

Comparison of three analytical methods in the determination of gold in six Finnish gold ores, including a study on sample preparation and sampling

R. Juvonen *, E. Kontas

Geological Survey of Finland, Betonimiehenkuja 4, P.O. Box 96, FIN-02151, Espoo, Finland

Received 15 July 1998; accepted 10 February 1999

Abstract

We used samples from six Finnish ore deposits to evaluate the efficiency of sample pretreatment procedures — crushing, splitting and grinding — and to compare three analytical methods based on the atomic absorption determination of gold following: (1) classical lead fire assay (FA); (2) the aqua regia leach (AR) followed by Hg coprecipitation of Au; and (3) the sodium cyanide (NaCN) leach. Sample size used for the method comparison is 20 g. The Au deposits and ore types were: Suurikuusikko and Osikonmäki, refractory ores in which Au is associated with arsenopyrite and pyrite; Pampalo and Kutemajärvi ores with metallic Au and Au tellurides; and Jokisivu and Pahtavaara ores containing coarse-grained metallic Au. After crushing, the samples were split into three parts, one of which was put aside into storage. Two splits were further divided into two subsamples which were ground to two grades of fineness (<0.03 and <0.06 mm). The four subsamples thus obtained were analysed for Au using the three analytical methods. Each determination was performed five times on each of the four subsamples. According to *t*-tests on the FA results of the two splits, crushing and splitting produced samples of equal Au content in all six cases. Grinding to a finer grain size gave a significant difference in Au results only for the Pahtavaara ore sample. If the FA results are assumed to represent 100% recovery of Au, we obtained greater than 95% recoveries for all but the Suurikuusikko sample (87% recovery) by the AR leach method. We also obtained recoveries of over 95% by the NaCN leach method for the Pampalo, Kutemajärvi and Pahtavaara samples, whereas recoveries for the other three samples varied between 73 to 92%. The AR leach was also performed on 1-g samples and the NaCN leach on 250-g samples. For three of the ore samples, decreasing sample size from 20 g to 1 g did not cause a significant difference in the variance of the Au results. Increasing the sample size from 20 g to 250 g significantly improves the representativity of only the Pahtavaara sample. For the Kutemajärvi, Pahtavaara and Jokisivu ores, a sample larger than 250 g is needed in order to obtain a precision equivalent to that for reference samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: gold ore analysis; representative sample; lead fire assay; aqua regia leach; mercury coprecipitation; cyanide leach

* Corresponding author.

1. Introduction

The present study was undertaken in an attempt to answer the following questions.

Is there any difference in the Au content of the splits of a large sample after crushing?

What is the sample size needed in order to obtain reproducible analytical results for Au of various types of ores?

Does grinding to a finer grain size improve the results?

How do the analytical methods based on either AR leach or NaCN leach compare with the classical, widely accepted lead fire assay in the determination of the Au content of these samples?

It is widely known that Au in geological samples is unevenly distributed which causes problems in sampling for Au analysis. Mathematical methods for determining the appropriate sample size developed by Clifton and others (Clifton et al., 1969) require knowledge of the size of the Au particles. It is difficult to apply these methods because Au is often not easily seen in the sample under the microscope and the particle sizes may vary. Gold may be invisible and often very fine-grained Au is predominant in the sample (Xuejing and Xueqiu, 1991), making the use of a large sample size for good repeatability of analytical results unnecessary.

In this study, we approach the problem by studying six Finnish Au ores. Samples of about 20 kg from each ore site were collected. Two of the ores, Suurikuusikko and Osikonmäki, are refractory or partially refractory ores; two others, Pampalo and Kutemajärvi, contain Au Te minerals; and two, Jokisivu and Pahtavaara, are known to contain fairly large nuggets of native Au. Pampalo is an Archean deposit whereas the other five deposits are Paleoproterozoic.

Two splits of about 5–7 kg of each ore were prepared for Au determination. Each split was further divided into two parts and ground to two grades of fineness, finally producing four subsamples of each ore. The following routine analytical methods of the Geological Survey of Finland (GSF) were used:

(1) Lead fire assay followed by determination of Au by flame atomic absorption spectrometry (AAS).

(2) Aqua regia leach followed by Hg coprecipi-

tation and determination of Au by graphite furnace atomic absorption spectrometry (GFAAS).

(3) Sodium cyanide leach followed by determination of Au by AAS.

The classical lead fire assay has been used at the GSF for decades (Juvonen and Väänänen, 1993). The method is used widely all over the world, and it is generally accepted as the most dependable analytical method for Au. The fusion flux may be varied to make it applicable to different types of samples (Haffty et al., 1977).

