Table XVII, continued

Sample	Corrected absorbances[1]			Mean absorbance	Corrected absorbance[2]	Concentration in solution (p.p.m.)	Weight (mgm.)	Volume (cc.)	Concentration (in sample) (p.p.m.)
S 19	.031	.028	.028	0.029	0.023	1.50	25.19	10	595.5
S 20	.018	.023	.019	0.020	0.019	3.60	30.32	10	1187.3
S 21	.012	.013	.014	0.013	0.012	2.25	11.12	10	2023.4
S 22	.014	.016	.014	0.015	0.009	0.56	24.75	10	202.0

1 - Absorbances corrected for instrument drift.

2 - Mean absorbance corrected for iron concentration in hydrochloric acid-aqua regia blank.

applied for the copper and iron contents in the solvents varies from sample to sample. This is because the analyses were carried out on different days and fresh blank solutions were prepared for each set of analyses. The copper concentration varies from 70 p.p.m. in G 40 to 6168 p.p.m. in G 34, with most of the samples having a concentration of less than 1000 p.p.m.. The iron concentrations range from 72 p.p.m. in G 42 to 3261 p.p.m. in G 45. Generally the iron concentrations seem greater than the copper concentrations, especially in the S samples.

2. Reproducibility of the method

The reproducibility of the method was investigated by carrying out a series of absorbance measurements on the standard solutions and the check solutions. The results are given in table XVIII.

Table XVIII. The variations in absorbance for replicate analyses of solutions of varying concentrations.

	Copper					Iron			
Solution	n	$\bar{x}$	s	v(%)	Solution	n	$\bar{x}$	s	v(%)
1	13	0.159	0.002	1.22	7	17	0.086	0.002	2.20
2	5	0.555	0.011	2.01	8	5	0.153	0.001	0.59
3	5	0.310	0.006	1.81	9	5	0.123	0.001	1.15
4	5	0.179	0.003	0.94	10	5	0.073	0.001	1.23
5	5	0.085	0.003	3.61	11	5	0.051	0.001	1.75
6	5	0.042	0.001	2.87	12	5	0.032	0.003	9.27

..48/...

Table XVIII continued.

Solutions:

1) Approximately 2 p.p.m. copper in hydrochloric acid.

2) 13.4 p.p.m. copper in acid-alcohol mixture.

3) 6.9 p.p.m. copper in acid-alcohol mixture.

4) 3.4 p.p.m. copper in acid-alcohol mixture.

5) 1.7 p.p.m. copper in acid-alcohol mixture.

6) 0.9 p.p.m. copper in acid-alcohol mixture.

7) Approximately 20 p.p.m. iron in hydrochloric acid.

8) 36.1 p.p.m. iron in acid-alcohol mixture.

9) 18.0 p.p.m. iron in acid-alcohol mixture.

10) 9.0 p.p.m. iron in acid-alcohol mixture.

11) 4.5 p.p.m. iron in acid-alcohol mixture.

12) 2.3 p.p.m. iron in acid-alcohol mixture.

N.B. n - number of determinations; $\bar{x}$ - mean absorbance;

s - standard deviation $= \sqrt{\frac{\Sigma (x-\bar{x})^2}{n}}$;

v - coefficient of variation $= \frac{100\ s}{\bar{x}}$.

From the results it appears that for copper the best reproducibility is obtained for concentrations in solution between 2 - 13 p.p.m.. For iron, the reproducibility is relatively good

..49/...

for all concentrations greater than 3 p.p.m.. The coefficients of variation are of the same order as those obtained by Strasheim, Butler and Maskew (1962) but are not quite as good as those obtained by Schuler, Jansen and James (1962).

