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Establishment of
Gold-Quartz Standard GQS-1

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ABSTRACT

A homogeneous gold-quartz standard, GQS-1, was prepared from a heterogeneous gold-bearing quartz by chemical treatment. The concentration of gold in GQS-1 was determined by both instrumental neutron activation analysis and radioisotope dilution analysis to be 2.61±0.10 parts per million. Analysis of 10 samples of the standard by both instrumental neutron activation analysis and radioisotope dilution analysis failed to reveal heterogeneity within the standard. The precision of the analytical methods, expressed as standard error, was approximately 0.1 part per million. The analytical data were also used to estimate the average size of gold particles. The chemical treatment apparently reduced the average diameter of the gold particles by at least an order of magnitude and increased the concentration of gold grains by a factor of at least 4,000.

INTRODUCTION

Frequently, the analyst determining the gold content of geologic materials is unable to estimate analytical precision because homogeneous standards are unavailable. To allow analysts to evaluate the accuracy and precision of procedures for determining the gold content we attempted to prepare a homogeneous standard reference material. We required that the standard be homogeneous with a maximum coefficient of variation of 10 percent for 200-mg (milligram) samples.

A gold-bearing quartz sample was chosen as the starting material because the quartz was readily available in large quantities and contained gold at the parts per million concentration level. When this material proved to be heterogeneous, we treated it chemically in an attempt to redistribute the gold. The concentration of gold in the treated material and the degree of homogeneity were evaluated by two different analytical techniques. Replicate analyses failed to reveal any heterogeneity within the treated material. Variation among the results was nearly equal to the precision of the analytical method. We were also able to derive from the analytical data information concerning the average sizes of gold particles in the treated and untreated materials.

EXPERIMENTAL PROCEDURES

Preparation of the Standard Powder

Some 120 pounds of gold-bearing quartz was collected from a quartz vein near the entrance to the Maryland mine at Great Falls, Md. This material was ground to about 200-mesh size by means of the procedures described by Flanagan (1967). When the powder was found to be heterogeneous with respect to gold, sufficient aqua regia was added to the quartz powder to make a paste. This paste was dried overnight on a steam bath and then was ignited at 900°C. The resulting dry powder was ground in a ball mill, mixed in a stainless steel V-blender, and poured into 120 12-ounce glass bottles. This material was designated gold-quartz standard 1 (GQS-1).

Instrumental Neutron Activation Analysis (INAA)

Splits amounting to 0.2 g (gram) of the gold-quartz standard 1 were divided into two equal portions, which were sealed in separate polyethylene snap-cap vials. Flux monitors were prepared by weighing two drops of a 92-µg (micrograms) Au per ml (milliliter) or one drop of a 5-µg Au per ml standard gold solution onto 100 mg of spectrographic-grade quartz powder. These monitors were also sealed in polyethylene snap-cap vials. The sample and monitor vials were placed in a polyethylene irradiation bucket in a cylindrical array such that the portions of each sample would occupy symmetrical positions in the neutron flux. The array was irradiated 4 minutes in the nuclear reactor at the Naval Research Laboratory, Washington, D.C. At 30-second intervals, the bucket was raised, rotated arbitrarily, and lowered into the reactor to randomize the orientation of the array in the neutron flux.

After irradiation, the ^{24}Na activity was allowed to decay several days, and the ^{198}Au was counted in a 3- by 3-inch NaI well detector. Gamma-spectra were collected in a 256-channel analyzer with a resolution

of 10 Kev (kilo electron volts) per channel over a period of 8 days. The area under the 412-Kev photopeak was measured and the concentration of gold in GQS-1 calculated by the equation:

$$C_{GQS-1} = \frac{A_{GQS-1}}{A_s} \cdot \frac{W_s}{W_{GQS-1}} \cdot \frac{C_s}{\rho_s}, \quad (1)$$

where C_{GQS-1} = concentration of gold in GQS-1 (μg per g),

C_s = concentration of gold in the standard gold solution (μg per ml),

A_{GQS-1} = counting rate for GQS-1, in counts per minute (cpm),

A_s = counting rate for the flux monitor (cpm),

W_s = weight of the standard gold solution (g),

W_{GQS-1} = weight of GQS-1 (g),

ρ_s = density of the standard gold solution (g per ml).

