl for 4 hours while a slow stream of Cl_2 was passed through the boiling solution. Only 0.01 g. of alloy was dissolved after this treatment. As indicated above at 300°C HCl is a very effective dissolving agent but at 110°C which is the boiling point of stabilized concentrated HCl the rate is much too slow for practical use.

D. Separation Methods

It is difficult to make a sharp distinction between separation methods to resolve the individual members of the group and separation methods that also result in radioactive decontamination or removal of base impurities. The chemistry of the platinum metals and of gold is direct and unique enough so that the production of the isolated element will materially accomplish, in some measure, all three of these effects. Accordingly the discussion of separations will be classified under techniques rather than desired results.

1. Ion Exchange Methods

Most of the reactions involved in this program will eventually be accomplished in a chloride medium. Thus the platinum metals will exist in solution as the complex chloride anions, i.e., $PtCl_6^{=}$, $IrCl_6^{=}$, etc. Since these are strong anions it makes possible to use cationic exchange resins to remove the trace impurities, whether radioactive or not, and allow the platinum metals to pass through

the column without absorption. It is possible therefore to utilize the ion exchange techniques in equipment of moderate dimensions for purification and decontamination purposes. As an example, a chloroplatinate solution containing 4000 ppm of iron and 4000 ppm of uranium was passed through a laboratory sized column of IR 120 ion exchange resin. After only one pass through the column the iron content was reduced to 3 ppm and the uranium content to 2 ppm. Such results are very encouraging and research in this area will be expanded.

The effectiveness of this technique for removal of very low levels of activity is illustrated in a very preliminary experiment using the solutions derived from B3 above. After removing HNO_3 by fuming, the pH was adjusted to 3.5 and passed through a short cation exchange colume (IR 120). The effluent solution was adjusted by evaporation to the original volume and beta counted in a windowless flow counter which had a 30 c/m background. The original solution had a counting rate of 27,500 c/m while the effluent had a rate of 1,250 c/m. A factor of ~25X was achieved in this simple experiment. The use of added Fe and Co holdback carriers would have assuredly achieved a much greater D.F. but the solution was retained to carry our exploratory experiments using scavenging techniques.

2. Scavenging Methods

Standard scavenging methods as used in radiochemical separations have proved of value even in large scale operations. At NUMEC the removal of traces of uranium from waste solutions in 1000 gallon

when it was assumed that the Au LY_1 peak would have to be used to eliminate tungsten interference (See below).

2. Trace Analysis by X-ray Fluorescence

The investigations regarding trace analysis of the noble metals by X-ray fluorescence methods has been directly correlated with the separations experiments. This was done in order to have rapid and reliable methods to follow the effectiveness of the separations and also to have a rapid method to establish the purity of the separated element. Accordingly, the first experiments involved Au, Pt and Pd.

A powerful tool for trace analysis is the utilization of X-ray fluorescence methods using spot test paper to contain the sample. Yagoda spot test papers are ideal for this purpose since a reproducible volume and sample area are conveniently obtained. When this method is combined with the "standard addition" method a procedure combining high sensitivity, reproducibility, quantitative measurement and freedom from matrix variation is available for rapid quantitative analysis. Including sample preparation and measurement, answers can easily be obtained in a half hour or less. These advantages make this technique practically ideal for quality control, process control as well as expediting the accumulation of data from the various scouting experiments in the development program. At NUMEC, this method has proved of tremendous value in heavy metal analysis such as U, Th, Nb and Zr.

In this program the method has been applied to:

1) The evaluation of precipitate purities after separation of an element.

2) The analysis fo filtrates to check the completeness of the separation.

Since the same basic technique is used in both cases, the following discussion applies equally well to either type of analysis. The following discussion is therefore divided into three parts (1) Pd, (2) Pt and (3) Au.

The sample preparation is the same for all three elements:

1) 0.2 cc of the solution to be analyzed is evaporated under an infra red lamp on Yagoda spot test paper. (Sample paper)
2) A 0.1 cc of a standard solution with a known concentration of the element to be analyzed is placed on a second spot test paper and 0.2 cc of the unknown also dried on this paper (addition paper).

