However, it was found that the iron tended to segregate out during the cooling and that neither the copper nor the silver distributed themselves uniformly throughout the gold lattice. To prevent the segregation of the iron, a gold-iron alloy containing 7.88% iron was obtained from the Central Metallurgical Laboratories and was combined with gold, silver and copper in proportions to give an alloy containing 10% silver, 0.5% copper and 0.2% iron. The homogeneity of the gold-iron alloy had been checked by replicate analyses over a long period of time. The constituents of the gold alloy were then sealed into a silica tube under a pressure of 1 micron of mercury and were placed in a furnace at 1000°C and heated to 1080°C. After keeping the molten constituents at this temperature for an hour, during which time the tube was shaken continuously, the tube was removed from the furnace and quenched in water. The ingot was then rolled out into a strip approximately 0.03 inches thick and three samples were taken, one from each end and one from the centre of the strip. These samples were submitted to a metallurgical laboratory for the determination of their silver, copper and iron contents. The results of the analyses were as follows:

Sample	Gold	Silver + base metals	Copper	Iron
1	89.45%	10.55%	0.80%	0.48%
2	89.57%	10.43%	0.55%	0.20%
3	89.66%	10.34%	0.70%	0.25%

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From the results it is seen that there were differences of up to 3000 p.p.m. in the copper and iron contents of the samples and that generally the alloy could not be regarded as homogeneous. It is possible, however, that at least part of the differences could be attributed to the inaccuracies of the analytical methods.

The remaining portions of the alloy were then remelted under vacuum and were kept molten at 1070°C, with continuous shaking, for two hours. The tube was removed from the furnace and allowed to cool rapidly in air before being placed in another furnace at 920°C. The alloy was annealed at this temperature for 48 hours. It was then rolled and resampled for analysis, the results being as follows:

Sample	Gold	Silver + base metals	Copper	Iron
1	88.97%	11.03%	0.50%	0.20%
2	89.03%	10.97%	0.63%	0.24%

Although these results indicated that the homogeneity of the alloy had increased, it seemed unlikely that the method could be used to prepare suitable spectrographic standards. If the above alloy were to be diluted with refined gold to the required copper and iron concentrations, the time required for melting and annealing would have to be increased greatly to ensure that the impurities were distributed uniformly throughout the alloy.

In view of this inability to prepare satisfactory standard alloys, it was decided not to use spectrographic methods for the

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quantitative analysis of the samples. Instead, a new method of using atomic absorption spectroscopy, was decided upon for the determination of the copper and iron contents of the gold.

(c) The determination of copper and iron in the gold samples by atomic absorption spectroscopy

The use of atomic absorption spectroscopy for analytical purposes was first proposed by Walsh (1955). Since then it has been developed by several workers and has been applied particularly to the determination of silver, gold, the platinum metals, copper, iron, mercury, magnesium, zinc and other impurities in solution. The method is very sensitive, being capable of detecting concentrations down to 1 p.p.m. and less, in some cases, in solution. Recently the method has been applied to the determination of impurities in high purity gold by Strasheim, Butler and Maskew (1962) and Schuler, Jansen and James (1962).

The theory behind the method has been discussed in detail by, amongst others, Russell, Shelton and Walsh (1957) and Menzies (1960), and will only be discussed briefly here. When a solution of a metallic element is introduced into a flame, the great majority of the metallic atoms are in the ground state. On excitation, therefore, these atoms will emit resonance lines of definite wavelength. If radiation of the same wavelength is passed through the flame, it will

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tend to be absorbed by the atoms in the flame, with a resultant decrease in the intensity of the radiation. This decrease in intensity will be directly proportional to the concentration of the absorbing atoms in the flame. Therefore, the method consists essentially of passing the radiation of the analytical element from a suitable source such as a hollow cathode or discharge lamp, through the flame into which the analytical solution is sprayed. The decrease in intensity of the resonance line of the analytical element is measured on a spectrophotometer, a monochromator being used to reject the resonance lines of the other elements. By measuring the variation in absorbances for a series of standard solutions, a graph of absorbance against concentration can be plotted and hence the concentrations of the elements in the unknown samples can be determined.