Radioisotope Dilution Analysis (RDA)

Ten-gram samples of the gold-quartz standard 1 were weighed in degreased glass beakers. To these, 10-ml portions of aqua regia were added to make a paste. Gold standards were prepared by pipetting 1.00 ml of a 10.0 μg Au per ml standard gold solution into separate degreased glass beakers. One ml of a 0.05 microcurie per ml [198]Au radio-tracer solution (< 0.1 μg Au per ml) was added to each sample paste and gold standard. The beakers were covered and heated and their contents stirred occasionally for 1 hour on a steam bath. An additional 20 ml of aqua regia was added to each beaker, the beakers were heated for half an hour, and the supernatants above the quartz were decanted. The residues were washed several times with a total of 30 ml 6N HCl and the washes were then combined with the supernatants. The supernatants and gold-standard solutions were evaporated to dryness and the residues dissolved in 1 ml aqua regia and diluted to 50 ml with 0.5N HCl. Each solution was then poured through an SB-2 anion exchange disk (H. Reeve Angel and Co.) and the disk washed with 100 ml of water.

The disks for the samples and gold standards were counted in a 3- by 3-inch NaI well detector and the counting rates were compared to radio-tracer standards prepared by weighing 2-drop portions of the [198]Au radio-tracer solution onto anion exchange disks.

The yields of gold on the disks from the GQS-1 samples and gold standards were calculated by the equation:

$$Y_x = \frac{A_x}{A_{rs}} \cdot \frac{W_{rs}}{\rho_{rs}} \cdot \frac{1}{V_{rs}}, \quad (2)$$

where Y_x = yield of gold from GQS-1 or from the gold standards,

A_x = counting rate for GQS-1 or the gold standards (cpm),

A_{rs} = counting rate for the radio-tracer standard (cpm),

W_{rs} = weight of the radio-tracer standards (g),

ρ_{rs} = density of the radio-tracer solution (g per ml),

V_{rs} = volume of the radio-tracer solution (ml).

The anion exchange disks were irradiated 5 minutes in the Naval Research Laboratory nuclear reactor and counted in a 3- by 3-inch NaI well detector. The [198]Au 412-Kev photopeak areas were corrected for activity due to the [198]Au radio-tracer and the amount of gold in GQS-1 was calculated by the equation:

$$C_{GQS-1} = \frac{A_{GQS-1}}{A_s} \cdot \frac{Y_s}{Y_{GQS-1}} \cdot \frac{W_s}{W_{GQS-1}}, \quad (3)$$

where W_s = weight of gold from the standard gold solution (μg),

Y_s = yield of gold from the gold standards,

Y_{GQS-1} = yield of gold from GQS-1,

and the other symbols have the same meaning as in equation 1.

The quartz residues remaining from the treatment of GQS-1 were washed several times with 6N HCl and water and then dried. To determine the quantity of unleached gold in these residues, portions of each were weighed out and irradiated along with untreated samples of GQS-1. After counting of the irradiated samples, the corrected concentration of gold in GQS-1 was calculated using the equation:

$$C^1_{GQS-1} = \frac{A_{GQS-1}}{A_{GQS-1} - A_r} C_{GQS-1} \quad (4)$$

where C^1_{GQS-1} = corrected concentration of gold in GQS-1 (μg per g),

A_{GQS-1} = counting rate for the untreated GQS-1 (cpm),

A_r = counting rate for the residue (cpm),

C_{GQS-1} = concentration of gold in GQS-1.

RESULTS AND DISCUSSION

The homogeneity of the original untreated gold-bearing quartz was estimated by determining gold in randomly selected 15-g samples by the fire assay-atomic absorption technique of Huffman, Mensik, and Riley (1967). The results shown in table 1 indicate that this sample was extremely heterogeneous and, therefore, not suitable for use as a standard reference material.

Results obtained by the two independent techniques chosen to evaluate the gold content and homogeneity of GQS-1 are given in table 2. Every 10th bottle of the first 100 12-ounce sample bottles was taken for measurement. Separate sets of samples were weighed for each run. Run 1 was irradiated twice using separately prepared flux monitors for each irradiation in an attempt to evaluate the precision of the INAA technique. The coefficient of variation for run 1 was 5 percent.

Two factors which might introduce error into the INAA technique are:

1. Self-shielding of the neutron flux by the large amounts of gold in the flux monitors,
2. Radiocontamination of the ^{198}Au photopeak in the GQS-1 spectra.