The analysis is carried out as follows:

1) The counts per second (a) obtained for the unknown at a suitable goniometer setting is corrected for background and the contribution from the tungsten interference if present.
2) Suitably corrected counts per second (b) for the addition paper are determined.
3) The difference b-a is then the counting rate per Y micrograms of element in the particular matrix used. Thus the matrix effect, geometry effect, etc. are cancelled out.

4) Then $\frac{a}{\frac{b-a}{Y}}$ is the concentration in micrograms of element in 0.2 cc and $\frac{5a}{\frac{b-a}{Y}}$ is micrograms of element per milliliter.

5) Thus the unknown concentration X is:

$$X = \frac{5aY}{b-a}$$

where a = c/s for element on sample paper corrected for background and tungsten interference

b = c/s for element + addition corrected for background and tungsten interference

Y = micrograms of element standard added

X = concentration of element in sample solution in micrograms per milliliter

a. Palladium

The Pd KA peak is used for the analysis; it is not interfered with by Au, Pt or W. Even in "dirty" scrap the only elements likely to be present which might interfere are Nb, Ru and Ag and then only if they are present in high concentrations.

The above procedure was used to determine the residual Pd in solution following a dimethylglyoxime precipitation (Sample No. 1002). Less than .002 mg Pd/ml was found in the filtrate. The Pd sensitivity is 3.5 c/s per microgram. Since 2 c/s is a significant rate measurement as little as 0.5 micrograms of Pd could be detected with confidence.

The Pd content of purified gold (Sample No. 1004) separated from a Au-Pd-Pt solution was measured by dissolving the gold in aqua regia, fuming off the nitric

acid, followed by the paper technique. The analysis indicated only .007 mg/ml in the gold solution but an unexpected observation was noted.

In the gold solution an enhancement of the Pd sensitivity was measured, i.e., the Pd sensitivity in this matrix was 4.5 c/s per microgram. Although enhancements of this sort have been previously observed in other applications, an attenuation of the Pd radiation by Au would be predicted based on density considerations.

A similar analysis was made for Pd in the Pt solution separated from Baker alloy. In this case the residual Pd content in the platinum was .01 mg/ml and the Pd sensitivity dropped to 2.1 c/s per microgram. In this case the expected attenuation of the Pd radiation occurs.

b. Platinum

The Pt LA_1 peak has been used for the trace analyses. In this application the contribution of the W LB_1 + W LB_2 (from the W target tube) to the Pt LA_1 peak must be corrected for. Based on NUMEC's extensive experience in correcting for the contribution of W LB_6 to the Zr KA peak, a similar method has been devised for the present case.

On theoretical considerations, the intensity ratio for two first order peaks of the same element should be the same over a wide range of intensity. This relationship should also hold for the ratio of intensities of an element peak to the same element contribution on the shoulder of

a peak where some intensity above background is still noted; this is true at least as a first approximation.

Thus the ratio of the unencumbered W LB_2 to the W LB_1 + W LB_4 is used to correct the observed intensity of the Pt LA_1 peak. Briefly, if the intensity ratio of

$$\frac{W\ LB_1 + W\ LB_4\ (peak)}{W\ LB_1 + W\ LB_4\ (Pt\ peak)} = constant = K_1 \text{ and } \frac{W\ LB_1 + W\ LB_4}{W\ LB_2} =$$

constant = K_2 then the intensity ratio $\frac{W\ LB_1 + W\ LB_4\ (Pt\ peak)}{W\ LB_2}$ is a constant and the contribution of the tungsten peaks to the platinum analysis peak (Pt LA_1) can be determined. The constant K_2 was determined using WO_3 powder and found to be, K_2 = .071. Thus to correct the observed counting rate at the Pt LA_1 peak, the intensity of the tungsten radiation is determined at the W LB_2 peak, multiplied by .071 and subtracted from the c/s obtained at the Pt LA_1 position.

Using this correction procedure, the sensitivity of trace platinum in gold solutions was found to be 1.5 c/s. When this work was done, the pulse height analyzer was not available so that the sensitivity using the PHA would undoubtedly be greater. However the Pt sensitivity will not equal that of Pd in any case since the intensity of the X-ray L spectrum is not as great as that of the K spectrum.

c. Gold

For gold the Au LB_1 peak is usable for trace analyses. The stronger Au LA_1 peak is too strongly interfered with by the W LA_1 peak and therefore cannot be used with a tungsten

target tube. There is a slight contribution to the Au LB_1 peak by W LY_1 but a correction can be applied as was done for the case of platinum.

