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PROPERTIES OF AN ION EXCHANGE RESIN WITH HIGH SELECTIVITY FOR GOLD

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By T. E. Green and S. L. Law

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PROPERTIES OF AN ION EXCHANGE RESIN WITH HIGH SELECTIVITY FOR GOLD

by

T. E. Green[1] and S. L. Law[1]

ABSTRACT

The Bureau of Mines Heavy Metals Program emphasizes the need for improved analytical methods for gold determination. A commercially available ion exchange resin with high selectivity for gold was investigated as a potential method to collect gold from solution. The resin was found to quantitatively collect gold from acid solutions over a wide range of acid concentrations. Common metals were not collected by the resin nor did they seriously interfere with the collection of gold. X-ray spectrographic and neutron activation methods based on the use of papers containing this resin are proposed.

INTRODUCTION

A paper by Koster and Schmuckler of the Israel Institute of Technology[2] disclosed information on the separation of noble metals from base metals by means of a new chelating resin described as a styrene-divinyl-benzene copolymer into which a resonating amino group has been introduced. They reported the quantitative collection of Os^{+8}, Rh^{+3}, Ir^{+4}, Pd^{+2}, Pt^{+4}, and Au^{+3} and gave data to show that the presence of Ni^{+2}, Cu^{+2}, and Fe^{+3} had little or no adverse effect on the collection of Pt^{+4}. Their statement that 1 gram of the dry resin had a capacity for 1.1 grams of gold was of particular interest.

Because of its potential importance in the Bureau of Mines Heavy Metals Program, additional tests were performed to obtain more detailed information on the use of this resin[3] in analytical operations.

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[1]Research chemist, College Park Metallurgy Research Center, Bureau of Mines, College Park, Md.

[2]Koster, G., and G. Schmuckler. Separation of Noble Metals From Base Metals by Means of a New Chelating Resin. Anal. Chim. Acta, v. 38, 1967, p. 179.

[3]Only one resin of this type could be found at the time of these investigations. It was obtained from the Ionac Chemical Co. under the trade designation SRXL. Its use in these tests does not imply endorsement by the Bureau of Mines.

EXPERIMENTAL PROCEDURE

The resin (minus 16 plus 50 mesh) was used as purchased. Solutions of known gold concentration were prepared from high-purity gold foil. All reagents and inorganic salts of the common metals were reagent grade. Gold radiotracer solutions were prepared from carrier-free ^{195}Au with a radiochemical purity of greater than 99 percent.

Ion exchange column tests were performed in a glass chromatographic tube with a 1-cm ID. The resin was supported in the column by means of a fritted glass plate. A glass delivery tube was connected to the lower end of a chromatographic tube by means of a short piece of rubber tubing. A screw clamp on this rubber tubing was used to control the flow rate from the column at approximately 2 ml/min. A 5-cm resin column was used in the initial acid studies; for other tests a 3-cm column of resin was used. A separatory funnel mounted above the chromatographic column served as a reservoir for the test solution and was used to maintain the test solution at a constant level in the chromatographic tube until all the test solution had passed through the resin. All test solutions contained sufficient ^{195}Au to provide good counting rates, and, except where otherwise noted, contained 20 μg/ml of inactive gold. A few drops of concentrated nitric acid were added to the ^{195}Au tracer solution and to the solutions of common metals to prevent reduction of gold by trace impurities in the chloride salts from which these metal solutions were prepared. The test solutions were diluted to 250 ml before they were passed through the ion exchange column.

An aliquot of the original test solution and an aliquot, or aliquots, of the column effluent were taken for counting of gamma activity. Counting was done by means of a well-type NaI (Tl) detector and single channel analyzer. The percentage of gold retained by the resin was calculated from the gamma activities of the initial test solution and the effluent:

$$\text{Au retained, percent} = 100\left(1 - \frac{A_2}{A_1}\right),$$

where A_1 = activity of the initial test solution

and A_2 = activity of the effluent.

