DATE ISSUED: DEC 17 1968

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ORNL-4338

UC-23 – Isotopes-Industrial Technology

EVALUATION OF FOUR METHODS USING GOLD-198 FOR SURFACE LABELING SAND AND A NEW TECHNIQUE FOR SIMULATING MASS LABELING

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ORNL-4338

Contract No. W-7405-eng-26

ISOTOPES DEVELOPMENT CENTER

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Isotopes Division

DECEMBER 1968

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

Procedures for tagging sand with ^{198}Au to be used in the study of sediment transport have been reported but not in sufficient detail to permit their use in obtaining reproducible results or to provide information concerning the characteristics of the labeled sand. Therefore two methods that were reported, one using direct reduction by stannous chloride and the other using displacement of silver with gold, were selected for further study. Two new techniques, based on direct labeling and reduction-displacement by using p-isopropylbenzaldehyde, were devised by the authors. The four methods were compared with respect to overall tagging efficiency and adherence of the gold to the sand after the samples were subjected to water leaching and mechanical abrasion. The most effective method was the one based on direct labeling using p-isopropylbenzaldehyde. This method was also adapted to simulate mass labeling; that is, the sand was labeled in such a way that the number of radiation counts detected per unit weight of sand appeared to be proportional to mass rather than to surface area.

INTRODUCTION

Many experiments have been conducted to obtain information concerning the processes in the littoral zone that cause sediment transport. Briefly, these experiments consist in labeling sediment material (sand), placing the material in the area to be studied, and surveying the area to determine movement. A number of different methods for labeling sand have been developed,[1] and are of two general types: surface labeling and mass labeling. Surface labeling consists of coating particle surfaces with resins, paints, and fluorescent dyes, as reported by Kidson and Carr[2] and by Gibert and Cordeiro,[3] or of plating a radioisotope onto

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the grain surfaces (by reduction, etc.), as reported by Petersen[4,5] in his work with ^{198}Au and ^{51}Cr sand tagging. Mass labeling is achieved when the radioactive tag is proportional to the weight of the particle being tagged. One example of mass labeling is the ^{133}Xe-tagging method used in a Radioisotopic Sand Tracer Study program directed by the U. S. Army Corps of Engineers Research Center.[6]

A search of the literature showed that sand studies have been carried out with ^{198}Au; however, the labeled-sand characteristics and the labeling procedures are not detailed. Therefore this study was initiated in order to establish these data and to compare two reported methods, direct reduction by stannous chloride[4] and displacement of silver by gold.[7]

During the study a question arose as to whether the gold was reduced on the surface of the sand particles or reduced in solution and deposited on the sand as a precipitate. Repeated testing indicated that much of the gold is deposited as a precipitate from the solution, thereby causing poor surface adherence. Therefore two new methods were developed based on the use of p-isopropylbenzaldehyde, which is insoluble in water.

Since surface labeling is a function of the surface area of the material to be labeled, inhomogeneous tagging on a weight basis will occur in materials that have a range of particle sizes. Therefore a second purpose for the study was to develop a technique whereby sand fractions can be labeled so that a reasonable approximation to mass labeling can be obtained.

EXPERIMENTAL PROCEDURE

The first two procedures are established methods found in the literature. In the two new methods, procedures C and D, p-isopropylbenzaldehyde was chosen as the labeling agent because of its insolubility in water, which reduces the possibility of the gold being precipitated in solution. In all cases the samples were given further treatment to determine the effect of heating on loss of gold by mechanical abrasion and leaching. Leach and abrasion tests were made on sand tagged by each method described. The tests consisted in stirring the sand with a mechanical stirrer in a beaker of distilled water for 15-min periods until

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loss of activity ceased. The counting was done with a 3-in. NaI crystal detector, which did not require standardization since the results were evaluated on a comparison basis. In all cases the sand was washed with HCl to destroy carbonates.

Procedure A - Direct Gold Reduction by Stannous Chloride

A 30-g sample of sand was treated with an excess of stannous chloride solution. The mixture was slurried and allowed to stand for 5 to 10 min. The excess solution was then decanted, and the sand was washed three times with 10 to 15 ml of water. The sand was dried and ^{198}Au chloride solution was added with stirring. The mixture was allowed to stand for about 30 min and was stirred occasionally. The gold solution was counted before it was added to the sand. After standing, the solution was decanted from the sand. Both the sand and decantate were counted at this point. The sand was dried and divided into three parts. One part underwent leaching tests before any further treatment, one part was heated in a furnace to 500°C before leach testing, and the third portion was heated to 1000°C before any testing.

Procedure B - Displacement of Silver by Gold

A 30-g sample of sand was treated with $SnCl_2$ as described in Procedure A. Silver nitrate solution was added to the sand with stirring. After the $AgNO_3$ treatment the sand was washed once with 10 to 15 ml of water and dried. The dried sand was then treated with ^{198}Au chloride solution and divided as described in Procedure A. Decantation and counting techniques were also the same as those described in the earlier procedure.

Procedure C - Silver Reduction by p-Isopropylbenzaldehyde Displacement of Silver by Gold

A solution of 2.5 to 3 ml of p-isopropylbenzaldehyde in 15 ml of absolute ethanol was added to 30 g of sand. The mixture was allowed to stand for 10 to 15 min and the excess solution was decanted. The sand was washed three times with 10-ml volumes of ethanol and three times with water. After drying, the sand was treated with an excess of Tollen's

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solution, $Ag(NH_3)_2OH$, and allowed to stand for 10 to 15 min. The Ag^+ was deposited onto the sand as metallic silver. Gold-198 chloride solution was added to the sand, which was then divided as before. Decantation and counting were carried out as previously described.