The method has several advantages over other analytical techniques, the most important being that the relative lack of interference allows the use of standards in a form different from the samples, i.e. it may be regarded as a fundamental method. In addition, it is extremely sensitive and the precision and accuracy are relatively good. However, the disadvantages include the facts that only one element can be analyzed at a time and that the sample must be in solution, which could introduce new errors.

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(ii) Laboratory procedure

1. Apparatus

The apparatus used was that described by Schuler and Janssen (1962). It consisted of a Zeiss M4QII monochromator and a Zeiss PMQII indicator unit for line isolation and intensity measurement; a specially designed water-cooled glass burner with a titanium grid; a titanium atomizer; a standard Hilger and Watts H909 atomic absorption unit hollow cathode lamp holder and quartz lenses. Plate 1 shows the burner, lamp holder, lenses and atomizer attached to the optical bar. The hollow cathode lamps were energized by a Hilger and Watts FA 41 hollow cathode lamp supply. 'Handigas', a mixture of propane and butane, was used for fuel for the burner. The composition of the gas mixture was kept constant by drawing the fuel off as a liquid and evaporating it in a thermostatically controlled, electrically heated unit attached to the gas cylinder. It was hoped in this way to obtain consistency in the burner operating characteristics.

2. Solution of the samples

After each homogenized sample had been rolled out, it was cut up into small pieces and definite amounts were accurately weighed out for the atomic absorption analyses. The amounts weighed out varied with the initial size of the sample.

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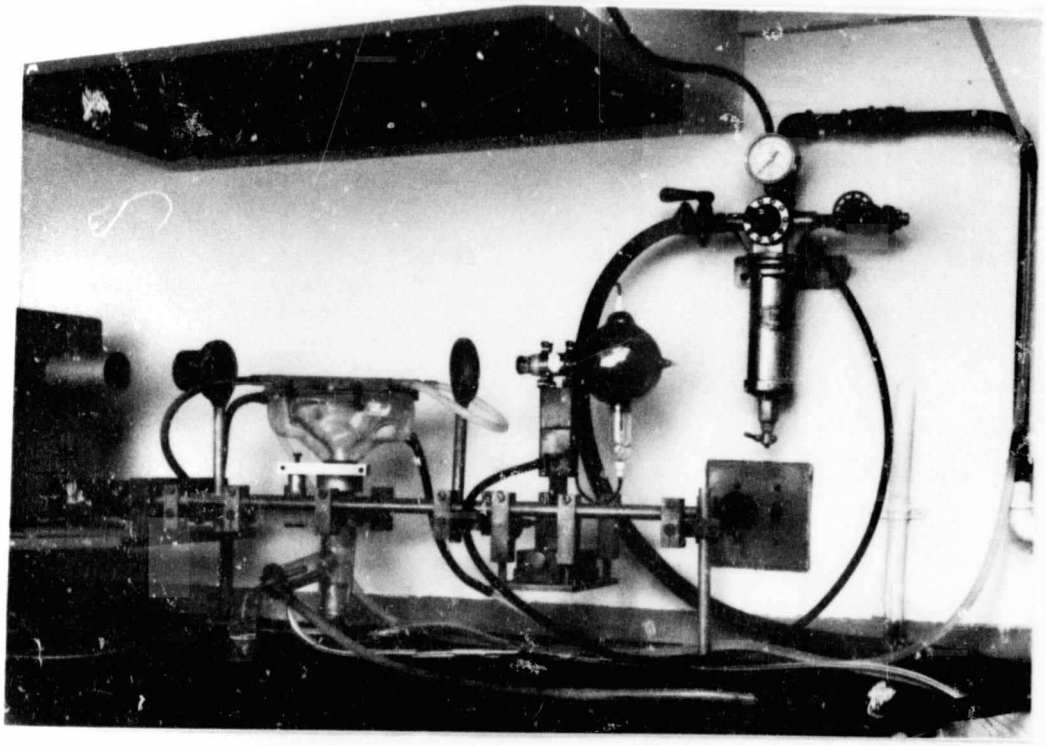

Plate 1 The atomic absorption apparatus used for the analysis of the gold solutions.