Tests involving the use of ion exchange resin-loaded paper disks were performed using the filtering apparatus and technique described by Campbell, Spano, and Green.[4] The resin-loaded disks used in these tests were prepared for the authors by the H. Reeve Angel Co.

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[4] Campbell, W. J., E. F. Spano, and T. E. Green. Micro and Trace Analysis by a Combination of Ion Exchange Resin-Loaded Papers and X-Ray Spectrography. Anal. Chem., v. 38, July 1966, p. 987.

RESULTS

Effect of HCl and HNO_3

In analytical methods, aqua regia is the preferred reagent for dissolving gold. Therefore, initial tests were performed to determine the effect of HCl, HNO_3, and mixtures of HCl and HNO_3 on the retention of gold by the resin. The results of these tests are given in table 1.

TABLE 1. - Collection of gold in the presence of HCl and HNO_3

HCl, normality	HNO_3, normality	Gold retained by resin, percent
0.12	0	98.7
.6	0	99.6
1.2	0	98.9
2.4	0	99.2
0	1.6	99.1
.6	.16	99.2
1.2	.48	99.7
2.4	.8	99.9-95.7

At the highest concentration of mixed HCl and HNO_3, a breakthrough was observed (fig. 1) after approximately 30 minutes' exposure of the resin to the mixed acid. Prior to this breakthrough, small aliquots of the effluent showed

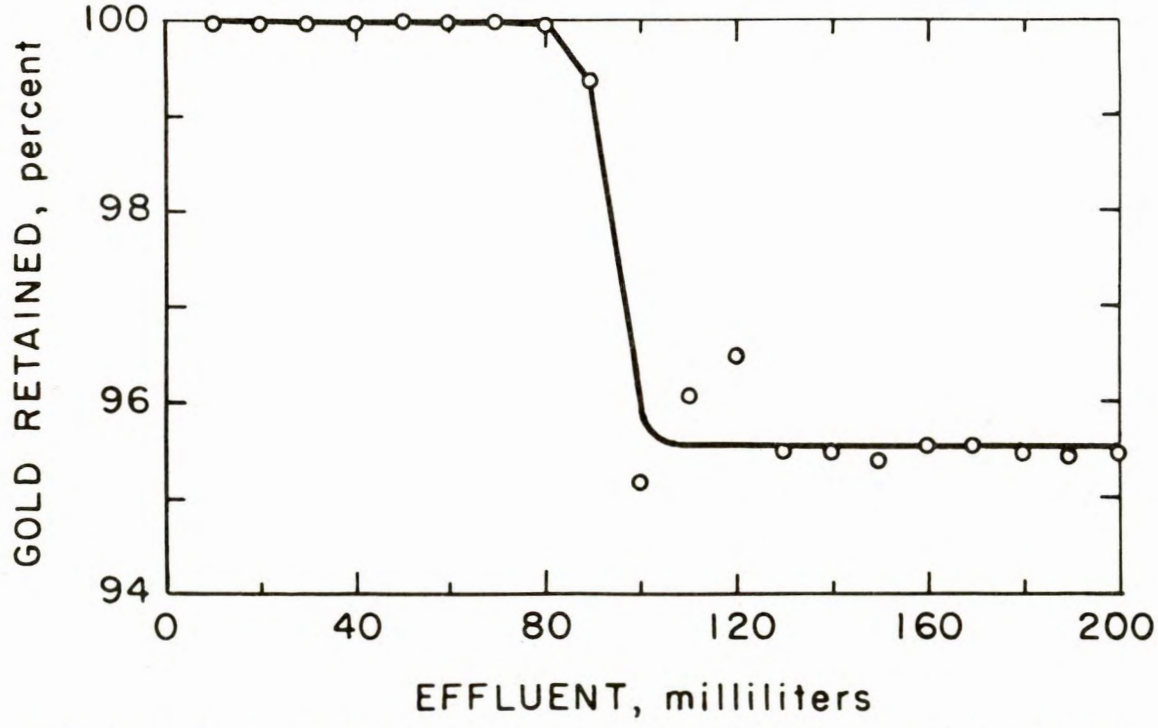

FIGURE 1. - Effect of $HCl+HNO_3$ on the Collection of Gold (2.4 *N* HCl+0.8 *N* HNO_3).

that essentially all the gold was collected from the solution. After the breakthrough, gold retention dropped to between 95 and 96 percent and remained at that level until the end of the test. During this test, darkening of the resin was observed. By the time the breakthrough point was reached, the entire column of resin had turned dark brown.

