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# The Separation of Gold, Platinum, and Palladium by Reversed-phase Partition Chromatography

Ikuko AKAZA, Toshiyasu KIBA and Tomoe KIBA

*Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa*

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For the separation of gold, platinum(IV), and palladium, and for the isolation of gold from other metals, the reversed-phase partition chromatography has been used as a column process in which TBP is adsorbed on Daiflon(polytrifluorochloroethylene moulding powder) as the stationary phase and hydrochloric acid, as the mobile phase. The separation of the above three noble metals was successfully achieved by carrying out the elution with 3—4 N HCl, and the isolation of gold was attained well of itself by virture of the fact that gold is tightly retained on the column and is only released by letting concentrated $HNO_3$ flow through the column. The concentration and separation of gold from various solutions, such as in the presence of a large amount of iron(III) or in the presence of 19 common metals and the above three noble metals, was achieved only by allowing gold to be retained on the column and allowing ther others to flow down with a 1 N HCl eluting solution. The behavior of the three noble metals in batch extraction was also examined under the same condition as in the partition chromatography employed here; a similarity was observed between the column and the batch extraction. The principal extracted species of the noble metals might be assumed to be a hydrated and solvated ion pair, such as $H(H_2O)_nTBP_6^+\cdot HPtCl_6^-$.

Reversed-phase partition chromatography has been used by many investigators for the separation of various metal ions. The present authors have also carried out investigations of the reversed-phase partition chromatography (not the ion-exchange) of alkali metals,[1] alkaline earth metals,[2] and hexacyanoferrate(II) and (III)[3] and established that the technique is very useful for the mutual separation of ions. In this work, reversed-phase partition chromatography was applied to the separation of gold, platinum, and palladium from each other, and to the isolation of gold from various metals. These three noble metals are the elements which come into the soluble fraction in the process of the treatment of the noble metals with aqua regia, which is still one of the best techniques available for the separation of the platinum group.[4]

With respect to the work on the reversed-phase chromatography of the noble metals, there have been descriptions by Hu *et al.*[5,6] on the chromatography using filter paper impregnated with TBP and a developing solution of hydrochloric acid. The quantitative separation of the noble metals has never been attained by means of reversed-phase partition column chromatography.

The chromatographic investigations previously performed by the present authors[1–3] have indicated that much valuable information on the chromatographic separation could be obtained from the extraction behavior of the element in question in the same system. Many articles dealing with the solvent extraction of noble metals have been cited in a review[7] and other papers; the TBP-HCl extraction system was preferred in this study as the one most suitable for a good separation of the three metals. This selection seemed to be pertinent in respect to the results of the reversed-phase partition paper chromatography by Hu[5,6], the $R_f$-spectra of many metals on reversed-phase thin-layer chromatography with TBP,[8] and the distribution data on the solvent extraction of the three metals in the TBP-HCl system[9] and in the counter-current extraction.[10]

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[2] I. Akaza, *ibid.*, **39**, 980 (1966).

[3] I. Akaza, T. Kiba and M. Taba, *ibid.*, **42**, 1291 (1969).

[4] I. M. Kolthoff and P. J. Elving, "Treaties on Analytical Chemistry," Part II. Vol. 8, Interscience Publishers, New York and London (1963), p. 384.

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[9] T. Ishimori, K. Watanabe and E. Nakamura, This Bulletin, **33**, 636 (1960).

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## Experimental

**Reagents and Equipments.** *Daiflon M-300.* Trifluorochloroethylene polymer moulding powder was obtained from the Daikin Kogyo Co., Osaka, Japan. The material was ground with a mixing grinder and sieved; particles of 42—80 mesh were used.

*TBP.* *n*-tributyl phosphate of the reagent grade was washed twice with a 5% sodium carbonate solution of equal volume and then with water to remove any dibutyl- or monobutyl phosphate.

*Metallic Salts Solutions.* The solutions were prepared from metallic gold, palladium chloride, and chloroplatinic acid hexahydrate, all of analytical-reagent grade respectively.

*Tracers.* $^{195}$Au, $^{113}$Sn, $^{203}$Hg, $^{59}$Fe, $^{207}$Bi, $^{110m}$Ag, $^{65}$Zn, $^{124}$Sb were employed as tracers of the stable ions.

The other chemicals used were all of an analytical grade.