Table XIII gives the amount of gold normally taken from each sample for analysis.

Table XIII Weights taken and the dissolution details of the atomic absorption samples.

Original weight of sample	Weight taken for analysis	Final solvent	Final volume of solution
>175 mgm	100 mgm	20% HCl	10 cc
75 - 175 mgm	50 mgm	20% HCl	10 cc
50 - 75 mgm	25 mgm	20% HCl - alcohol mixture.	10 cc
30 - 50 mgm	10 mgm	20% HCl - alcohol mixture	5 cc

Those samples which weighed less than 30 mgm were not normally analyzed by this method.

In considering the weights taken for analysis, it should be noted that they were far less than those used by other workers. For example, Strasheim, Butler and Maskew (1962) used a 5 gram sample to determine two elements, though they do mention that less gold is required.

The aqua regia for the dissolution of the gold was prepared from analar grade acids and distilled water in the ratio of 200 HCl (S.G. 1.19) : 45 HNO_3 (S.G. 1.4) : 245 H_2O, following the method of Strasheim, Butler and Maskew.

The gold samples were dissolved in 10 cc. of the aqua regia and

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the solutions were evaporated to incipient dryness. The residue was redissolved in 10 cc of a 20% hydrochloric acid solution and once more evaporated to dryness. The samples were then redissolved in the solvents given in table XIII, according to their weights, and the solutions made up to the required volumes in the table. The addition of ethyl alcohol to the hydrochloric acid used to dissolve the smaller samples, was done to enhance the sensitivity and, thus, to try and ensure the detection of the very small amounts of copper and iron in the solutions. Schuler et al (1962) have shown that by adding organic solvents to the solutions, it is possible to increase the absorption signal and that a mixture of 20% hydrochloric acid and ethyl alcohol, in the proportion of 70 : 30 parts respectively, doubles the sensitivity. It was this particular mixture of acid and alcohol that was used as the final solvent of the smaller samples.

No attempt was made to filter of the silver chloride precipitated during the dissolution of the gold, as it was feared that some of the gold solution would be lost during the filtration. Strasheim, Butler and Maskew have, however, shown that the presence of silver chloride has no effect on the absorption signals of copper and iron.

Those samples which were dissolved in the acid-alcohol mixture were only taken into solution shortly before being analyzed and were stored in tightly stoppered bottles to prevent, as much as possible, the evaporation of the alcohol. However, during the actual analyses,

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the solutions were exposed to the air and it is possible that evaporation of the alcohol may have affected the results.

The gold concentration in the solutions can affect the absorbance recorded, particularly at high concentrations, (Schuler et al, 1962; Strasheim, Butler and Maskew, 1962). However, the maximum concentration of gold in the sample solutions was approximately 1% (w/v) and therefore the effect on the absorbances may be ignored.

3. The preparation of the blank solutions

Blank solutions were prepared by evaporating 10 ccs of aqua regia to dryness, dissolving the residue in 10 cc of 20% hydrochloric acid, evaporating to dryness and then redissolving in either 10 cc of hydrochloric acid or the acid-alcohol mixture.

4. The preparation of the standard solutions.

Two stock solutions were prepared by carefully dissolving accurately weighed amounts of spectrographically pure copper oxide and iron sponge in 20% hydrochloric acid. These two solutions were then transferred to two volumetric flasks, great care being taken not to lose any, and were made up to the mark. From these copper and iron stock solutions, two sets of standard solutions were prepared for each element by diluting them with 20% hydrochloric acid and the 20% hydrochloric acid-ethyl alcohol mixture. These

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standard solutions covered the following ranges of concentration:

Copper		Iron	
HCl	HCl-alcohol	HCl	HCl-alcohol
---	13.4 p.p.m.	---	72.3 p.p.m.
9.9 p.p.m.	6.9 p.p.m.	51.6 p.p.m.	36.1 p.p.m.
5.0 p.p.m.	3.4 p.p.m.	25.8 p.p.m.	17.5 p.p.m.
2.5 p.p.m.	1.7 p.p.m.	12.9 p.p.m.	9.0 p.p.m.
1.2 p.p.m.	0.9 p.p.m.	6.5 p.p.m.	4.5 p.p.m.