At higher concentrations of aqua regia, the resin is slowly attacked and its ability to quantitatively collect gold is destroyed. The following test was performed to determine whether the gold initially collected by the resin was retained after prolonged treatment with 50 percent aqua regia (3 volumes HCl, 1 volume HNO_3, 4 volumes H_2O). A 1-gram portion of the resin was continuously stirred in a 50-percent aqua regia solution containing 20 mg of inactive gold and ^{195}Au tracer. The percentage of gold remaining in the solution was periodically determined. The results given in table 2 show that the collection of gold is slow and not quantitative, but that the gold which has been collected is retained by the resin. In practical applications it would not be necessary to work at such high acid concentrations.

TABLE 2. - Effect of 50 percent aqua regia on the collection of gold

Time of contact, hr	Gold remaining in solution, percent
1/12	53.0
3/4	14.1
1	11.3
1-1/2	9.1
3	6.6
4	5.9
6	5.2
24	4.2
30	4.6
96	4.5

Effect of Common Metals

Koster and Schmuckler reported that nickel, cobalt, and iron had little effect on the collection of platinum by the resin. They did not report the effect of common metals on the collection of gold. In our tests, 100-ml portions of solutions containing 20 mg/l of gold and a wide range of concentration of the common metals were adjusted to 1.2 N with HCl and passed through 3-cm-long columns of the resin at the rate of 3 ml/min. The results are given in table 3.

Retention of gold by the resin was essentially quantitative in the presence of all the common metals except copper. Because the effect of copper was different, the test in the presence of 150 g/l of copper was repeated under the same conditions except that the gold was determined in small consecutive fractions of the eluate. The results of this test, shown in figure 2, indicate that the quantity of gold retained gradually decreased and that no sharp breakthrough occurred.

TABLE 3. - Gold retained in the presence of individual common metals, percent

Added metal, g/l	Added metal							
	Al	Ca	Cu	Fe	K	Ni	Pb	Zn
1.....	99.8	100.0	99.8	99.9	-	100.0	99.9	100.0
5.....	99.9	99.8	99.8	99.8	-	99.9	(1)	99.9
10.....	99.9	100.0	99.8	99.9	-	99.9	(1)	99.9
50.....	99.2	99.9	99.5	99.6	-	99.8	(1)	100.0
100.....	(1)	99.7	98.5	99.8	100.0	99.2	(1)	99.7
150.....	(1)	(2)	97.2	(2)	-	(2)	(1)	-
200.....	(1)	(2)	96.3	(2)	-	(2)	(1)	99.5

[1] Limited solubility of the chloride prevents preparation of this concentration.

[2] Resin floats because of high specific gravity of the test solution.

The effect of combinations of common metals on the retention of gold was determined using the same experimental technique. The results given in table 4 indicate that the combined effect of these metals is greater than the effect of any single metal. It should be noted that these interelement effects were studied at concentrations that greatly exceed those anticipated in practical applications. If such high concentrations were encountered, simple dilution would restore the ability of the resin to quantitatively collect gold.