The ratio $\frac{W\ LY_1\ (31.22)}{W\ LB_2} = .0128.$

Using this value the sensitivity for gold was determined to be a little less than 1 c/s per microgram. This work was also done with the use of the pulse height analyzer.

On the basis of the work accomplished to date four immediate conclusions are obvious:

1) The pulse height analyzer definitely enhances sensitivity.
2) The pulse height analyzer could conceivably be used to eliminate the W interference in the case of Pt and Au trace analyses. However the correction factors are so small it is very doubtful that the PHA need be used with such a narrow window. Also the Pt and Au intensities would be correspondingly decreased with an overall decrease in sensitivity.
3) The validity of the correction technique postulated should be checked with synthetic samples in order to rule out the possibility of any significant effect of Compton scattering. Theoretically such pertubations should be insignificantly small.
4) The relative advantages and disadvantages of using a Mo target tube in place of the W tube currently in use must be investigated. The advantages of eliminating the W interferences may be outweighed by the lower intensity of the Mo tube.

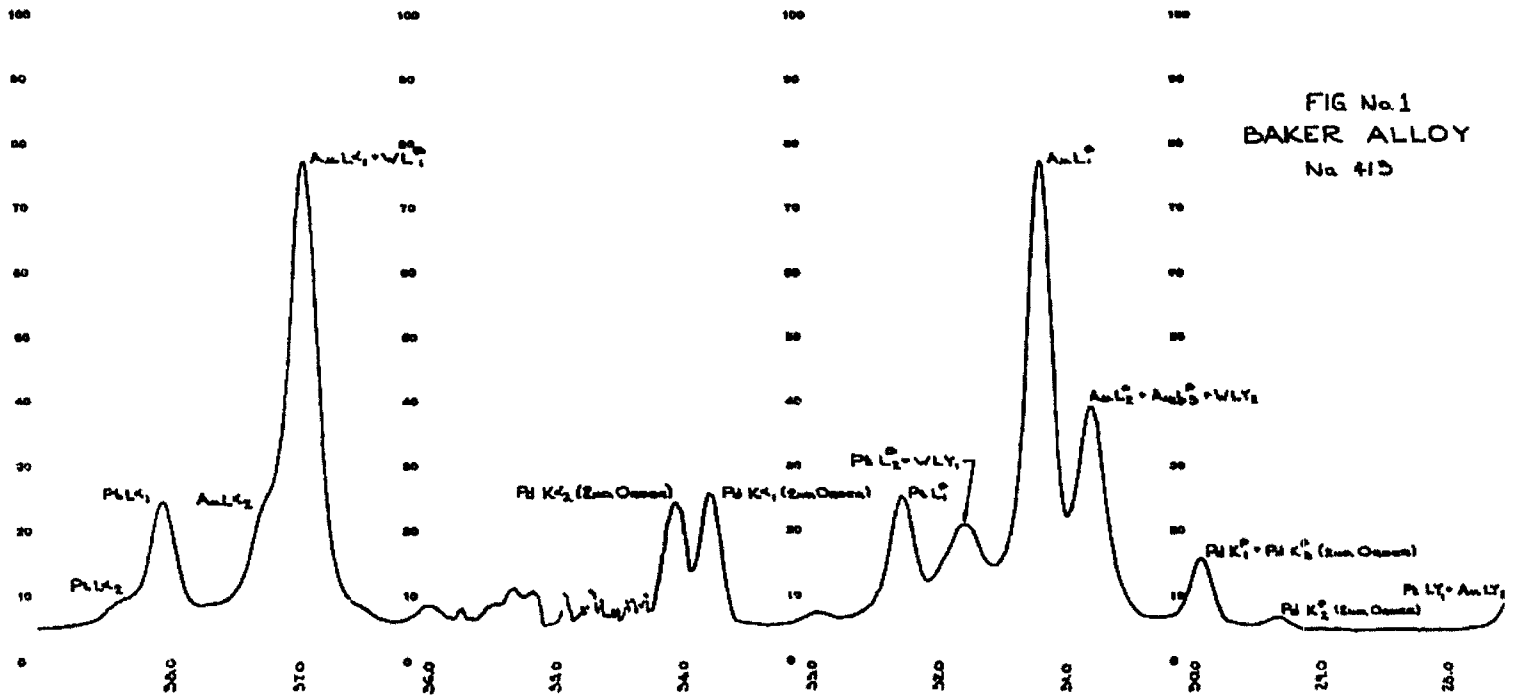
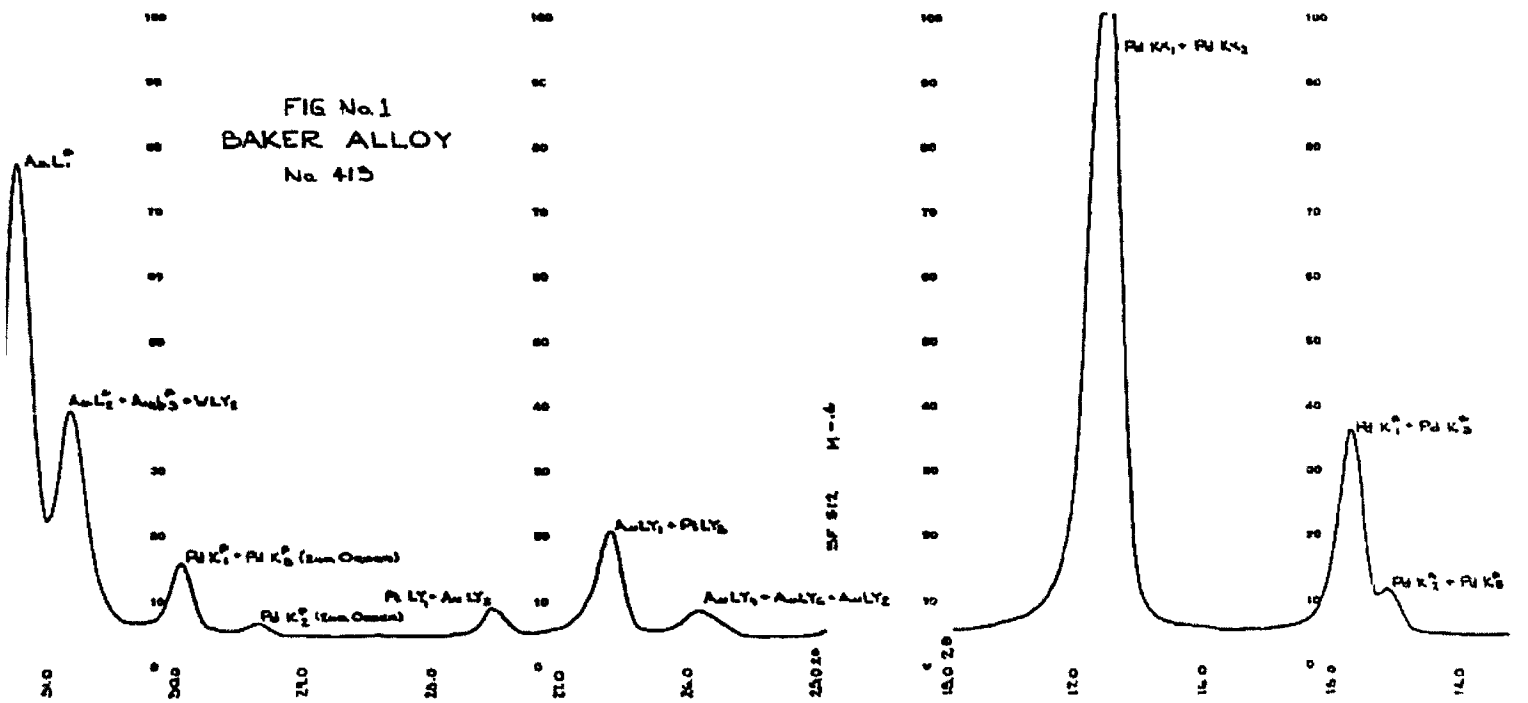


FIG No. 1
BAKER ALLOY
No. 415

Figure 1



APPENDIX I

Literature Survey

A. Introduction

A comprehensive survey of precious metal chemistry may be found in Gmelin (1). A less complete but more critical survey is given by Sidgwick (2). A very complete literature survey with 813 references was presented by R. Gilchrist (3) in 1943. More recently Beamish (4) has prepared a comprehensive review of methods of isolation and seperation of the precious metals. Major emphasis was on application to precious metal ore assay. Beamish lists 157 references.