The method of Au determination based on AR leach and Hg coprecipitation has been developed at the GSF (Kontas, 1981, 1993). The method has been used extensively in Finland since the beginning of the 1980s for geochemical mapping and prospecting (Koljonen, 1992). A 1-g sample has been used in geochemical mapping; in this study both 1-g and 20-g samples are used. Gold is extracted from the acid solution by reductive coprecipitation using stannous chloride as reducing agent and Hg in the form of Hg nitrate as the coprecipitant. The precipitate containing the Au is dissolved in AR prior to determination with GFAAS.

A basic cyanide solution is known to leach Au from rock samples upon the oxidation of Au and the formation of the easily soluble $[\text{Au}(\text{CN})_2]^-$ complex. Leaching with a basic solution of NaCN has been used widely in Au production since the turn of the century. Quantitative determination of Au can also be based on the cyanide leach. The method has been used, for example, in the analysis of siliceous limestone ores (Olson, 1965) and in geochemical exploration for Au (Fletcher and Horsky, 1988; Collis et al., 1991). The NaCN leach was introduced as an analytical method for Au at the GSF in 1995, to enable the use of a large sample size, 250–1000 g. In this study the method was tested on 20-g samples; a sample size of 250 g was also used.

The study compares analytical methods and evaluates the efficiency of the sample pretreatment procedures: crushing, splitting and grinding. Size of the subsample is varied using both the AR leach and the cyanide leach methods. The results of the Au analyses, comparing analytical methods and the effect of sample size, are compared statistically.

2. Samples and sample preparation

2.1. Description of the six Au ores

In choosing the ore samples for the study an attempt was made to select a variety of ore types. Suurikuusikko and Osikonmäki are refractory ores. Pampalo and Kutemajärvi contain native Au and Te minerals. Jokisivu and Pahtavaara are known to contain free-milling native Au of fairly large grain size. Details on the geology and mineralogy of the Au ore deposits are presented in Table 1.

2.2. Sample pretreatment

The 20-kg samples were crushed with a jaw crusher (Retsch BB3) in two steps: first, a crude crushing and then a finer crushing, after which 80–90% of the sample was reduced to a particle size of less than 3 mm.

The crushed sample was split with a Jones splitter into three parts of about 5–7 kg each. One part was saved for further studies and two parts, splits A and B, were further split into two. The two splits, of about 3 kg each, were ground with a swing mill (Labtechnics LM 5), to two grain sizes. The first split was ground using the routine grinding time of 6 min and the other split was ground using 12–18 min (Fig. 1).

Grain size determinations of the ground samples were made with a laser diffraction instrument (Sympatec Helos). At least 75% of the sample particles were of the grain size presented in Table 2 or smaller. With the exception of the Osikonmäki sample, the grain size was substantially reduced with prolonged grinding time. The Jokisivu and Kutemajärvi samples were ground for 18 min because the 12 min grinding time for these samples gave particle sizes of 0.06 mm for Jokisivu and 0.04 mm for Kutemajärvi.

Table 1
Geology and mineralogy of the six gold ore deposits and their S concentration determined by X-ray fluorescence spectrometry

Gold ores	Ore mineralogy	Host rocks and structures
Suurikuusikko ^a , S, 3.61%	disseminated sulfides, mainly pyrite and arsenopyrite; Au correlates with arsenopyrite	quartz breccia, metavolcanic rocks, graphite-rich schist
Osikonmäki ^b , S, 2.57%	disseminated bands of sulfides, main ore minerals pyrrhotite, arsenopyrite, löllingite and chalcopyrite, accessory ilmenite or rutile, sphalerite, galena, stannite, tetrahedrite, boulangerite and molybdenite; Au occurs as native Au and electrum in arsenides, sulfides and silicate grains with native Bi	synorogenic tonalite, ductile shear zones
Pampalo ^c , S, 5.51%	Au in variable associations, native Au as inclusions in potassium feldspar and between silicate grains intergrown with tellurides and with pyrite grains	contact zone of ultramafic talc-carbonate rock, quartz-feldspar porphyry and altered intermediate schist
Kutemajärvi ^d , S, 0.03%	pyrite, pyrrhotite, chalcopyrite, tellurides include calaverite; Au mainly included in tellurides	sericite-quartz schist, abundant quartz veins
Pahtavaara ^e , S, 6.72%	low contents of sulfide, mainly pyrite; Au associated with pyrite at contact zones with quartz-barite lenses	hydrothermally altered tuffitic komatiites, biotite schist quartz-barite lenses
Jokisivu ^d , S, 0.88%	pyrrhotite, ilmenite, arsenopyrite, chalcopyrite, löllingite, scheelite, sphalerite, pyrite, marcasite, magnetite, galena; Au occurs as native Au and in Te minerals	skarn-banded quartz rock with variously deformed quartz veins

^a Härkönen and Keinänen, 1989.

^b Kontoniemi et al., 1991; Kontoniemi, 1998.