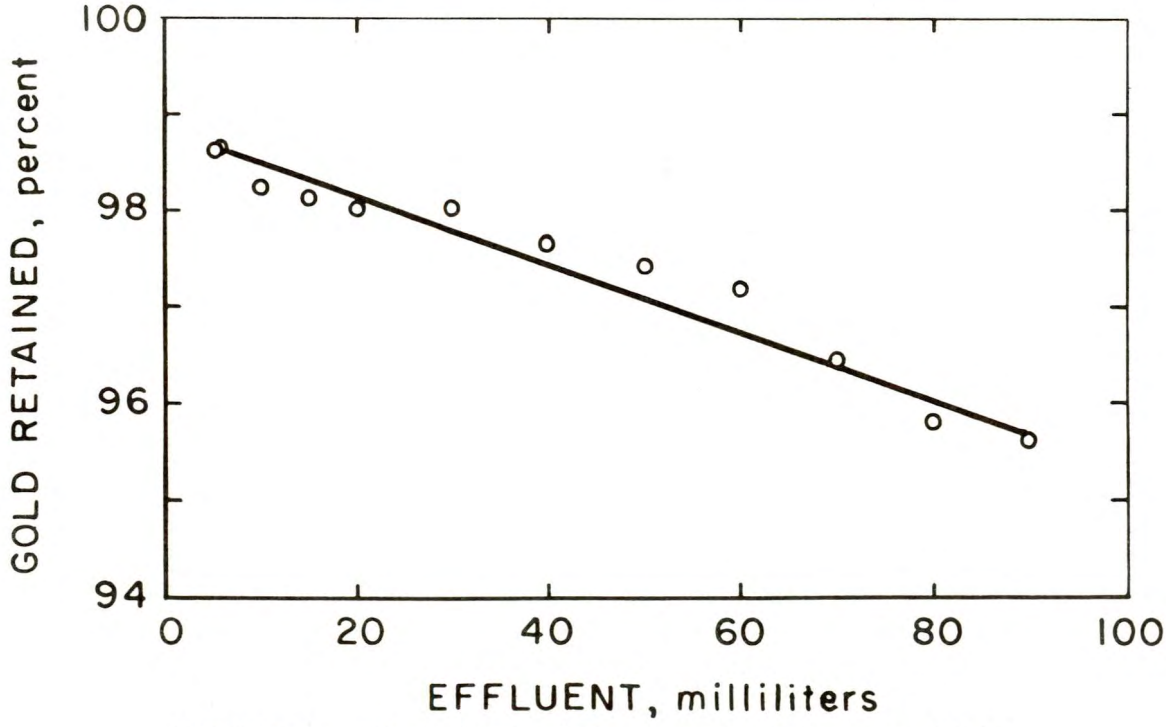

FIGURE 2. - Effect of 150 g/l Copper on the Collection of Gold.

TABLE 4. - Gold retained in the presence of mixtures of common metals

Gold retained by resin, percent	Added metal, g/l					
	Al	Ca	Cu	Fe	Ni	Zn
99.8.....	1.25	2.5	5	2.5	2.5	5
99.6.....	2.5	5	10	5	5	10
98.0.....	5	10	20	10	10	20
94.8.....	6.25	12.5	25	12.5	12.5	25
93.3.....	8.3	16.7	33.3	16.7	16.7	33.3

Use in Alkaline Cyanide Solutions

Koster and Schmuckler stated, "The noble metals must be adsorbed on the resin in an acidic medium, as in an alkaline environment, hydrolysis of the metals as well as of the amine groups of the resin takes place." Tests which we performed showed that cyanide solutions containing either NaOH or CaO as the alkaline constituent slowly attack the resin. However, during initial contact between 0.25 percent cyanide solution and the resin, gold is nearly quantitatively collected by the resin. The gold which has been collected is retained by the resin after the capability of the resin to collect gold has been destroyed.

Table 5 shows the results of a test in which a 1-gram portion of the resin was added to a flask containing 50 ml of 0.25 percent NaCN solution in which 1,000 µg of gold and ^{195}Au tracer were dissolved. The flask was shaken periodically, portions of the solution were temporarily removed for counting, and comparison was made with the radioactivity of an identical solution to which no resin had been added.