*Column.* The glass tube had a diamter of 0.92 cm and a length of 30 cm, and was equipped with a fritted glass disk at one end.

*Measurement of Radioactivity.* A scintillation counter, Kobe Kogyo Co., Model EA-14, with a NaI(Tl) crystal, and a Model SA-2 scaler were employed.

The other pieces of equipment such as a fraction collector and a spectrophotometer, were all those in ordinary use.

*Organic Solvent for the Stationary Phase of the Column as Well as for the Batch Extraction.* The TBP used in each experiment had been pre-equilibrated with hydrochloric acid of the same concentration as that of the acid used for the mobile phase in the column or the aqueous phase in the batch. No such diluent as benzene was added except when it was necessary to vary the TBP concentration of the organic phase.

*Eluting Solution of the Column Extraction.* Hydrochloric acid of various concentrations and concentrated nitric acid were used as the eluting solutions; they had been pre-equilibrated with TBP or TBP-benzene. These solutions were also used in the batch-extraction experiments as an aqueous phase.

*Test Solution.* Hydrochloric acid of various concentrations and of varying volumes, each portions containing 0.5 mg of a metal ion, was prepared; in this case, the concentration of hydrochloric acid was adjusted to be the same as that of the eluting solution for the column or the aqueous phase in the batch extraction.

**Experimental Procedure.** *The Stationary Phase of the Column.* A 5.5-g portion of Daiflon was placed in an Erlenmyer flask fitted with a stopper, and 6 m*l* of the organic solvent, prepared as above, was poured onto it. This volume of the organic solvent had been established previously to be an adsorbable amount of TBP on Daiflon.[3] The stoppered flask was shaken gently by hand until the content became homogeneous; then it was left standing over three hours. The product was then slurried with an eluting solution and packed in a column tube by gentle pressing with a glass rod every time a small portion of the slurry was added. After the column had then been washed with an eluting solution with the acidity same as the test solution, a 5 m*l* or 3 m*l* portion of the test solution was allowed to soak into the column bed at the rate of about 0.25 m*l*/min. The elution was carried out with a suitable eluting solution at the rate of 0.5 m*l*/min. The effluent was collected in suitable fractions, and the metal ion in each fraction was determined. In this study the colorimetric methods of platinum with $SnCl_2$ and of palladium with dimethylglyoxime were adopted. The gold was estimated colorimetrically with rhodamine B or radiometrically with $^{195}$Au. When radioactive tracers, involving gold and other elements; were employed, all being mixed together, the nuclide separated in a fraction was identified by taking its $\gamma$-ray spectra with a 200-channel pulse-height analyzer, not only by counting the radioactivity with a scintillation counter.

## Rusults and Discussion

**Preliminary Experiments.** *Behavior of Au, Pt, and Pd in the Batch Extraction.* The distribution behavior of the three metals was examined between the TBP adsorbed on Daiflon and an aqueous solution, not by means of liquid-liquid extraction between TBP and hydrochloric acid, in search of good conditions for separation. In this case, 4.6 g of Daiflon, adsorbing 5 m*l* of TBP, and 15 m*l* of a hydrochloric acid solution containing 0.5 mg of the metal were employed. The contents of a stoppered flask were gently shaken for a while, set aside a while, then poured them on a coarse glass filter. The aqueous solution coming through the filter was submitted to the determination of the metal ions in it. Gold shows a very high distribution in TBP on Daiflon, so this measurement method can not be applied in the case of gold. Therefore, the distribution ratio of gold was estimated only by an

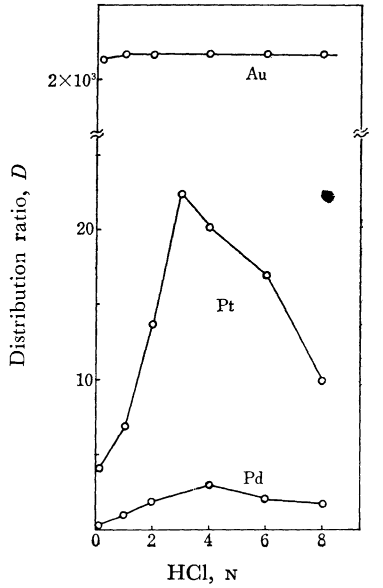

Fig. 1. The distribution curves of Au, Pt and Pd in the batch extraction.