At concentrations greater than those above, the absorbances are unreliable and the calibration graph tends to depart from linearity.

As the analyses were carried out on three different days, fresh standard solutions were prepared for each day.

5. The analytical method

The following table gives the standard experimental conditions used for all analyses:

Element	Wavelength	Slit width	Lamp current	Air pressure
Copper	3247 A	0.07 mm	12 mA.	20 lbs/sq inch
Iron	2483 A	0.10 mm	32 mA.	20 lbs/sq inch

The absorbance measurements for the standard solutions, samples and blank solutions, were all taken consecutively in one run. Before

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the run, after each fourth measurement and at the end of the run, the absorbance given by a check solution was noted to control any drift in the recording unit. Five measurements were made on the standard solutions and three on the sample solutions. After each solution had been sprayed into the flame, the atomizer was cleaned with hydrochloric acid followed by distilled water. Throughout the analyses, the conditions were kept as constant as possible. The same type of beaker was used as a container for all the solutions and the heights of the solutions in the beakers were kept the same.

(iii) Results

1. Calculation of the results

The absorbances given by the check solution were plotted against the number of the reading to give a graph showing the variation in absorbance due to instrument drift. The mean absorbance value for the solution was calculated and all the absorbance values obtained were corrected from the graph to this mean value. Figure 5 shows the variation in absorbance for the copper check solution with instrument drift. The mean value for the absorbance is 0.097 and all readings are corrected to this value. For example, reading number 36 must be reduced by 0.003 of an absorbance unit to allow for the effect of instrument drift on the absorbance measurement.

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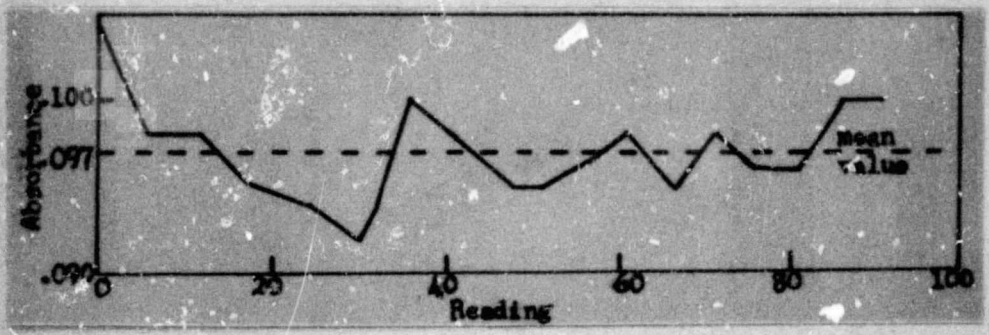

Figure 5 The variation in absorbance of the copper check solution with instrument drift.

After correcting the absorbance values of the standard solutions for instrument drift and for the concentrations of copper and iron in the solvents (from the blank solvent absorbances), graphs relating absorbance to concentration were plotted for the two elements. Figures 6 and 7 show these graphs for copper and iron in hydrochloric acid and hydrochloric acid plus ethyl alcohol. The graphs for copper depart very slightly from linearity over the range of concentration covered by the standards. However, those for iron show a marked departure from linearity at high concentrations as the absorbance fails to increase at the same rate as the concentration. From the graphs, the absorbance values for the sample solutions (corrected for instrument drift and the absorbances of the blank solvents) are converted into concentrations of the elements in solution. These concentrations in solution are then converted into concentration in the sample as is shown in the following hypothetical example:

Weight of sample dissolved in solution = 100 mgm = 0.1 gm

Volume of solution = 10 cc

Therefore concentration of sample in solution = 0.01 gm/cc

Concentration of metal in solution = 5 p.p.m. = 5×10^{-6} gm/cc (as determined from the graph)

Therefore concentration of metal in sample = $\frac{5 \times 10^{-6}}{0.01}$ = 500 p.p.m.