TABLE 5. - Gold retained by resin in 0.25 percent cyanide

Time of contact, hr	Gold retained, percent
1/60.....	66.1
1/12.....	87.8
1/4.....	97.5
1/2.....	98.9
3/4.....	99.2
1-1/6.....	99.3
43.....	99.4
49.....	99.4
66.....	99.3
138.....	97.4
166.....	96.8
310.....	96.2

An ion exchange column test was performed using an alkaline 0.25 percent solution of NaCN containing 20 mg/l of gold and ^{195}Au radiotracer. The flow rate through the 10- by 30-mm column was adjusted to 2 ml/min. The gold

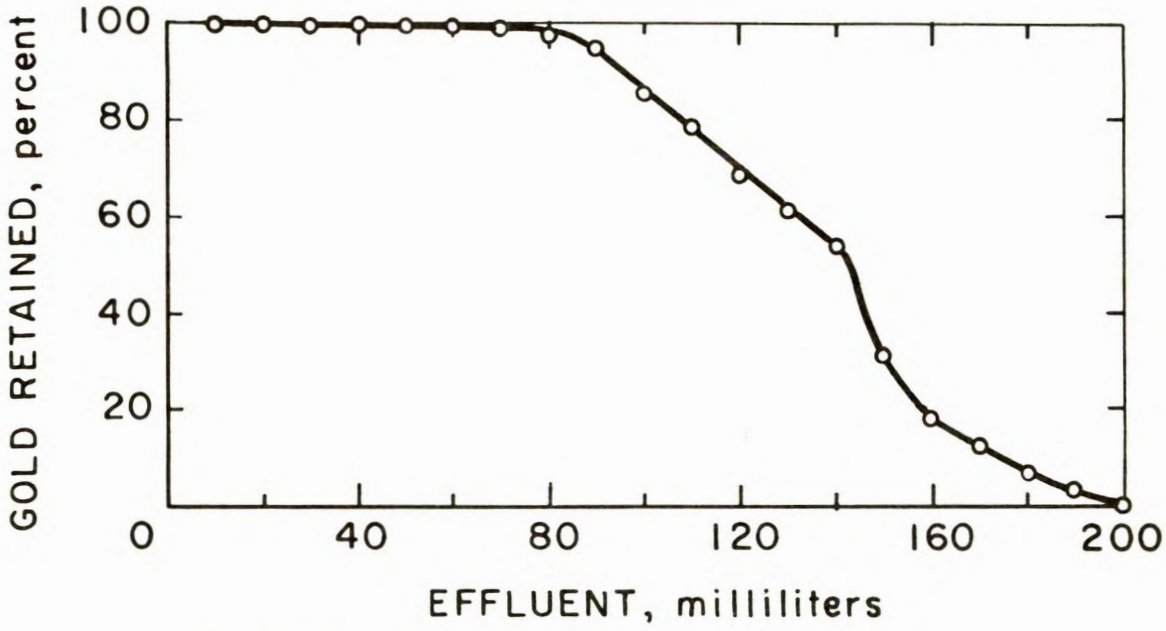

FIGURE 3. - Effect of Cyanide on the Collection of Gold.

content of successive small fractions of the effluent were determined by gamma counting. The results are shown in figure 3.

During the passage of the first 100 ml of solution through the column, a yellow discoloration of the effluent was observed indicating a reaction between the resin and the alkaline solution. After the passage of the first 100 ml, the yellow discoloration was no longer observed. Even though the resin rapidly lost its ability to retain gold at this point, no tendency was observed for the resin to lose the gold it had already collected.

Ion Exchange Resin-Loaded Papers for Analytical Use

Thin disks, 3.5 cm in diameter, consisting of 50 percent cellulose and 50 percent resin were used to explore the possibility of collecting gold for determination by X-ray spectrography or neutron activation. Previous work with similar disks containing nonselective ion exchange resin[5] had shown that such disks provided an excellent medium for collecting trace metals for X-ray spectrographic determination. The efficiency of resin-loaded disks for collecting gold was evaluated by filtering 50-ml portions of 5 percent HCl solutions containing 500 μg of ^{197}Au and tracer quantities of ^{195}Au. Gamma counting of the filtrates showed that one filtration resulted in the collection of 93 percent of the gold; five to seven passes of the solution through the paper resulted in collection of 99.5 percent of the gold. A similar test using 0.25 percent NaCN solutions resulted in less than 10 percent of the gold being collected. For analytical purposes cyanide solutions could be converted to chloride solutions from which the gold is quantitatively collected. X-ray spectrographic sensitivity was determined on 3.5-cm disks of this paper on

[5]Work cited in footnote 4.

which 500 µg of gold had been collected. Using a tungsten target tube at 50 kv and 40 ma, a sensitivity of 2.2 counts per second per microgram above a background of 300 counts per second was obtained. Fifty micrograms of gold on a 1.0-cm-diam disk produced a sensitivity of 6.5 counts per second per microgram above a background of 140 counts per second.