Pt, Pd: Batch extraction with TBP-Daiflon
Au: Liq.-liq. batch extraction
TBP: 5 m*l*, Aqueous solution: 15 m*l*, Metal: 0.5 mg

ordinary liquid-liquid extraction between 5 m*l* of TBP and 15 m*l* of the aqueous solution. The results are shown in Fig. 1, from which the optimum condition for the mutual separation of the metals may be seen to be in the range of acidity between 3 to 4.

*Chromatographic Behavior of Individual Ions.* With 3 m*l* of a test solution containing only one of the three metals, the chromatographic behavior of the metal ion was examined by means of elution with hydrochloric acid of various concentrations. The results are shown in Fig. 2, where gold is omitted because of its absence in the effluent. Gold showed so high a distribution in TBP on the column that, even after as much as 1 *l* of the eluting solution had passed through, gold did not appear in the effluent. Thus, the separation of the three metals seemed to be attained satisfactorily by elution with 3—4 N hydrochloric acid.

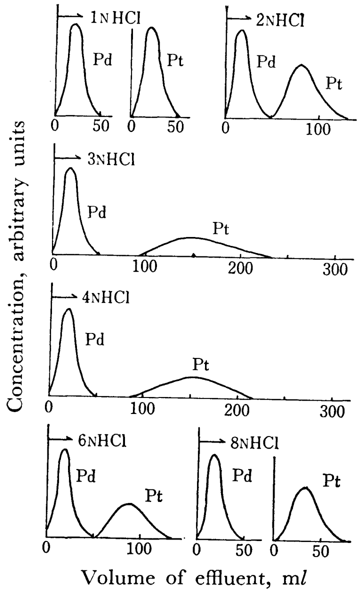

Fig. 2. The chromatographic behavior of individual ions. Gold was not eluted even after 1 *l* of eluting solution flowed.

Test solution: 3 m*l* containing metal of 0.5 mg.

**Separation of Au, Pt, and Pd in the Presence of Fe(III).** With the help of the results obtained for an individual ion, the separation from a test solution containing all three metals was carried out by elution with 3—4 N hydrochloric acid. Gold, which was tightly retained on the column, could be at last removed from the column by passing through concentrated nitric acid. The features of this elution scheme are shown in Fig. 3. Some interesting applications of this separation are also shown in Fig. 4, in which: (a) the quantity of each metal is in proportion to its Clarke number, (b) there is separation from a test solution of large a volume such as 50 m*l*, and (c) there is the separation of the three noble metals in the presence of iron(III). In the last case, iron(III) could be eluted with 1 N hydrochloric acid after the elution of Pd and Pt with 3.5 N hydrochloric acid. This seems to be very noticeable because

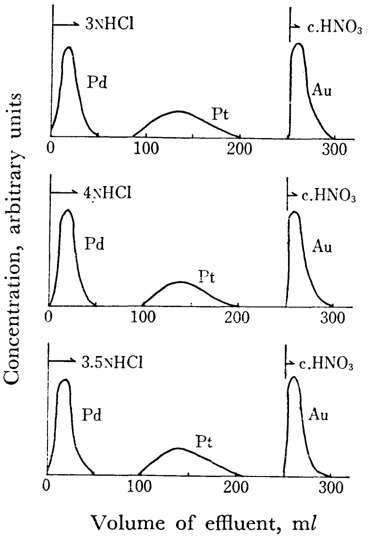

Fig. 3. The separation of Au, Pt and Pd from a mixed solution.

Test solution: 5 m*l* containing 0.5 mg of each metal.

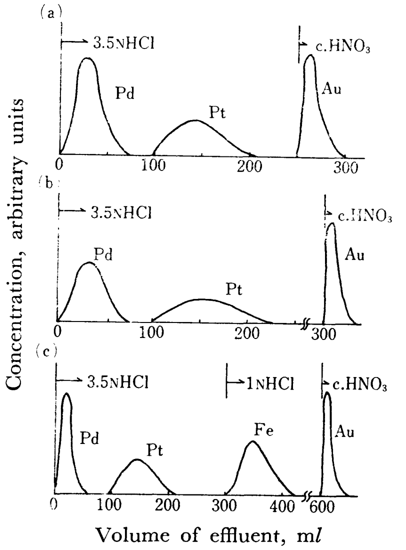

Fig. 4. The separation of Au, Pt and Pd from a mixed solution.