^c Kojonen et al., 1993.

^d Luukkonen et al., 1992.

^e Korkiakoski et al., 1989.

Pretreatment of gold ore samples

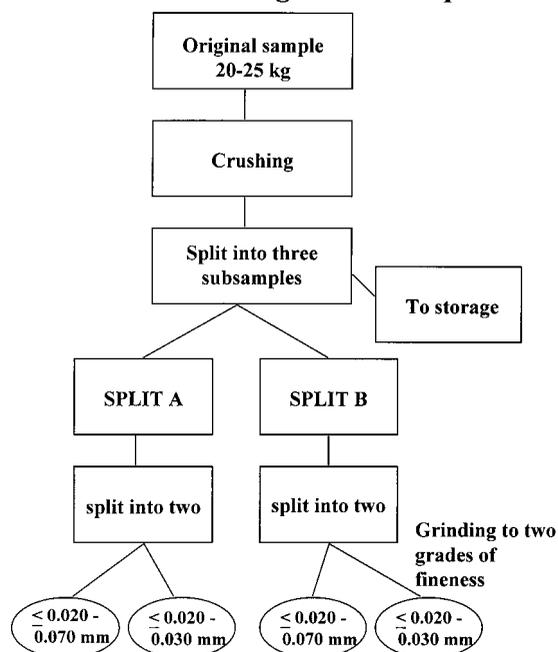


Fig. 1. Pretreatment of gold ore sample.

Table 2

Grain sizes of the ore samples after grinding, 75% of the sample particles being of the grain size given in the table or smaller

Sample	Particle size, mm	
	6 min grind	12–18 min grind
Suurikuusikko	0.06	0.02
Osikonmäki	0.02	0.02
Pampalo	0.04	0.02
Kutemajärvi	0.04	0.03
Pahtavaara	0.05	0.03
Jokisivu	0.07	0.03

3. Analytical methods

3.1. Lead fire assay

The 20-g sample is mixed in a plastic bag with 50 g PbO and about 200 g of the flux containing 32 g Na₂CO₃, 44 g Na₂B₄O₇, 52 g K₂CO₃, 52 g KHC₄H₄O₆ and 20 g quartz. After mixing, the bag with its contents is put into a fire-clay crucible, and Ag is added as AgNO₃ solution. The crucible is transferred into a preheated furnace and fused at

1100°C for 1 h. The contents of the crucible are poured into an iron mold to cool. After cooling, the Pb regulus is hammered and brushed clean, after which it is cupelled in a magnesite cupel at 940°C. The Ag bead remaining after the cupellation is flattened with hammer and anvil, transferred into a graduated test tube and dissolved by adding 0.5 ml HNO₃ (65% v/v) and 1.5 ml HCl (37% v/v). To avoid overboiling, the test tubes are allowed to stand at room temperature overnight before heating on an electric block heater. When the bead is dissolved, the volume is made up to 10 ml with 6 M HCl. The solution is ready for AAS measurement of Au, using a Varian SpectrAA 400 instrument with an air–acetylene flame.

3.2. Aqua regia leach

The sample is first roasted in a porcelain crucible at 600°C in order to oxidise organic material, graphite and sulfides. The sample (20 g) is transferred into a 250-ml disposable plastic bottle. The acids — 50 ml of 12 M HCl and 10 ml of 16 M HNO₃ — are added in several portions by computer-controlled dispensers, while the bottles are on a horizontal shaker which shakes them automatically after each addition. The bottles are covered with plastic wrap and allowed to stand at room temperature overnight, after which 40 ml of water are added. The solution is mixed well, and about 10 ml are transferred into a test tube and centrifuged. A 0.5-ml aliquot (or 5.0 ml in the ppb range) of the clear solution is pipetted into a test tube into which 6 ml of 4 M HCl, 2 ml of stannous chloride solution (20%) and 1 ml of mercurous nitrate solution (1 mg Hg/ml) are added. The test tubes are centrifuged, whereby the Hg precipitate containing the Au settles at the bottom. The supernatant liquid is discarded, the test tube filled with water and centrifuged again. The Hg precipitate is dissolved by adding 0.7 ml of 12 M HCl and 0.3 ml of 16 M HNO₃. The test tube is agitated with a test tube agitator, after which 0.9 ml of HNO₃ (20%) are added. It is assumed that 0.1 ml of water remains in the test tube after the Hg precipitation, therefore the final volume of the solution prepared for the GFAAS determination is 2 ml.

For a 1-g sample, volumes in the digestion step are divided by 20. The dissolution procedure for

the Hg precipitate is the same as that for the 20-g sample. The 0.5-ml aliquot allows measurement at the ppm range. The GFAAS measurements were made with the Perkin-Elmer P-E Z3030 instrument, with the standard solution of 50 ng/ml used as the lowest standard, being equivalent to a sample Au concentration of 1.00 ppm.