Procedure D - Direct Labeling by p-Isopropylbenzaldehyde

A 30-g sample of sand was treated with a p-isopropylbenzaldehyde-ethanol solution as described in Procedure C. After the sand was washed and dried, it was treated directly with the gold chloride solution. After standing for 30 min, the solution was decanted and the sand was dried. The dried sand was divided into three portions for leach tests as described in Procedure A.

Simulated-Mass-Labeling Technique

Two liters of sand was separated into various particle-size fractions by repeated dry and wet sieving. Each fraction was treated with p-isopropylbenzaldehyde and ^{198}Au chloride solution as described in Procedure D, so that the same amount of ^{198}Au per gram of sand was added. The samples were stirred frequently during a 30-min period and excess solutions were decanted. Both the sand samples and decantates were counted.

EVALUATION OF VARIOUS METHODS

Surface-Labeling Methods

Of the four methods evaluated the most satisfactory one was Procedure D, using p-isopropylbenzaldehyde. The retention of gold was slightly better than with the other methods when the sand underwent no heating or heating at 500°C after labeling. This was due to the fact that the initial gold adsorption by the p-isopropylbenzaldehyde-treated sand was 15 to 20% higher than by any of the other methods. There was no marked difference in the resistance of the gold to leaching and abrasion by any of the four methods. However, when the sand was heated to 1000°C after labeling, Procedure D showed significant advantages over the other three methods.

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The amount of gold removed from the sand by leaching and abrasion was 10 to 20% less than that removed from sand labeled by the other methods.

Procedure B, which involved the reduction of silver by $SnCl_2$ followed by the displacement of silver by gold, was unsatisfactory. The silver was not reduced when it came into contact with $SnCl_2$-treated sand, but instead reacted with the Cl^- ions present to form AgCl. Therefore when gold chloride was added to the sand, the gold was not reduced by the displacement of silver but by the Sn^{2+} ions present.

No change in tagging efficiency was observed when the amount of gold used was varied from 10 mg of gold per 145 g of sand to 1.2 g of gold per 145 g of sand.

The effect of heating the sand to 500°C for about 30 min after labeling was to increase the retention of gold on the sand during abrasion and leach tests. Heating to 1000°C further increased the retention of the gold on the sand. After the sand was labeled and heated to 1000°C it appeared that all the gold was in the elemental state, and washing the sand with dilute HCl removed only a negligible amount of activity.

The methods are compared in Table 1, and the effects of heating and abrasion are given in Tables 2 and 3.

Table 1. Comparison of Labeling Methods[a]

Labeling method	^{198}Au removed from tagging solution, %	^{198}Au retention, %		Overall process efficiency, %
		After 1st leach	After 2nd[b] leach	
Direct reduction by $SnCl_2$	68	63	60	41
Reduction of Ag by $SnCl_2$ displacement by gold	68	63	60	41
Reduction of Ag by *p*-isopropylbenzaldehyde displacement by gold	62	63	58	36
Direct labeling by *p*-isopropylbenzaldehyde	92	65	60	55

[a]Data reported in table represent average values.

[b]No significant loss after third leach test.

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Simulated-Mass-Labeling Technique

It was found that simulated mass labeling could be achieved by sieving the sand into fractions and then labeling each fraction with the same amount of ^{198}Au per gram of sand (Procedure D). When the various labeled fractions were counted and counts per milligram of sand were calculated, the agreement among fractions was within ±20%. With strict surface labeling, there is a deviation of 500 to 600% between the largest and the smallest sand particles. A comparison of the two types of labeling is given in Table 4. In the simulated mass labeling, within each fraction the labeling was found to be uniform. Less than 0.1% deviation existed among the counts per milligram of sand, calculated from 1-min counts on several 1-g samples.

Table 2. Effect of Heating Sand to 500°C After Labeling

Labeling method	^{198}Au removed from tagging solution, %	^{198}Au retention, %		Overall process efficiency, %
		After 1st leach	After 2nd leach	
Direct reduction by $SnCl_2$	68	68	63	43
Reduction of Ag by $SnCl_2$ displacement by gold	68	68	63	43
Reduction of Ag by *p*-isopropylbenzaldehyde displacement by gold	62	73	73	45
Direct labeling by *p*-isopropylbenzaldehyde	92	70	70	64

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Table 3. Effect of Heating Sand to 1000°C After Labeling

Labeling method	^{198}Au removed from tagging solution, %	^{198}Au retention after 1st leach, %[a]	Overall process efficiency, %	Overall retention
Direct reduction by $SnCl_2$	68	82	56	82
Reduction of Ag by $SnCl_2$ displacement by gold	68	82	56	82
Reduction of Ag by *p*-isopropylbenzaldehyde displacement by gold	62	83	51	82
Direct labeling by *p*-isopropylbenzaldehyde	92	98	90	98

[a]There was no significant loss after the second leach.

Table 4. Comparison of Surface- and Simulated-Mass-Labeling Methods

Surface labeling		Simulated mass labeling	
Particle size, μ	Counts per mg	Particle size, μ	Counts per mg
+500	68	+500	462
-500 +297	78	-500 +297	496
-297 +210	103	-297 +250	554
-210 +177	164	-250 +208	578
-177 +149	235	-208 +125	553
-149 +44	312	-125 +88	592

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