3. The limits of detection of the method

The detection limit is relatively high because of the small amounts of the samples dissolved in the solutions. For example, assuming the limit of detection for copper to be 0.04 p.p.m. in a hydrochloric acid-ethyl alcohol solution (Schuler et al, 1962, table I), the concentration of copper in a 10 mgm sample dissolved in 5 cc of solvent, would have to be 20 p.p.m. to be detected. Similarly, assuming a limit of detection of 0.15 p.p.m. in solution for iron (Strasheim, Butler and Maskew, 1962, table VIII), the concentration of iron in a 10 mgm sample in 5 cc of solvent, would have to be 75 p.p.m. to be detected.

..50/...

(d) The determination of the fineness of the gold samples by the fire assay method.

(i) Introduction

The origin of the method of assaying is obscure, though it undoubtedly dates back many centuries. Smith (1947) gives a detailed account of the development of assaying and the following data are taken from his book.

The first explicit records of assaying were published anonymously in German at the beginning of the 16th century. However, much earlier than this, assaying was being used to test the purity of gold by observing the surface appearance of the molten metal as impurities produced a dross to the clear and bright surface of the pure metal. This testing by fire was probably the forerunner of the cupellation process, which was said to be in use in the 2nd century B.C.

The parting assay, in which gold is separated from an alloy of gold and silver by the action of nitric acid, was known to the early alchemists. However, the first official acceptance of its use was in France in 1343, when the process was adopted in the French Mint.

(ii) The theory of cupellation.

The principles of cupellation have been discussed in detail by several workers including Beringer and Beringer (1921), Rose and Newman (1937) and Smith (1947). The method has as its object the removal, as oxides, of base metals in gold and silver, which can not be oxidized. The operation is carried out in a furnace

../51...

in porous vessels, known as cupels. Cupellation is based on the fact that when molten lead is exposed to the action of air at a temperature much greater than redness (above 746°C on Fulton's colour temperature scale, Fulton and Sharwood, 1929), it is oxidized to litharge (PbO). At these temperatures, litharge is a liquid and, therefore, if the lead is contained in a porous vessel, which allows the fused litharge to drain away as it is formed, a fresh surface of lead will be continually exposed to the air and the operation will continue until all the lead has been oxidized and absorbed. However, since silver and gold do not oxidize, cupellation of alloys of these metals and lead will result in the removal of the lead, leaving behind a button of gold or silver.

Of the other base metals which may be present in gold, bismuth is the only one whose oxide can be absorbed by the cupel. Molten litharge, however, acts as a solvent for the oxides of copper, tin, iron and antimony, allowing them also to be removed from the gold. The surface tension of molten gold and silver remaining after the removal of the base metals, is too high to allow them to be absorbed by the cupel.

The temperature of the muffle furnace during cupellation is important. Generally, the furnace temperature required for absorption of the litharge by the cupel should be above 900°C (Rose and Newman, 1937, p. 500).

..52/...

The loss of gold and silver during cupellation is not normally great though it does occur. According to Smith (1947), too high a temperature and the use of too much lead can increase the loss. The presence of base metals such as copper can also cause absorption of the precious metals, though it is found that if gold is alloyed with silver, the cupellation loss decreases due to the protective action of the silver. This loss by absorption of the gold is thought to be due partly to infiltration of lead-gold alloys into the cupel and partly to the formation of gold oxides either by the action of atmospheric oxygen, during cupellation, or by the action of base metals oxides which act as 'oxygen carriers'.

The determination of the loss during cupellation is very important and is usually carried out by assaying check samples of proof gold (or silver) under the same conditions as the material being assayed.

(iii) Laboratory Procedure

1. The inquartation and cupellation of the gold samples

To ensure that as much silver as possible is removed from the gold during the parting assay, it is necessary to add silver to the gold so that the proportion of gold to silver in the resultant alloy is approximately 2:5. The addition of silver to the gold is known as inquartation and it may be carried out by fusion of the two metals using blow-pipes or, better, by cupellation (Rose and Newman, 1937; Smith, 1947). Therefore, the required amount of silver is usually wrapped

..53/...

with the gold in as small a piece of lead foil as possible, and cupelled, resulting in the combining of the gold and silver and the simultaneous removal of the base metals from the gold.