In previous ion exchange column tests, the resin had been shown to be highly selective for gold in the presence of large quantities of common metals. Additional tests were performed to determine the effect of common metals on the collection of gold by the ion exchange resin-loaded paper disks. The experimental conditions and results of these tests are given in table 6. The percentage of gold retained on the disks was determined by measuring the activity of the ^{195}Au in the filtrate. Other tests were performed under the same conditions as in test 3 of table 6, except that the volume of the solution was increased. Results are shown in table 7.

TABLE 6. - Effect of common metals on the collection of gold by resin-loaded disks

Test	1	2	3
Gold added, µg Au+^{195}Au.....	500	500	500
Total Cu+Fe+Ni+Zn in ratio of 1:1:1:1, g.....	0	2	5
Volume of solution, ml.....	50	50	50
Gold retained,[1] percent:			
1st disk.....	99.5	95.8	72.2
1st+2d disks.....	100.0	100.0	92.7
Metals observed in X-ray scan of disk:			
Copper.....	Negligible	Negligible	Small Kα peak
Iron.....	Small Kα peak	Small Kα peak	Small Kα peak
Nickel.....	Negligible	Negligible	Negligible
Zinc.....	Negligible	Negligible	Negligible

[1]Solutions filtered 6 times through each disk.

TABLE 7. - Effect of solution volume and common metals on the collection of gold by resin-loaded disks

Volume of solution, ml	Gold collected, percent	
	1st disk	1st+2d disks
50.....	62.5	91.0
100.....	74.2	94.0
250.....	78.0	98.8
500.....	83.3	-

Although increasing the volume of the solution reduced the interference of the common metals, the filtering rate of 10 ml/min places a limit on the volume which can be conveniently used.

These results show the advantage of using ^{195}Au as a collection monitor. For analytical purposes, the collection of gold need not be complete as long as the percentage of collection is known. The small amounts of the common metals collected caused no interference in the measurement of the L_{β_1} X-ray peak of gold.

Greater sensitivity can be obtained if the gold collected on the disks is determined by neutron activation. During activation, the naturally occurring ^{197}Au from the sample is converted to ^{198}Au with a gamma peak at 0.412 mev. The ^{195}Au, which has a gamma peak at 0.130 mev, is essentially unaffected by the neutron flux. Gamma counting over these two energy ranges provides a means to determine the gold content of the original sample. Standard disks containing known quantities of ^{197}Au and ^{195}Au, and test disks containing ^{197}Au collected from weighed quantities of Bureau of Mines reference ore plus known quantities of ^{195}Au were sent to Gulf General Atomic for neutron activation and gamma counting. A linear relationship between gamma intensity and amount of gold added was obtained over the 0.1 μg to 1.0 μg range of these tests.

A major advantage of collecting gold in the presence of ^{195}Au monitor prior to neutron activation is the elimination of high levels of activity which are produced if the entire sample is activated. A technical publication describing both the X-ray spectrographic and neutron activation methods is now being prepared.

CONCLUSIONS

An ion exchange resin was found to quantitatively and selectively collect gold from acid solutions over a wide range of acid concentrations. Common metals at high concentration are not collected by the resin and they do not seriously interfere with the collection of gold. Alkaline cyanide solutions gradually destroy the capability of the resin to collect gold, but do not cause the release of the gold initially collected.

Ion exchange resin-loaded papers containing 50 percent resin are an excellent medium for collecting gold in a form suitable for X-ray spectrographic and neutron activation determination. In both analytical methods, cyclotron-produced ^{195}Au can be used as a collection monitor.

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