(a) Pd: 1 mg——Test soln.: 5 m*l*; Pt, Au: 0.5 mg
(b) Test soln.: 50 m*l*——Metal: 0.5 mg each
(c) In presence of Fe——Test soln.: 5 m*l*; metal: 0.5 mg each

iron(III) is an ion which has a high distribution ratio in an ordinary TBP-HCl extraction system and is apt to exist in various samples as an impurity. All in the above experiments, gold could not be eluted by elution with hydrochloric acid, but instead was retained on the column tightly; therefore, a minute amount of gold could be successfully concentrated and separated by this column technique. As an example, 200 m*l* of a test solution containing 0.5 mg of gold and 6 g of iron(III) was adjusted to 1 N of a hydrochloric acid solution and allowed to flow through the column; followed by elution with 500 m*l* of 1 N hydrochloric acid. The iron(III) in the effluent was determined colorimetrically by the thiocyanate method, and gold-(III) was detected by the tracer method with $\gamma$-counting. It was found that the gold was retained on the column completely; was concentrated and separated from a large amount of iron(III). With the elution of concentrated nitric acid, the gold could also be recovered quantitatively in the effluent. This method might be used in the chemical analysis of gold-plating materials.

**Separation of Gold from Many Other Metals.** To confirm the above use of this method, 50 m*l* of a test solution of 1 N hydrochloric acid was prepared, in which 0.5-mg portions of each of the following metal ions were put: Sn(IV), Hg-(II), Fe(III), Zn, Bi, Ag, Co, Sb(III), Cd, Cu, Ni, Al, Mn, Pb, Ca, Sr, Ba, Mg, Pd, Pt, and Au(III). The test solution was soaked on the column, and then 950 m*l* of 1 N hydrochloric acid eluting solution was passed through. After examining all of the fractions of the effluent, it was found that only two metal ions, Au(III) and Sn(IV), were retained on the column. Then, Sn(IV) was released from the column by passing through 300 m*l* of 1 N nitric acid, and there after. Au was eluted by concentrated nitric acid. From the distribution data of the liquid-liquid extraction in the TBP-HCl system, it had been established that none of the metal ions except Sn(IV), Hg(II), Fe(III), Bi(III), Ag, Zn and Sb(III) participated in the extraction,[9] therefore, in this study the radioactive tracers of the latter seven metals and Au(III) were preferentially employed in order to detect the behavior of these metal ions. Thallium(III) is only the ion, the distribution ratio of which is so close to that of Au(III) in the TBP-2 N HCl extraction, but it was omitted in this experiment because of the lack of its $\gamma$-emitting tracer. It seems that this separation method can be used for various purposes, such as the milking of $^{195}$Pt from $^{195}$Au and the preparation of carrier-free $^{199}$Au from irradiated platinum. The applications will be described elsewhere.

**The Distribution Ratio in the Chromatographic Column and That in the Batch Extraction of the Same System.** The distribution ratio in the column extraction can be calculated by the following equation by putting the data of the elution into it: $D=(E-F)/B$, where $E$ is the volume of the effluent before the emergence of the peak of the curve; $B$, the volume of the stationary phase, and $F$, the volume of the mobile phase. In the present column, $B$ was 6 m*l* and $F$ was 6.4 m*l*; 0.5 mg of platinum was loaded on and eluted with hydrochloric acid of varying concentrations. The TBP concentration of the stationary phase was also varied by diluting the organic solvent with benzene.

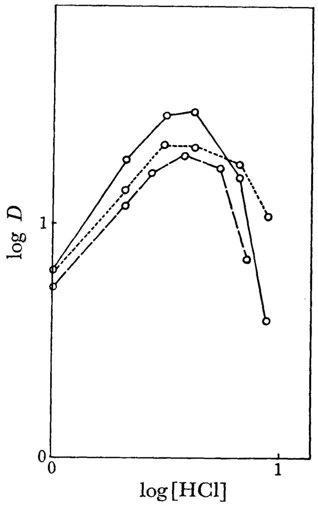

Fig. 5. Dependence of the distribution ratio of Pt on the concentration of HCl.