For small amounts of gold bullion, Rose and Newman (1937) have suggested that the proportion of silver to gold should be increased to ensure maximum parting and that for 10 mgm samples a gold - silver ratio of 1:4 is suitable. However, gold-silver alloys containing this much silver tend to break up during parting, resulting in a possible loss of gold. Therefore, for the assay of the samples in this investigation it was decided to adopt a gold:silver ratio of 1:3, to allow for the small size of the samples and to prevent the breaking up of the alloys.

The amount of gold weighed out for assay varied from 5 mgm, for those samples containing only a small quantity of gold, to 25 mgm for the larger samples. Wherever possible, duplicate assays were weighed out. Samples of proof gold, which had been shown to contain 999.7 parts of gold per 1000 (Finkelstein and Lock, 1962, table VI, sample S.3), were weighed for check assays. One of these samples was included with each batch of gold assays to control losses during cupellation and parting. After the samples had been accurately weighed out, the amount of silver wire required to give a silver to gold ratio of 3:1 was calculated on the assumption that the samples already contained 10% silver alloyed with the gold, and weighed out.

The gold and silver wire were then wrapped in as small a piece of lead foil as possible, as suggested by Rose and Newman (1937),

..54/...

Smith (1947, table XXXV) gives the recommended amounts of lead which should be used for cupellation, depending on the fineness of the bullion. However, as the finenesses of the samples were not known, it was decided to use approximately the same amount of lead foil for each sample.

The cupellation was carried out as follows. After the furnace had reached a temperature a little above the required temperature, as indicated by the colour (orange to light orange), the cupels were placed in the furnace and allowed to remain there for 15 minutes, to ensure that they reached the temperature of the furnace and that all the moisture was driven out of them. The samples were then charged in as quickly as possible and the door was closed to raise the temperature until all the lead buttons had cleared, after which it was partly opened to allow a stream of air to pass through the furnace. As check assays were being used to control any errors during the cupellation, it was necessary to keep the temperature as uniform as possible. This was done by surrounding the sample cupels with a row of blank cupels, as suggested by Smith (1947, p.277). Cupellation was allowed to continue for 25 minutes. The door was closed just before removing the cupels and the temperature increased to remove the last traces of lead.

..55/...

2. Parting of the assay buttons

After the buttons had been removed from the cupels, they were flattened on an anvil with a polished hammer. Both the anvil and the hammer were cleaned and polished before being used and were used only for hammering gold and silver. Great care was taken to hammer the buttons as flat as possible to ensure that the maximum surface area was presented to the acid for attack during parting. The flattened buttons were annealed in the furnace at low red heat before parting. The first assays carried out were not given this preliminary annealing but it was found that these buttons tended to break up during the parting and that the surcharge (the variation in weight of the check sample due to the retention of silver or loss of gold) was very high. The annealing, suggested by Rose and Newman (1937, p. 522), eliminated these faults. It was not thought necessary to roll the flattened assays to reduce the thickness of the buttons.

The parting acid was prepared by mixing equal volumes of concentrated nitric acid (S.G. 1.4) and distilled water. A small amount of silver nitrate was added to the acid before use to remove any chlorides which may have been present. The acid was also kept free from sulphuric acid, which in the presence of nitric acid will dissolve gold. Smith (1947) recommends that two parting acids, one of 50%

..56/...

of water, be used to ensure that as much silver as possible is removed from the alloy. However, as parting with the weaker acid usually leaves less than 0.25% silver in the gold, it was decided that this amount could be corrected from the check assays and that parting with the stronger acid was unnecessary.

The parting was carried out in porcelain crucibles, the acid being brought to the boil before the addition of the samples. When the flattened buttons were placed in the acid, a violent reaction ensued as the acid attacked the silver. Parting was allowed to continue for half an hour to ensure that as much silver as possible was removed. The temperature was kept at approximately 90°C throughout the parting, as recommended by Rose and Newman (1937, p. 523).