3.3. Sodium cyanide leach

The sample (20 g) is weighed into a bottle and 40 ml of water are added. The pH is adjusted to 11 by the addition of about 0.1 g of CaO. The solution is made 0.3% with respect to NaCN by adding 0.12 g of the solid reagent. The open bottle is laid on its side on a bottle roller and allowed to roll for 24 h. The bottle with its contents is weighed before and after the cyanide leach to estimate the amount of evaporation. After replacing the evaporated water, some solution is transferred into a test tube and centrifuged. A 5-ml aliquot of the solution is pipetted into a test tube and 5 ml of HCl (37% v/v) are added. After evaporation of the HCN gas in the fume hood, the Au content of the solution is determined by AAS. Sample-to-water ratio and the concentration of the NaCN solution are kept constant regardless of sample size.

4. Results and discussion

The four subsamples of each ore were analysed for Au using the three analytical methods described above. Each determination was performed five times, and the sample weight used in all of the determina-

tions was 20 g. The Pb fire assay method is used as the reference method. Reference sample results, which have been collected over several years using the FA and the AR methods, are presented in Table 3. The effect of sample size on the variance is studied by comparing the results obtained for subsamples of 1 g for the AR leach and subsamples of 250 g for the NaCN leach with the 20-g subsample results. Mean recoveries for Au using the AR and the NaCN methods are given in Table 4.

4.1. Evaluation of homogeneity of the samples after crushing and splitting

For both split A and split B of each of the six Au ore samples, two subsamples of different grain size were prepared. Because each subsample was analysed five times, there are ten Au results for samples of both splits. Even distribution of Au in splitting is tested by applying the *t*-test on all ten Au results obtained for splits A and B regardless of grain size. The results of the *t*-test are presented in Table 5. None of the *t*-test values for the six ore samples is above the critical value, indicating that there are no significant differences in the Au contents of the splits A and B.

4.2. Effect of sample grain size on the Au results

The effect of sample grain size on the Au results was studied by applying the *F*-test on the standard deviations of the ten results of the finer grain size of splits A and B and the ten results of the larger grain size of splits A and B. A value above the critical value in this test indicates that the difference between the variances of the tested sets of values is

Table 3

Results for reference samples using the aqua regia leach method and the lead fire assay method (sample size is 5 g in each determination)

Method	Reference sample	Result of GSF Au (ppm)	RSD (%)	Number of determinations	Reference value ^a Au (ppm)
Aqua regia leach	GXR-1	3.10 ± 0.20	6.5	5	3.10 ± 0.20
	GXR-4	0.42 ± 0.01	2.4	3	0.44 ± 0.16
	SARM 7	0.36 ± 0.066	18.3	65	0.31 ± 0.015
Fire assay	MA-1a	19.91 ± 1.2	6.0	31	21.4 ± 0.4
	MA-3	7.4 ± 0.3	4.1	9	7.49 ± 0.19

GXR-1 jasperoid and GXR-4 copper-mill head, United States Geological Survey; SARM 7 platinum ore, Council for Mineral Technology, South Africa; MA-1a and MA-3 gold ore, Canada Centre for Mineral and Energy Technology.

^a Reference values from certificates.

Table 4

Mean recoveries for Au using aqua regia leach and NaCN leach for different sample sizes of the six Au ores; the fire assay recovery for the 20-g sample is assumed to be 100%

Ore	Mode of occurrence of Au	Recovery (%)			
		AR leach		NaCN leach	
		1 g	20 g	20 g	250 g
Suurikuusikko Osikonmäki	Au associated with arsenopyrite, pyrite and in silicate inclusions id.	93.7	86.8	73.1	n.d.
		98.5	95.7	85.6	88.9
Pampalo Kutemajärvi	metallic Au and Au tellurides id.	104	98.9	94.9	105
		105	102	99.3	103
Pahtavaara Jokisivu	coarse-grained metallic Au id.	76.4	95.7	97.5	111
		121	102	92.2	110

n.d. = not determined.

statistically significant. The results are presented in Table 6.

From these results, it can be seen that grinding to a finer particle size did not improve the variance of the results, except in the case of the Pahtavaara sample. According to the *F*-test, statistically significant differences in variances of different grain size fractions were also found for the Pampalo and the Kutemajärvi samples. However, in these cases, the

standard deviation values are higher for the subsamples of finer grain size.