Tables XIV, XV, XVI and XVII give the results obtained for the analyses of the samples. It will be noticed that the correction

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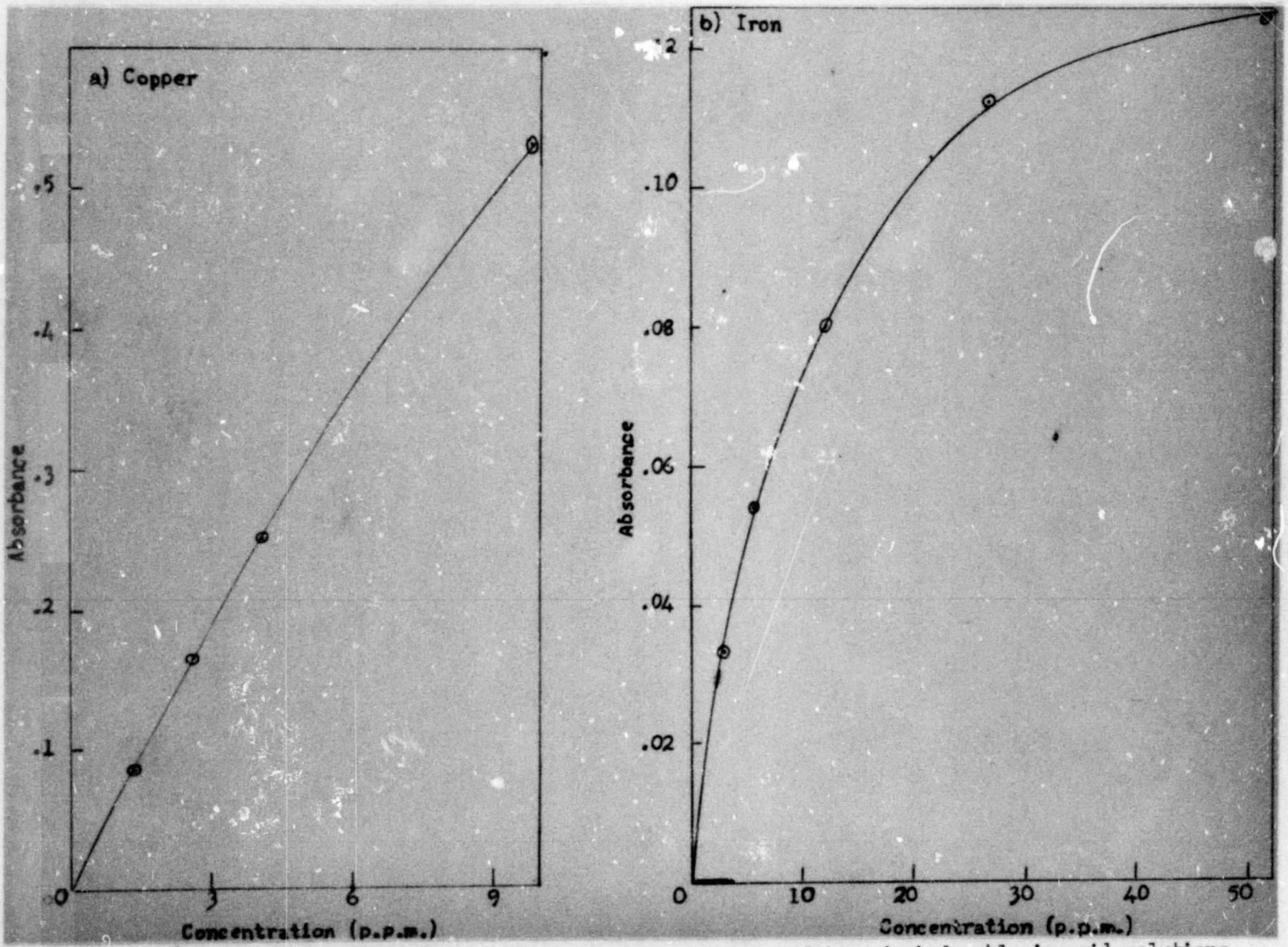

Figure 6 The atomic absorption working curves for copper and iron in hydrochloric acid solutions