After parting, the samples were washed twice with distilled water and were annealed in the furnace at red heat. They were then carefully weighed on the same balance as used for the initial weighings.

(iv) Results

1. The calculation of the gold content and the fineness of the samples

From the initial and final weights of the check samples, the surcharge (the increase or decrease in weight of the check sample due to the retention of silver or loss of gold) was calculated. This surcharge was then applied as a correction to the samples which were cupelled with the check assay. The gold and silver plus base metals

..57/...

contents were then calculated using the corrected weights. The fineness for each sample was calculated from the formula:

$$\text{fineness} = \frac{Au}{Au + Ag} \times 1000 \quad \text{(Fisher, 1945)}$$

The silver content was obtained from the silver plus base metals content by assuming that the copper and iron contents (obtained by atomic absorption) represented the total concentration of base metals. The following example shows the calculation of the results for sample S 13.

Initial weight of check assay	= 15.10 mgm
Final " " " "	= 15.12 mgm
Increase in weight	= 0.02 mgm
Therefore, surcharge	$= \frac{0.02}{15.12} \times 1000$
	= +1.3 parts per thousand
Final weight of sample	= 11.18 mgm
Corrected final weight	$= 11.18 - \frac{(1.3 \times 11.18)}{1000}$
	= 11.17 mgm
Initial weight of sample	= 12.02 mgm
Therefore, gold content	$= \frac{11.17}{12.02} \times 100$
	= 93.01%
Silver + base metals content	= 100 - 93.01
	= 6.99%
Copper + iron contents	= 1026 + 274
	= 1300 p.p.m.
	= 0.13%
Therefore, silver content	= 6.86%
Therefore, fineness	$= \frac{93.01}{6.86 + 93.01} \times 1000$
	= 931.3

..58/...

Tables XIX and XX give the results for all the samples assayed. Where duplicate assays were carried out, the results agreed to within 1% for most of the samples and all agree within 2.5%. For the G samples, the fineness varied from 757 for G 34 to 980 for G 41. Along the Zwartkopje shoot the fineness varied from 846 in S 1 to 983 in S 16. Most samples had finenesses greater than 900.

2. Causes of error in the parting assay

The main inherent sources of error in the parting assay are due to (a) the loss of gold by volatilization, absorption of silver by the cupel and by solution in the parting acid; and (b) the retention of silver in the parted gold. The losses due to volatilization amounts to one part in a million (Rose and Newman, 1937, p.523) and may be ignored. Most of the gold lost is due to absorption by the cupel, the amount absorbed varying with the conditions of cupellation such as the temperature, the amount of lead used, and the proportion of silver to gold, as has been described in a previous section. The percentage of copper in the alloy affects the amount of gold absorbed considerably; the greater the percentage copper, the greater the absorption. Smith (1947, p.284) states that for a copper content of less than 10%. the amount of gold absorbed is 0.3 - 0.4 parts per thousand. Other factors which affect the loss during cupellation include the nature of the cupel and the draught through the furnace, (Finkelstein, 1962, p. 702). The loss of gold in nitric acid by solution is very small, Beringer and Beringer

..59/...

Table XIX. The gold and silver contents and the finenesses of the G samples of native gold.