4.3. Statistical comparison of results obtained with the three analytical methods

Results for the median, mean and standard deviation of all twenty analyses obtained for each of the six Au ore samples using lead fire assay, AR leach

Table 5

The *t*-test is used to evaluate whether there are statistically significant differences in the averages of the results for Au determinations of splits A and B

	Split	Mean \pm SD Au (ppm)	Value <i>t</i> -test
Suurikuusikko	A	10.68 \pm 0.14	1.56
	B	10.49 \pm 0.36	
Osikonmäki	A	12.03 \pm 0.97	0.21
	B	11.93 \pm 0.92	
Pampalo	A	322.61 \pm 9.34	1.02
	B	312.75 \pm 29.23	
Kutemajärvi	A	136.18 \pm 4.52	0.64
	B	134.79 \pm 4.49	
Pahtavaara	A	37.86 \pm 16.72	0.49
	B	45.17 \pm 43.64	
Jokisivu	A	15.62 \pm 1.58	0.12
	B	15.50 \pm 2.90	

For 18 degrees of freedom ($n_1 + n_2 - 2 = 18$, where $n_1 = 10$ samples of split A and $n_2 = 10$ of split B) the critical value of the *t*-test is 2.1. Gold is determined using the fire assay pre-concentration and AAS determination.

Table 6

The *F*-test is used to evaluate whether there are statistically significant differences in variance of the results for the two different grain size fractions of the six Au ore samples

	Grain size	Mean \pm SD, Au (ppm, $n = 10$)	RSD (%)	Value <i>F</i> -test
Suurikuusikko	0.06 mm ^a	10.43 \pm 0.27	2.6	1.61
	0.02 mm ^b	10.74 \pm 0.21	2.0	
Osikonmäki	0.02 mm ^a	12.76 \pm 0.49	3.8	1.28
	0.02 mm ^b	11.20 \pm 0.44	3.9	
Pampalo	0.04 mm ^a	332.3 \pm 10.1	3.0	4.16
	0.02 mm ^b	303.1 \pm 20.6	6.8	
Kutemajärvi	0.04 mm ^a	132.1 \pm 1.92	1.5	3.57
	0.03 mm ^c	138.8 \pm 3.63	2.6	
Pahtavaara	0.05 mm ^a	52.29 \pm 44.0	84.1	77.4
	0.03 mm ^b	30.91 \pm 5.00	16.2	
Jokisivu	0.07 mm ^a	14.61 \pm 1.70	11.6	2.09
	0.03 mm ^c	16.51 \pm 2.46	14.9	

The critical value for the *F*-test is 3.18 (degrees freedom are 9 and 9) at $\alpha = 5\%$. Values above the critical value are in **bold** print.

Grinding time: ^a 6 min, ^b 12 min, ^c 18 min.

Table 7

Median, mean, standard deviation (SD) and relative standard deviation (RSD) of the determinations using the three analytical methods

	Au (ppm)		
	fire assay	AR leach	NaCN leach
Suurikuusikko, <i>n</i> = 20			
median	10.53	9.19	7.80 ^a
mean	10.58	9.18	7.73 ^a
SD	0.28	0.21	0.44
RSD (%)	2.7	2.3	5.7
Osikonmäki, <i>n</i> = 20			
median	12.04	11.38	10.19
mean	11.98	11.47	10.26
SD	0.92	0.82	0.57
RSD (%)	7.7	7.2	5.6
Pampalo, <i>n</i> = 20			
median	323.8	312.2	308.0
mean	317.7	314.1	301.5
SD	21.72	8.65	16.41
RSD (%)	6.8	2.8	5.4
Kutemajärvi, <i>n</i> = 20			
median	133.8	138.5	133.0
mean	135.5	138.3	134.6
SD	4.45	5.44	6.9
RSD (%)	3.3	3.9	5.1
Pahtavaara, <i>n</i> = 10			
median	29.04	27.46	28.68
mean	30.91	29.57	30.14
SD	5.00	6.96	9.31
RSD (%)	16.2	23.5	30.9
Jokisivu, <i>n</i> = 20			
median	15.50	15.18	13.74
mean	15.56	15.84	14.34
SD	2.28	2.77	1.76
RSD (%)	14.6	17.5	12.3

A 20-g sample weight was used for all determinations. Presented are the results of five repetitions of the two finer grain size subsamples of the Pahtavaara ore sample and of four subsamples of the five other Au ore samples.

^a Sample roasted at 600°C before the sodium cyanide leach.

and NaCN leach are presented in Table 7. The *t*-test is used to test for statistically significant differences between the results for the AR leach method and the NaCN leach method as compared with the fire assay method. Differences in variance of the results are evaluated with the *F*-test.

According to the *t*-test (Table 8), significant differences between the results of the AR leach and the

fire assay method are found only in the results for the Suurikuusikko sample. The slightly lower recovery with the AR leach method for this sample can be explained by the mineralogical composition of the sample: Au has been found as inclusions in the silicate minerals which are not attacked by AR (Section 5.1). The standard deviation of the results for Pampalo with the AR leach method is significantly lower than that of the fire assay method. This could be explained by the high Au content of the sample: unlike in the case of samples of lower Au concentration, variable and detectable amounts of Au remain in the slag after fire assaying causing variation in the results.