The literature survey presented here was undertaken in order to review some of the developments that have appeared since the Gilchrist articles; major emphasis was placed in seeking information pertinent to the problem of decontamination, methods for dissolving precious metal alloys and methods for separation of solutions of alloys into their pure components. With these ends in mind a complete survey of the chemical reactions and properties of compounds of the precious metals was not attempted. A short survey of these topics is presented by Emeleus and Anderson (5). Basolo and Frost (6) give a very complete discussion of the present state of knowledge of the kinetics and mechanisms of the complex ions of the precious metals.

B. Removal of Impurities by Surface Treatment

Classical methods for cleaning platinum laboratory apparatus by acid treatment or treatment with fused potassium hydrogen sulfate are given in standard textbooks on quantitative analysis (7). These books also discuss the deleterious effects of certain fused salts and

concentrated mineral acids on platinum laboratory ware. It is interesting to note that the solubilizing effect of hot sulfuric acid on platinum crucibles is completely inhibited by bubbling SO_2 through the boiling acid.

The corrosion resistance of platinum crucibles and crucibles made of a 90 Au-10 Pt alloy has been studied (8). It is reported that at temperatures above 600°C fused potassium hydrogen sulfate attacks platinum. Thus, a 50 ml platinum crucible containing 11 g. potassium hydrogen sulfate lost 1.9 mg after 20 minutes fusion at 600°C. A similar Au-Pt alloy is several times more resistant to fused Na_2CO_3 or K_2CO_3 at 720°C and to fused NaOH at 600°C than is Pt. Below 600°C NaOH-KNO_3 mixtures have practically no effect on the Au-Pt alloy.

C. Methods of Dissolving Precious Metals and Their Alloys

The classical methods for the solution of precious metals are aqua regia treatment, fusion with alkaline oxidizing fluxes and high temperature chlorination of the material usually in contact with a sodium chloride bed. Another method involves heating the material with concentrated HCl and an oxidizing agent such as fuming nitric acid, sodium chlorate, perchloric acid or chlorine at high temperature under pressure. The last method is reported to be effective for dissolving iridium and iridium alloys.

It is also reported (9) that Au, Pt and the other metal of the Pt group can be rapidly rendered soluble by subjecting, at a high temperature, to the simultaneous action of boiling 38% HCl and gaseous Cl_2. Among other examples 3.3 kg of Au was converted to soluble $AuCl_3$-HCl by treating it for 5 hours with 1900 kg Cl_2 and 1735 kg 38% aq. HCl at the boiling point of the latter.

In all cases the rate of solubilization of a given precious metal or precious metal alloy can be enhanced by reduction of particle size of the material. The standard method for accomplishing this has been fusion with zinc followed by treatment with HCl to remove excess zinc. Iridium does not form an alloy with zinc and advantage has been taken of this fact to separate Ir from rhodium (10). After fusion and dissolution of excess zinc, the rhodium was dissolved in aqua regia. The insoluble residue was iridium which was separated from the aqua regia solution, dried and weighed. The residue obtained from zinc fusion is, in general, a very finely divided alloy of zinc with the precious metal. This method has been criticized by Hill and Beamish (11) who object to the zinc introduced by this operation.

Other metals may prove superior to zinc for alloying purposes. The following systems have been studied from the metallurgical point of view; Pt-Co (12); Pt-Cr (13); Pt-Cd (14). Os is insoluble in Sn while all the other Pt metals are soluble (15). Three distinct chemical compounds are formed in the Cu-Pt system (16) these are $CuPt$, $CuPt_3$ and $CuPt_7$. It has benn reported (17) that when CuO or Cu_2O are heated with Au, Pt or Pd oxygen is evolved with the formation of metallic Cu which forms solid solutions with the noble metals. Pt is not very soluble in Hg under ordinary conditions, its solubility being 1.77 atom % at 200°C (18).