Sample	Initial weight (mgm.)	Final weight (mgm.)	Surcharge (parts per thousand)	Corrected weight (mgm.)	% Au	% Ag	% (Cu + Fe)	Fineness	Mean fineness.
G 2	12.21	10.14	+20.2	9.94	81.41	18.16	0.43	817.6	
G 4	10.75	10.40	+22.0	10.17	94.60	5.30	0.10	946.9	
G 5	9.55	9.10	+18.5	8.93	93.51	5.95	0.54	940.2	
G 6	7.50	6.62	+20.2	6.49	86.53				
G 7	14.46	12.72	+18.5	12.48	86.31	13.63	0.06	863.6	
G 8	10.51	9.78	+20.2	9.58	91.15	8.80	0.05	912.0	
G 9	10.72	10.27	+18.5	10.08	94.03	5.79	0.18	942.0	948.4
	16.41	15.72	+ 0.5	15.64	95.30	4.52	0.18	954.7	
G 10	13.74	12.66	+18.5	12.43	90.47	9.51	0.02	904.1	896.6
	10.00	8.90	+ 2.5	8.88	88.80	11.18	0.02	888.2	
G 14	9.60	9.06	+20.2	8.88	91.64	9.29	0.07	917.0	
G 15	11.80	10.31	+18.5	10.12	85.76				
G 16	10.21	9.68	+22.0	9.47	92.75	7.20	0.05	928.0	926.0
	12.81	11.85	+ 1.3	11.83	92.35	7.60	0.05	924.0	
G 17	13.77	12.51	+22.0	12.23	88.82	11.07	0.11	889.2	
G 18	11.01	8.84	+20.2	8.66	78.66	21.27	0.07	787.2	
G 19	10.52	10.02	+20.2	9.82	93.26	6.67	0.07	933.3	929.5
	8.95	8.30	+ 2.5	8.28	92.51	7.42	0.07	925.7	

Table XIX, continued.

Sample	Initial weight (mgm)	Final weight (mgm)	Surcharge (parts per thousand)	Corrected weight (mgm)	% Au	% Ag	%(Cu + Fe)	Fineness	Mean fineness
G 20	8.79	8.50	+ 22.0	8.31	94.54	5.40	0.06	946.9	
G 21	9.78	8.81	+ 18.5	8.65	88.45				
G 22	5.22	5.08	+ 22.0	4.97	95.21	4.67	0.12	953.2	
G 23	15.42	13.71	+ 1.3	13.68	88.78	11.01	0.21	889.7	885.1
	8.65	7.62	+ 2.5	7.60	87.86	11.93	0.21	880.4	
G 24	7.21	6.11	+ 20.2	5.99	83.08	16.70	0.22	832.6	
G 25	2.00	1.82	+ 20.2	1.78	89.00				
G 26	20.32	18.34	+ 1.3	18.32	90.16	9.81	0.03	901.9	905.2
	19.05	17.31	+ 0.5	17.30	90.81	9.16	0.03	908.4	
G 27	10.82	9.89	+ 18.5	9.80	90.57	9.40	0.03	906.0	903.6
	16.83	15.20	+ 2.5	15.16	90.08	9.89	0.03	901.1	
G 28	11.08	10.48	+ 22.0	10.25	92.51	7.39	0.10	926.1	
G 29	11.61	10.10	+ 22.0	9.88	85.10	14.85	0.05	851.4	
G 30	8.95	9.05	+ 22.0	8.85	97.79	2.15	0.06	978.5	979.7
	14.22	13.95	+ 0.5	13.94	98.03	1.91	0.06	980.9	
G 31	7.81	6.22	+ 18.5	6.10	78.10	21.84	0.06	781.5	781.3
	8.20	6.41	+ 1.6	6.40	78.05	21.89	0.06	781.0	
G 32	12.10	10.72	+ 20.2	10.50	86.78	13.15	0.07	868.4	878.1
	14.70	13.05	+ 0.5	13.04	88.71	11.22	0.07	887.7	