Solid line: Column chromatography
Dotted line: Batch extraction with TBP-Daiflon
Dashed line: liq.-liq. batch extraction

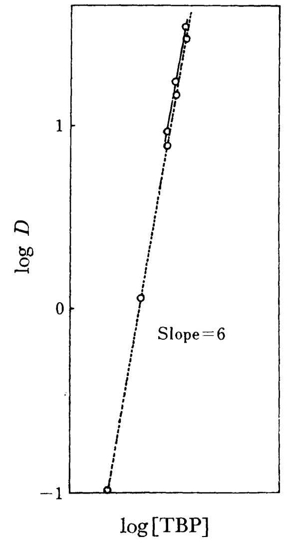

Fig. 6. Dependence of the distribution ratio of Pt upon the concentration of TBP.

Solid line: Column method
Dotted line: Batch method

Thus, the dependence of the distribution ratio on the hydrochloric acid concentration of the aqueous phase, log *D* *vs.* log [HCl], and that on the TBP concentration of the organic phase, log *D* *vs.* log [TBP], were found to be as shown in Fig. 5 and Fig. 6 respectively. Along with these experiments, two other extractions were carried out by the batch system: a liquid-liquid extraction between each 5-m*l* portin of the aqueous and the organic phases, and a liquid—TBP on Daiflon extraction between 15 m*l* of the aqueous phase and 5 m*l* of the organic phase held on the adsorbent. From the distribution data thus obtained, log *D* *vs.* log [HCl] and log *D* *vs.* log [TBP] were also obtained; they are shown in Fig. 5 and Fig. 6. From the figures, it can be seen that platinum behaves similarily in all the above three extraction processes, and the chromatographic data can contribute to a knowledge of the distribution behavior of the metal ion. The lowering of the distribution ratio in the range of higher acid concentrations in Fig. 5 raises some questions to the extraction mechanism and the extracted species, but it is assumed to be caused by the competition between hydrochloric acid and the platinum ion in the extraction with TBP. Therefore, when the concentration of the chloride ion was fixed at 4 M by adding lithium chloride, the lowering of the distribution disappeared and log *D* *vs.* log [HCl] showed a straight line with a slope unity, as shown in Fig. 7.

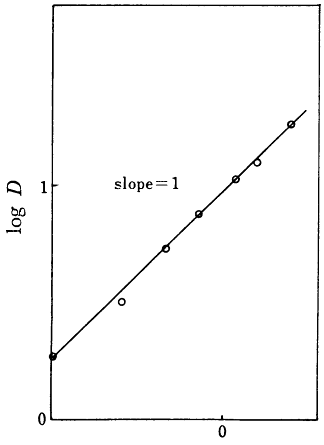

Fig. 7 Dependence of distribution ratio of Pt on the concentration of HCl.

$[Cl^-]$ is adjusted to 4 M with LiCl

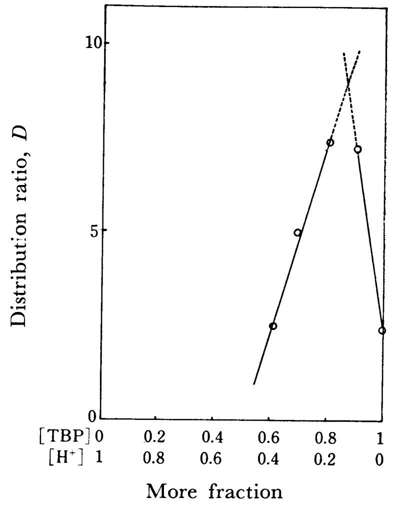

Fig. 8. Distribution of Pt under continuous variation of [TBP] and [HCl].

$[Cl^-]$ is kept at 4 M with LiCl

[TBP] and [HCl] are 0—3.66 M each

At last, it may be of interest to establish the extracted species of platinum in this TBP-HCl system since the species in the organic phase has not been stated anywhere. A continuous-variation method was applied to the extraction system with two variables of TBP and hydrochloric acid concentrations with a fixed concentration of 4 M lithium chloride in the aqueous phase. As is shown in Fig. 8, the maximum distribution appears at the [H] : [TBP] ratio of 1 : 6; this fact agrees well with the results shown in Figs. 5, 6, and 7. In consequence of this distribution study, though it was far from ideal, the main extracted species may be assumed to be an ion-associated one, $H(H_2O)_nTBP_6{}^+HPtCl_6{}^-$, especially in view of a previous paper concerning the extraction of metals and mineral acids,[11] and Ref. 8.

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[11] Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).