Lead has long been used as a collector for precious metals. The excess Pb can be removed by oxidation of the Pb-precious metal alloy in a special bone ash crucible. During this operation, called cupellation, the PbO is taken up in the walls of the crucible while the precious metals are left behind as a button called a regulus. Slight losses of precious metals occur during the process. Silver is sometimes added to prevent

losses of precious metals. N. Plabisin and E. A. Marenkov (19) studied the loss of precious metals during cupellation with and without added Ag; very complex behavior was found. In general it was noted that the losses of precious metals, either with or without added Ag were Ir > Pd > Pt > Rh. In all cases Ag inhibited the loss but did not change the order.

Chlorination has often been used to convert aqua regia insoluble materials, particularly those rich in rhodium, into a soluble form. Carbon tetrachloride passed over Pt metal and an alkali chloride at 550-600°C (20) and a mixture of NH_4Cl and the precious metal heated to red heat in the presence of O_2 (21) have been used as chlorinating agents. Usually the chlorination is carried out by passing gaseous Cl_2 over a mixed bed of NaCl and the precious metal at 700°C. In the absence of NaCl the chlorination is slow and volatile products often result (11). A 4 mg sample of Iridosmine required 217 hours for complete chlorination at 700°C in the absence of NaCl. 4 mg of Iridosmine mixed with 40 mg NaCl was completely chlorinated in 10 hours.

A mixture of HF and H_2O_2 was reported to be effective in the solution of Rh, Os, Pt, Au and Pd (22).

The reaction of F_2 with Os and Pt have recently been investigated (23). The formation of PtF_6 and OsF_6 is said to be rapid and complete at low temperatures.

D. Methods of Separation

Methods of separation and purification for large scale operations are described by Gilchrist (3). Analytical procedures for the accurate determination of Au and the Pt metals are described in detail by Hillebrand, Lundell, Bright and Hoffman (7). Later workers seem to have added little

to the classical procedures given in the references above. A few papers are worth noting however. Pshenitsyn (24) reports the use of $CrCl_2$ for the separation of Rh and Ir. This operation was carried out in 10% HCl and must be done in the absence of atmospheric oxygen. The use of thioacetanilide as a reagent for the separation of Rh from Ir is described by Jackson (25). A trivalent Rh-thioacetanilide complex is precipitated when $CrCl_2$ is added to the soluble trivalent Rh-thioacetanilide complex in 0.2 N HCl solution. Au, Pd and Pt among the precious metals also form insoluble thioacetanilide complexes.

A new method for the preparation of spectrally pure Pt is reported by Chernyaev and Rubinshtein (26). The method required the preparation of Blomstrands salt $[(NH_3)_2(NO_2)_2Cl_2Pt]$ and recrystallization of this compound. Impure Pt sponge is dissolved in aqua regia, converted to chloroplatinic acid and treated with 10% KCl to precipitate K_2PtCl_6. The K_2PtCl_6 is treated with $NaNO_2$ and 20% NH_4OH to give an abundant precipitate of $[(NH_3)_2(NO_2)_2Pt]$. The precipitate is suspended in cold H_2O and Cl_2 bubbled through the solution until the reaction is complete as judged by color change. The resulting salt is crystallized from water and calcined to give spectrally pure Pt. It is claimed that spectrally pure Pt containing no Ir, Pd or Fe can be prepared from Pt containing as much as 2% Pd.

Beamish (4) has reviewed the application of ion exchange and chromatographic procedures to the separation of precious metals. A paper by Butler (27), not mentioned by Beamish, reports the use of a cation exchanger for the separation of base metal contaminants from Pt-Rh solutions. The adsorption of base metal impurities varies with the free acid concentration and is about 98.5% efficient. The precious metals in the effluent are recovered by the addition of hydrazine which converts

them to the metal. If the metal blacks are treated with E.D.T.A. the efficiency of separation is increased to 99.5%.

MacBryde (28) has reviewed solvent extraction procedures. The compounds extracted by solvents include halogen complexes, oxides, complexes with $SnCl_2$ and organic complexes. The choice of method is usually governed by the environment of the metal which is being separated and by the subsequent operations in the overall analysis.

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