Table XIX, continued

Sample	Initial weight (mgm.)	Final weight (mgm.)	Surcharge (parts per thousand)	Corrected weight (mgm.)	% Au	% Ag	% (Cu + Fe)	Fineness	Mean fineness
G 33	5.42	4.90	+ 18.5	4.81	88.75				
G 34	3.92	2.95	+ 1.6	2.95	75.26	24.10	0.64	757.4	
G 35	7.60	6.91	+ 22.0	6.76	88.95	10.99	0.06	890.0	
G 36	10.80	9.62	+ 22.0	9.41	87.13	12.84	0.03	871.6	874.6
	17.92	15.73	+ 0.5	15.72	87.72	12.25	0.03	877.5	
G 37	10.58	9.48	+ 22.0	9.27	87.62	12.34	0.04	876.6	884.3
	17.80	15.89	+ 1.3	15.87	89.16	10.80	0.04	892.0	
G 38	12.11	11.01	+ 18.5	10.81	89.27	10.70	0.03	893.0	
G 39	12.35	11.00	+ 20.2	10.78	87.29	12.49	0.22	874.8	885.6
	16.46	14.76	+ 2.5	14.72	89.43	10.35	0.22	896.3	
G 40	20.00	18.58	+ 1.3	18.56	92.80	7.18	0.02	928.2	928.8
	22.74	21.18	+ 2.5	21.13	92.92	7.06	0.02	929.4	
G 41	14.19	14.20	+ 22.0	13.89	97.89	2.09	0.02	979.1	980.1
	11.51	11.31	+ 0.5	11.30	98.09	1.89	0.02	981.1	
G 42	11.42	10.33	+ 18.5	10.14	88.79	11.19	0.02	888.1	
G 43	10.62	9.60	+ 1.3	9.59	90.30	9.59	0.11	904.0	
G 44	9.90	9.05	+ 20.2	8.87	89.60	10.37	0.03	896.3	906.5
	16.85	15.45	+ 0.5	15.44	91.64	8.33	0.03	916.6	
G 45	9.85	9.50	+ 20.2	9.31	94.52	5.14	0.34	948.4	942.9
	9.72	9.10	+ 2.5	9.08	93.42	6.24	0.34	937.4	
G 46	10.31	10.00	+ 18.5	9.81	95.15				
	5.52	5.20	+ 0.5	5.20	94.20				

Table XX. The gold and silver contents and the finenesses of the S samples of native gold.

Sample	Initial weight (mgm.)	Final weight (mgm.)	Surcharge (parts per thousand)	Corrected weight (mgm.)	% Au	% Ag	% (Cu + Fe)	Fineness	Mean fineness.
S 1	9.31	7.88	+ 1.3	7.87	84.53	15.39	0.08	846.0	
S 2	6.93	6.51	+ 18.5	6.39	92.20	7.69	0.11	923.0	930.4
	4.42	4.15	+ 1.3	4.14	93.67	6.22	0.11	937.8	
S 3	28.75	27.21	+ 2.5	27.14	94.40	5.47	0.13	945.2	
S 4	10.86	10.31	+ 22.0	10.08	92.82	7.08	0.10	929.1	922.2
	16.91	15.40	+ 1.6	15.46	91.43	8.47	0.10	915.2	
S 7	11.30	10.67	+ 20.2	10.45	92.48	7.46	0.06	925.4	931.6
	18.32	17.21	+ 2.5	17.17	93.72	6.22	0.06	937.8	
S 8	6.60	6.15	+ 1.3	6.14	93.06	6.81	0.16	931.3	
S 9	5.07	4.63	+ 2.5	4.62	91.13	8.74	0.13	912.5	
S 10	23.23	22.26	+ 0.5	22.25	95.78	4.08	0.14	959.1	
S 11	12.02	11.18	+ 2.5	11.15	92.76	8.08	0.16	929.1	
S 13	12.02	11.18	+ 1.3	11.17	93.01	6.86	0.13	931.3	939.1
	17.12	16.20	+ 0.5	16.19	94.57	5.30	0.13	946.9	
S 15	12.92	11.85	+ 1.3	11.83	91.56	8.32	0.12	917.9	920.2
	13.85	12.79	+ 2.5	12.76	92.13	7.75	0.12	922.4	
S 16	10.00	10.00	+ 20.2	9.80	98.00	1.90	0.10	981.0	983.0
	16.[illegible]	16.00	+ 2.5	15.96	98.40	1.50	0.10	985.0	