Both of these effects would increase the value for gold in GQS-1. The flux monitors contained 0.2–9 μg of gold. Other experiments indicated that the specific activities (cpm per g Au) produced in monitors containing from 0.04 to 4 μg gold varied by less than 2 percent. Therefore, the first effect should be negligible. In any case, the flux monitors in run 2 contained the same amount of gold as GQS-1 and the effect of self-shielding should have been the same in both.

The presence of radiocontamination under the ^{198}Au photopeak can be detected by energy discrimination and half-life discrimination. Spectra taken with a high resolution Ge(Li) detector yielded a value of 412±5 Kev for the ^{198}Au gamma peak (literature value = 412 Kev). No significant contamination peaks were observed within the energy range covered by the NaI detector. To measure the half-life, the decay of ^{198}Au in one sample of GQS-1 was followed for a period of 10 days. The measured half-life was 2.7±0.1 days (literature value = 2.7 days). Therefore, any radiocontaminant for ^{198}Au in the GQS-1 samples must have a half-life in the range of 2.6–2.8 days, an energy in the range of 402–422 Kev, and must be produced in high yield by neutron bombardment. The only nuclide that fulfills these requirements is ^{191}Pt with a 3.0-day half-life and a 410-Kev gamma energy. However, other more abundant gammas from ^{191}Pt, which should be present at 352, 361, and 540 Kev, were missing from the spectra and, therefore, a significant ^{191}Pt contamination was not present.

The RDA results may be in error owing to contamination of the GQS-1 samples by gold during the analysis or to failure to equilibrate the gold in the standards or GQS-1 samples with the radiogold spike. Contami-

nation as a source of error is unlikely. A reagent blank carried through the same procedure at the same time showed less than 0.05 percent of the gold present in the samples. An attempt was made to eliminate the second source of error by adding the radiogold as soon as possible after the aqua regia to prevent loss of gold on the container walls before equilibration.

An analysis of variance was carried out for runs 1 (irradiation 1), 2, and 3 using the model, $Y_{CR} = \mu + \alpha_C + \beta_R + \varepsilon_{CR}$. This model employs a two-way classification in which the two criteria are independent and there is one observation per cell (Beyer, 1966, p. 106). The subscript C refers to the column of data (that is, the analytical method), R refers to the row of data (the bottle), the Y_{CR}'s are the measured gold concentrations, μ is the grand mean of all the Y_{CR}'s, the α_C's and β_R's are the column and row effects, and the ε_{CR}'s are the residual effects. α_C is a fixed effect because the analytical methods are not a random effect produced by variation among bottles (the individual bottles are assumed to be homogeneous). The presence of both fixed and random effects makes this a "mixed" model. Table 3 shows the results of the analysis of variance. The F test was used to evaluate the significance of the mean squares for the column and row effects as compared to the residual effects. The variation among columns is highly significant ($0.001 < P < 0.005$, where P is the probability of occurrence for this ratio of column effect mean square to residual mean square); the variation among rows is negligible ($P > 0.2$). Stated differently, these analytical methods fail to detect any significant heterogeneity among the bottles.

Although heterogeneity among the bottles could not be demonstrated in this test, some degree of heterogeneity almost certainly exists. Its detection, however, will require the use of an analytical method with considerably better precision than the precision of the methods now available. The precision of the methods used in this test is about ±0.10 ppm (parts per million) (standard error). Unless the precision of the method used is considerably better than this, the determinations made on a group of bottles should vary little more than or no more than repeated determinations on the same bottle.

The gold content of GQS-1 has also been measured by other analytical techniques. The results are summarized in table 4. These values are in excellent agreement with those obtained by INAA and RDA.

It should be noted that the estimated gold content of the gold-bearing quartz (table 1) was only one-tenth that of GQS-1 (tables 2, 4). About 100 mg of gold would have had to have been added to account for this increase. Such a level of contamination is extremely unlikely. One explanation for the apparent increase in content may lie in the particle size-frequency distribution. If most of the gold in the gold-bearing quartz was contained in relatively few large grains which were not included in the samples taken for analysis,

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then the aqua regia treatment would have made the gold content of these grains available for analysis in GQS-1. The difficulty of obtaining accurate values for gold in heterogeneous materials is apparent, and the estimate given in table 1 is thought to be low.