The first three of the *t*-test values comparing the NaCN leach with the fire assay (Table 8) are above the critical value, indicating that the lower recoveries obtained with the cyanide leach are statistically significant. Gold has been found as inclusions in pyrite and silicates in these ores. For samples in which Au is present as metallic Au or Au tellurides, good recoveries with the cyanide leach are obtained. In comparing the NaCN leach with the fire assay method, a significant difference in the variance of the results is found for all except the Pampalo and Jokisivu samples. In three cases, the standard deviation for the fire assay results is lower than for the NaCN leach, and in one, the reverse is true.

4.4. The effect of sample weight on the analytical results for Au

The NaCN leach was carried out on 250-g subsamples and the AR leach on 1-g subsamples. The results of these determinations together with the results for the previously presented 20-g subsamples by both methods are presented in Table 9. The NaCN leach was not performed on the 250-g Suurikuusikko sample because preliminary tests showed that less than 10% of the Au is leached with NaCN if the sample is not roasted prior to leaching. Roasting of the 250-g subsamples was not undertaken.

The results with the higher sample weight have a general tendency to be higher. This can clearly be seen in the NaCN leach results. Increasing sample size to 250 g significantly lowered only the SD of the Pahtavaara sample. Variance of the Kutemajärvi results increased with increase in sample size.

Table 8

The fire assay method is compared with the aqua regia leach and with the sodium cyanide leach

	Fire assay vs AR		Fire assay vs NaCN	
	<i>t</i> -test value	<i>F</i> -test value	<i>t</i> -test value	<i>F</i> -test value
Suurikuusikko	17.7	1.82	24.3	2.40
Osikonmäki	1.85	1.26	7.11	2.60
Pampalo	0.69	6.31	2.66	1.75
Kutemajärvi	1.78	1.50	0.50	2.41
Pahtavaara	0.57	1.94	0.27	3.46
Jokisivu	0.35	1.47	1.90	1.67

Values for the *t*-test and the *F*-test are calculated using the means and the standard deviations given in Table 6 for the 20 determinations of each sample using the three analytical methods (10 determinations of the Pahtavaara sample). The critical value for the *t*-test is 2.03 (2.1 for the Pahtavaara sample) at 5% significance level, and the critical value for the *F*-test is 2.2 (2.9 for Pahtavaara). Values above the critical value are indicated by **bold** print.

When comparing results for the 1-g and 20-g samples, using the AR leach, SD is lower for all six samples with the 20-g sample weight, but variance is significantly higher in only half of the cases.

5. Evaluation of the results according to ore type

5.1. Suurikuusikko

A diagnostic leach procedure according to the method of Lorenzen (1995), involving alternating leaches with acids and NaCN solution, was used to identify minerals with which Au is associated in this sample. It was found that the highest concentration of Au was liberated after digestion of the sample with nitric acid, which attacks the sulfides. The silicate phase of the sample was also found to contain appreciable amounts of total Au (20–30%). According to the *t*-test, a significantly higher result is obtained with the lead fire assay than with either the AR or NaCN leach for this ore. Roasting of the sample prior to the cyanide leach was found necessary. Without roasting, the recovery of Au was only about 6% of the fire assay recovery.

5.2. Osikonmäki

The arsenic content of the sample is high, 6.61%. The highest recovery is obtained with the fire assay method, where the Au contained within the crystal lattices of the arsenopyrite and silicate minerals is

released upon fusion of the minerals. Leaching with NaCN does not liberate all of the Au. According to the *t*-test, the difference in favour of the fire assay method is statistically significant for the NaCN leach, but not for the AR leach. According to Table 2, the grain size did not become smaller by increasing the grinding time and, consequently, the grinding time did not have any effect on the repeatability of the Au results (Table 6).

5.3. Pampalo

Grinding of the sample to a finer grain size causes the standard deviation of the Au results to increase. According to the *F*-test result (Table 6), the difference is statistically significant. However, the RSDs of the results are very low compared to the RSDs of the certified reference samples presented in Table 3, making it questionable to draw the conclusion that Au nuggets might be joining together and the sample becoming more inhomogeneous due to prolonged grinding. What can be stated is that increased grinding time and smaller grain size do not give better repeatability. The highest Au values are obtained with the cyanide leach on a 250-g sample and the lowest SD with the AR leach on a 20-g sample. This is in agreement with the fact that Au is present as visible Au. The slightly lower results obtained with the Pb fire assay may be due to the extremely high Au concentration of this sample. Upon refusing the slag, it was found that about 5% of the Au remained in the slag.