Table XX, Continued

Sample	Initial Weight (mgm.)	Final Weight (mgm.)	Surcharge (parts per thousand)	Corrected weight (mgm.)	% Au	% Ag	% (Cu + Fe)	Fineness	Mean fineness
S 17	9.95	9.68	+22.0	9.47	95.18	4.65	0.17	953.4	944.8
	11.75	11.00	+ 1.6	10.98	93.45	6.38	0.17	936.1	
S 18	8.43	8.20	+18.5	8.05	95.49				
S 19	11.68	11.09	+22.0	10.85	92.89	7.02	0.09	929.7	
S 20	11.11	10.38	+ 1.3	10.37	93.34	6.51	0.15	934.8	936.7
	26.24	24.65	+ 2.5	24.59	93.71	6.14	0.15	938.5	
S 21	10.58	10.08	+ 0.5	10.07	95.18	4.52	0.30	954.7	955.0
	4.82	4.60	+ 2.5	4.59	95.23	4.47	0.30	955.2	
S 22	10.01	9.60	+22.0	9.39	93.81	6.11	0.08	938.9	

(1921) giving it as 0.01 - 0.03%. The loss increases with the strength of the acid and with the proportion of silver present, but usually is so small that it may be ignored (Rose and Newman, 1937, p.524).

The gold obtained by parting always retains some silver, the amount varying with the thickness of the pellets and the proportion of silver present in the original alloy. After parting with the 50% nitric acid, 2.5 - 3 parts per thousand are retained. However, boiling in the stronger acid reduces the silver content to 0.06 - 0.09%, depending upon the length of time of the boiling. It has been shown that effective annealing of the cornets before parting is vital if the amount of silver retained is to be low and reproducible, (Law, 1928; Coxon, 1961).

Since the amount of silver retained usually exceeds the amount of gold lost during cupellation, the surcharge is usually positive. With a decrease in the proportion of gold, the loss is greater and the surcharge decreases until for bullion 700 - 800 fine there is usually no surcharge. The surcharge for gold 800 - 900 fine generally varies from 0.5 - 0.7 parts per thousand (Smith, 1947, p. 265).

The errors discussed above are inherent in the fire assay method. However, although the nett error (or surcharge) usually exceeds one part per thousand, accuracies of a much higher order are obtained by the application of control standards and rigidly reproducible

..60/...

procedures. Indeed Hanrahan (1962) has shown that for the routine assay procedure at the Rand Refinery, the standard error of the mean fineness is 0.058 parts per thousand.

C. THE SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THE GOLD SAMPLES

(a) Introduction

(i) General principles and techniques

As a single general method, spectrographic analysis is unsurpassed for the qualitative and quantitative analysis of minerals and rocks. The advantages of the method include very high sensitivity, speed, low cost, the very wide range of elements which can be detected and the provision of a permanent record of analysis in the form of a photographic plate. In addition, spectrographic methods are especially suitable for the analysis of gold as the gold spectrum is relatively simple and there is little chance of line coincidence with any of the impurities sought. Other favourable factors include the small amounts of material required, and the fact that the samples require almost no pretreatment before analysis.

In order to understand fully the methods of spectrographic analysis, it is essential to know something about the origin of spectra. When an element is heated to a high temperature, its atoms become excited and emit radiant energy in the form of radiation with characteristic wavelengths. In optical spectrography, this radiation is allowed to

..61/...

pass through a slit into the spectrograph where it is dispersed by a grating or a prism and emerges in the form of a spectrum which can be recorded on a photographic plate. A series of lines formed by the image of the slit, each of which corresponds to a particular emitted wavelength, appears on the plate. The structure of the spectrum, i.e. the number and wavelength of the component lines, is determined by the electronic configuration of the energized atoms. Therefore, the spectrum emitted by the atoms of an element is characteristic of the particular element and can be used for identification purposes. The intensity of the spectrum may serve as a measure of the concentration of the element.