It is instructive to estimate the average sizes of the gold particles in the gold-bearing quartz and in GQS-1. Wickman (1963) and Wilson (1964) published mathematical treatments of this problem. They assumed that the gold grains are equivoluminal and distributed within the sample binomially. If the number of grains is large, the distribution approximates the normal or Gaussian distribution; if the number is small, the distribution approximates the Poisson distribution. Considering the precision of our data, the method used by DeGrazia and Haskin (1964) is adequate to estimate the size of the gold particles. They assume a uniform particle size and apparently assume a Poisson distribution of the grains. Table 5 shows the computed grain diameters and number of grains of gold before and after the aqua regia treatment. According to these calculations, the aqua regia treatment reduced the average diameter of the gold particles by at least an order of magnitude and increased the concentration of gold grains by at least a factor of 4,000.

CONCLUSION

We have succeeded in preparing and calibrating a gold-quartz standard which contains about 2.61 ppm gold. The coefficient of variation, 5 percent, is well within our goal of 10 percent for 200-mg samples, and thus, this standard reference material should be useful for the evaluation of analytical techniques for gold. The concentration of gold grains in this material is greater than 2,200 per g and the average diameter of the grains is less than 5μ.

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Table 1.--Values for gold content, in parts per million, in the
gold-bearing quartz powder prior to the aqua regia treatment

[Analyses by Leo Mei and Carroll Burton by the fire assay-atomic
absorption method on 15-gram samples]

Gold content------------------------	0.18, 0.17, 0.44, 0.46, 0.23, 0.42
Mean and standard error--------------	0.32+0.06
Standard deviation-------------------	0.14
Coefficient of variation percent------	44

Table 2.--Gold content, in parts per million, of the gold-quartz standard GQS-1

[Analyses by H. T. Millard, Jr., by instrumental neutron activation analysis (INAA) and radio-
isotope dilution analysis (RDA)]

GQS-1 bottle No.	INAA (0.2-gram samples)		Run 2	RDA (10-gram samples Run 3
	Run 1			
	Irradiation 1	Irradiation 2		
10-------------------------	2.58	2.67	2.66	2.50
20-------------------------	3.01	3.08	2.61	2.45
30-------------------------	2.77	2.75	2.56	2.55
40-------------------------	2.69	2.69	2.52	2.61
50-------------------------	2.80	2.85	2.69	2.55
60-------------------------	2.65	2.69	2.54	2.61
70-------------------------	2.62	2.67	2.58	2.56
80-------------------------	2.59	2.64	2.54	2.39
90-------------------------	2.65	2.63	2.55	2.63
100------------------------	2.60	2.64	2.54	2.47
Mean and standard error----	2.70+0.04	2.73+0.04	2.58+0.02	2.53+0.02
Standard deviation---------	.13	.14	.06	.08
Coefficient of variation--percent--	4.8	5.1	2.2	3.1

Grand mean and standard deviation = 2.64+0.10 ppm

Table 3.--Analysis of variance for data from runs 1 (irradiation 1), 2, and 3

Source of variation	Sum of squares	Degrees of freedom	Mean square	F test
Column, or method, effects-----	0.143	2	0.071	8.20
Row, or bottle, effects--------	.086	9	.010	1.09
Residual effects---------------	.157	18	.009	
Total--------------------	.386	29		

Table 4.--Gold content, in parts per million, of GQS-1

[Cyanide leach-atomic absorption and fire assay-atomic absorption (Denver) analyses by Claude Huffman. Fire assay-atomic absorption (Washington) analyses by P. J. Aruscavage, and neutron activation-fire assay analyses by J. J. Rowe and Frederick Simon (Washington). Numbers in parentheses are number of samples]

Type of analysis	Sample size (grams)	Gold content	Average gold content
Cyanide leach-atomic absorption-	15 (4)	2.60, 2.63, 2.68, 2.65	2.64
Fire assay-atomic absorption (Denver)----------------------	15 (4)	2.64, 2.65, 2.65, 2.64	2.65
Fire assay-atomic absorption (Washington)------------------	15 (2)	2.61, 2.47	2.54
Neutron activation-fire assay---	0.1 (10)	2.71, 2.15, 2.22, 2.40, 2.30, 2.02, 2.23, 3.00, 2.77, 2.72	2.45

Table 5.--Average grain sizes of gold particles in the gold-bearing quartz and in GQS-1 as computed from the analytical data

	Coefficient of variation (percent)	Sample size (grams)	Grain diameter (microns)	Number of grains—	
				per gram	per cm^3
Gold-bearing quartz (before aqua regia treatment--------	45	15	70	0.33	0.9
GQS-1 (after aqua regia treatment)--	<5	.1	<5	>2,200	>6,000

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