Table 9

Effect of changing sample size on the results of Au determinations of the six Au ores

	Au, ppm NaCN leach		<i>F</i> -test value	Au, ppm AR leach		<i>F</i> -test value
	20 g	250 g		20 g	1 g	
Suurikuusikko <i>n</i> = 20						
median	7.80	n.d.		9.19	9.87	
mean	7.73			9.18	9.91	
SD	0.44			0.21	0.31	2.18
RSD (%)	5.7			2.3	3.1	
Osikonmäki <i>n</i> = 20						
median	10.19	10.54		11.38	11.13	
mean	10.26	10.65		11.47	11.8	
SD	0.57	0.55	1.07	0.82	2.85	12.08
RSD (%)	5.6	5.2		7.2	24.1	
Pampalo <i>n</i> = 20						
median	308.0	334.1		312.2	325.9	
mean	301.5	334.3		314.1	330.1	
SD	16.41	21.1	1.65	8.65	37.21	18.50
RSD (%)	5.4	6.32		2.8	10.6	
Kutemajärvi <i>n</i> = 20						
median	133.0	143.6		138.5	135.2	
mean	134.6	139.6		138.3	142.4	
SD	6.9	14.08	4.16	5.44	7.74	2.02
RSD (%)	5.1	10.1		3.9	5.4	
Pahtavaara <i>n</i> = 10						
median	28.68	33.13		27.46	22.60	
mean	30.14	34.36		29.57	23.60	
SD	9.31	4.59	4.11	6.96	7.94	1.30
RSD (%)	30.9	13.35		23.54	33.6	
Jokisivu <i>n</i> = 20						
median	13.74	17.24		15.18	11.42	
mean	14.34	17.13		15.84	18.87	
SD	1.76	1.54	1.31	2.77	14.53	27.51
RSD (%)	12.3	9.0		17.5	77.0	

All 20 determinations are included in the medians and the mean values. For the Pahtavaara sample only the finer grain size subsamples are included. Critical value for the *F*-test is 2.2 (2.9 for Pahtavaara). Values above the critical value are indicated by **bold** print; n.d. = not determined.

5.4. Kutemajärvi

The sulfide content of the Kutema sample is low, at 0.03% S. Comparing results of the three analytical methods of Table 7, we can see that all methods give equivalent results, with the NaCN leach method giving a higher standard deviation value than the other two methods. Increasing the sample size from 20 g to 250 g gives higher results (Table 9). A *t*-test value of 6.4 is obtained, which indicates a

significant difference in the results. This may be due to the larger sample increasing the probability of having more of the larger nuggets in the sample. The smaller grain size again gives inferior repeatability, as with the Pampalo sample.

5.5. Pahtavaara

The Ba content of this sample was high at 18%, indicating the presence of the quartz–barite lenses

mentioned in Table 1. Increasing the grinding time to produce a sample of smaller grain size lowered the variance of the analytical results for this sample significantly (Table 6). For this reason, only the finer grain size fractions of splits A and B are considered in Tables 7–9. Nevertheless, the RSDs of the results for 20-g subsamples with all three methods are quite high, between 16 and 31%, indicating that Au is inhomogeneously distributed in the sample. The highest results and the lowest RSD are obtained with the NaCN leach on 250-g subsamples.

5.6. Jokisivu

According to the results presented for the 20-g subsamples in Tables 7 and 8, all three analytical methods give equivalent results for this sample. The variance of the results is higher, but not significantly higher, for the finer particle size sample. The highest Au value and the lowest SD are obtained with the NaCN leach on a 250-g sample. The high SD in Table 9 of the results by the AR leach on 1-g samples indicates the presence of Au nuggets.

6. Conclusions

The crushing and splitting procedures produced subsamples of equivalent Au content. Further comminution of the sample, after the routine grinding, improved the subsample representativity in only one case: the Pahtavaara sample.

For three of the ore samples — Suurikuusikko, Kutemajärvi and Pahtavaara — increasing the sample size from 1 g to 20 g does not change the variance of the results significantly. Increasing the sample size from 20 g to 250 g gives a significantly lower SD only for the Pahtavaara sample. A sample weight higher than 250 g is needed for Kutemajärvi, Pahtavaara and Jokisivu in order to obtain RSDs equivalent to those obtained by the laboratory for reference samples.

A significant difference between the results of the fire assay and the AR leach method is found only for the refractory ore of Suurikuusikko. A significantly higher variance for results by fire assay than by AR leach is obtained for the Pampalo sample. This is due to low recovery by the routine fire assay method

because of the unusually high Au content of the sample.

For the three ore samples — Suurikuusikko, Osikonmäki and Pampalo — the NaCN leach results are significantly lower than fire assay results. For the other three ore samples — Kutemajärvi, Pahtavaara and Jokisivu — the results do not differ significantly.