The common sources of excitation are the flame, the arc and the spark. The flame has been discussed briefly in the section dealing with the atomic absorption spectroscopy and for further details Twyman (1951) may be consulted. Spark spectra are particularly useful in the quantitative analysis of metals and alloys because of the high reproducibility and accuracy of the method. Examination of the references listed by Wichelstein (1962, p. 707-708) shows that ten workers used spark sources to determine impurities in gold, whereas only six used d.c. arc sources and a further six a.c. arc sources. However, the d.c. arc has one important advantage over the spark, namely, its greater sensitivity. This is particularly important for qualitative and semi-quantitative analysis and, therefore, the d.c. arc finds its

..62/...

greatest use in these fields. Ahrens and Taylor (1961) discuss the theory and application of the d.c. arc in spectrochemical analysis in great detail and from their work, it appears that satisfactory accuracy in quantitative analysis can only be obtained by standardising operating conditions and choosing suitable internal standards. Indeed, it should be stressed, that for all spectrochemical analyses, standard analytical procedures should be strictly adhered to and arcing conditions, especially, should be kept as uniform as possible to overcome the many possible causes of error inherent in the method.

The most sensitive spectral lines of an element are normally used to detect whether the element is present in a given sample. Ahrens and Taylor (1961) give tables of the most sensitive lines of all the elements, with the interfering lines of other elements. The lines are identified by comparing them with master plates containing the spectra of the elements sought, or by determining their wavelengths and looking up the elements in reference tables (e.g. Harrison, 1939). An iron spectrum is usually exposed on the photographic plate to simplify determination of the wavelength. Mistaken identification of the lines may occur due to interference of lines of other elements. This is especially the case when the matrix material or elements in large amounts in the samples, have complex spectra. However, with regard to the present work, the gold spectrum is relatively simple and interference by weak lines is not marked.

..63/...

In quantitative analysis, it is assumed that the intensity of the lines is proportional to the concentration of the atoms emitting the radiation, which, in turn, is dependent on the concentration of the element. To overcome errors introduced by variations in the conditions of arcing, it is normal practice in quantitative analysis to use an element which is burnt with the sample as an internal standard. The internal standard should be present in the samples in constant amounts and the variations in the intensity of its lines, therefore, indicate variations in the arcing conditions. The internal standard element may be either already present in the sample to be analyzed or else may be added to it. In either case, its concentration must be accurately known.

The choice of a suitable internal standard depends on several factors, including the following: the volatilization rates of the internal standard and the analysis elements should be similar; the particular analysis and internal standard lines used should have approximately the same wavelength and similar excitation and ionization potentials; the internal standard line should be free from self-absorption. Ahrens and Taylor (1961, chap. 8) discuss these and the other factors in great detail.

The instrument used to measure the intensity of the lines is known as a microphotometer or densitometer. It measures the amount of light transmitted through a spectral line by means of a photocell,

..64/...

Author Gay N C (nicholas Gay)
Name of thesis A Study Of The Trace Elements Associated With Gold From The Barberton District. 1963

PUBLISHER:

University of the Witwatersrand, Johannesburg
©2013

LEGAL NOTICES:

Copyright Notice: All materials on the University of the Witwatersrand, Johannesburg Library website are protected by South African copyright law and may not be distributed, transmitted, displayed, or otherwise published in any format, without the prior written permission of the copyright owner.

Disclaimer and Terms of Use: Provided that you maintain all copyright and other notices contained therein, you may download material (one machine readable copy and one print copy per page) for your personal and/or educational non-commercial use only.

The University of the Witwatersrand, Johannesburg, is not responsible for any errors or omissions and excludes any and all liability for any errors in or omissions from the information on the Library website.