A study of the analytical method and sample size best suited for a particular ore occurrence could amount to financial savings. This study shows that both the AR and NaCN leach methods, as alternatives for the fire assay method, give good recoveries for Au in various types of Au ores.

Acknowledgements

The idea for the study originated from the director of the Chemical Laboratory of the GSF, Harry Sandström. The mining companies, Outokumpu Mining Oy and Terra Mining Oy, co-operated by providing samples. Kari Kojonen participated in selecting the samples for the study. Satu Vuoriainen did much of the analytical work involving the NaCN leach. Maija Hagel-Brunnström did the XRF analyses of the ore samples. The text was improved by the constructive criticism of Gwendy E.M. Hall. All of them are gratefully acknowledged by the authors.

References

- Clifton, H.E., Hunter, R.E., Swanson, F.J., Phillips, R.L., 1969. Sample size and meaningful gold analysis. U.S. Geol. Surv. Prof. Pap. 625-C, 1–17.
- Collis, G.D., Moles, C.M.E., Mazaiwana, I., 1991. Exploration for gold by use of cyanide leach analytical techniques on soil samples in the greenstone belts of Zimbabwe. *African Mining '91*, pp. 99–110.
- Fletcher, K., Horsky, S.J., 1988. Determination of gold by cyanidation and graphite furnace atomic absorption spectroscopy. *J. Geochem. Explor.* 30, 29–34.
- Haffty, J., Riley, L.B., Goss, W.D., 1977. A manual on fire assaying and determination of the noble metals in geological materials. U.S. Geol. Surv. Bull. 1445, 8–18.
- Härkönen, E.A., Keinänen, V., 1989. Exploration of structurally controlled gold deposits in the central Lapland greenstone belt. *Geol. Surv. Finl. Spec. Pap.* 10, 79–82.
- Juvonen, R., Väänänen, P.J., 1993. Determination of gold in geological materials by atomic absorption after lead fire assay

- separation. In: Kontas, E. (Ed.), *Analytical Methods for Determining Gold in Geological Samples*. Geol. Surv. Finl. Rep. Invest. 114, pp. 13–16.
- Kojonen, K., Johanson, B., O'Brien, H.E., Pakkanen, L., 1993. "Mineralogy of gold occurrences in the late Archean Hattus schist belt, Ilomantsi, eastern Finland". Geol. Surv. Finl. Spec. Pap. 17, 233–271.
- Koljonen, T., 1992. *The Geochemical Atlas of Finland, Part 2: Till*. Geol. Surv. Finl. 25.
- Kontas, E., 1981. Rapid determination of gold by flameless atomic absorption spectrometry in the ppb and ppm ranges without organic solvent extraction. *At. Spectrosc.* 2, 59–61.
- Kontas, E., 1993. Determination of gold and palladium by aqua regia digestion, stannous chloride–mercury coprecipitation and flameless atomic absorption. In: Kontas, E. (Ed.), *Analytical Methods for Determining Gold in Geological Samples*. Geol. Surv. Finl. Rep. Invest. 114, pp. 29–32.
- Kontoniemi, O., 1998. "Geological setting and characteristics of the Paleoproterozoic tonalite-hosted Osikonmäki gold deposit, Southwest Finland". Geol. Surv. Finl. Spec. Pap. 25, 39–80.
- Kontoniemi, O., Johanson, B., Kojonen, K., Pakkanen, L., 1991. Ore mineralogy of the Osikonmäki gold deposit, Rantasalmi, southeastern Finland. In: Autio, S. (Ed.), *Current Research*. Geol. Surv. Finl. Spec. Pap. 12, pp. 81–89.
- Korhikoski, E.A., Karvinen, A., Pulkkinen, E., 1989. Geochemistry and hydrothermal alteration of the komatiite-hosted Pahtavaara gold mineralization, Finnish Lapland. In: Autio, S. (Ed.), *Current Research*. Geol. Surv. Finl. Spec. Pap. 10, pp. 83–89.
- Lorenzen, L., 1995. Some guidelines to the design of a diagnostic leaching experiment. *Miner. Eng.* 8, 247–256.
- Luukkonen, A., Grönholm, P., Hannila, T., 1992. *Eräiden Etelä-Suomen kulta- ja sen seuralaismetalliesiintymien geologiset pääpiirteet*. English summary: Main geological features of certain gold and tungsten–tin–gold prospects in southern Finland. Geol. Surv. Finl. Rep. Invest. 113, 90 pp.
- Olson, A.M., 1965. Gold assay by atomic absorption spectrophotometry: a preliminary report. *At. Absorpt. Newsl.* 4, 278–280.
- Xuejing, X., Xueqiu, W., 1991. Geochemical exploration for gold: a new approach to an old problem. *J. Geochem. Explor.* 40, 25–48.