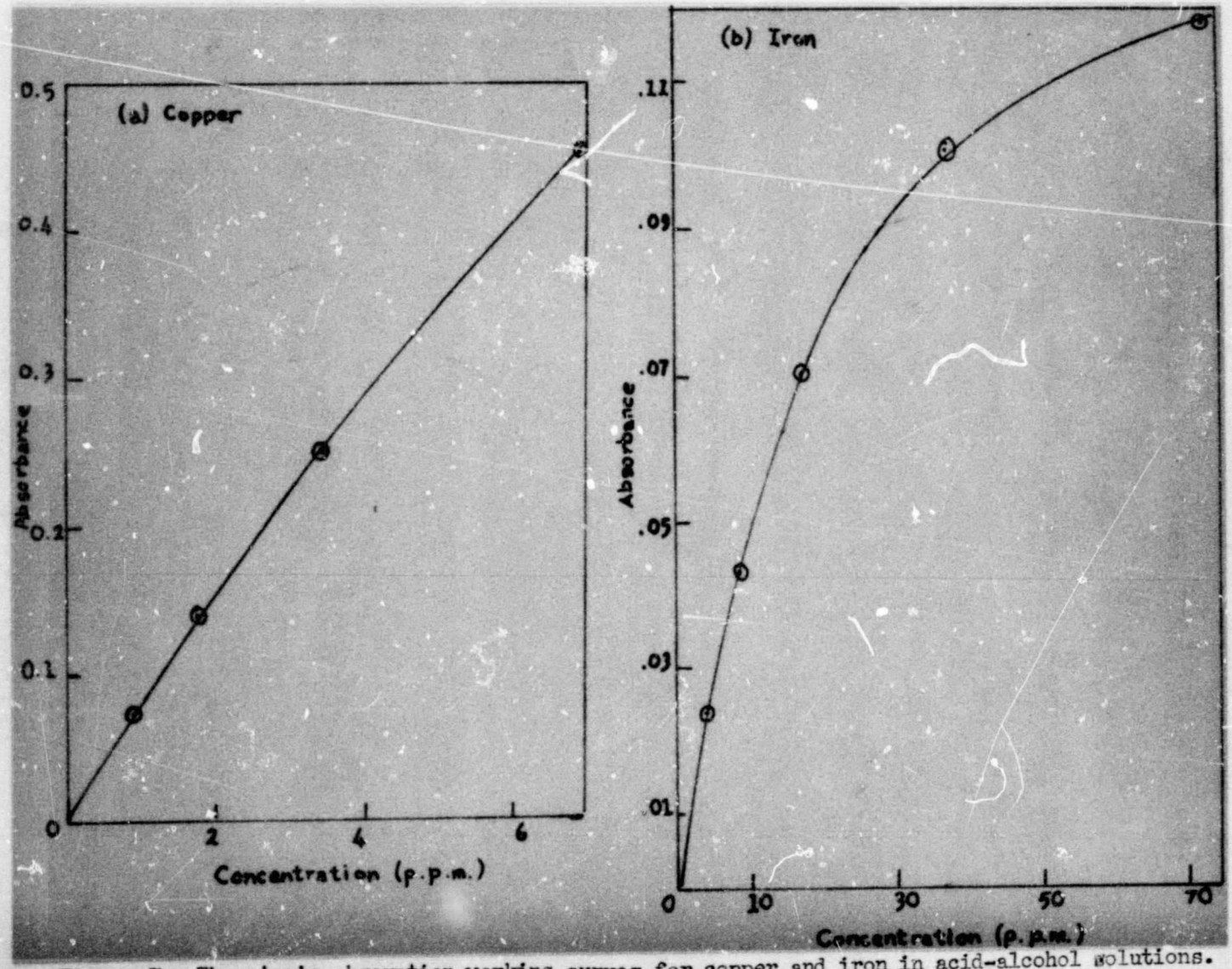

Figure 7 The atomic absorption working curves for copper and iron in acid-alcohol solutions.

Table XIV. The Copper concentrations in the G native gold samples, as determined by atomic absorption.

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.)
G 1	.050	.047	.047	0.048	0.045	0.55	9.95	5	276.4
G 2	.434	.427	.428	0.430	0.427	6.46	10.35	5	3120.8
G 4	.195	.199	.200	0.198	0.187	2.90	93.60	10	309.8
G 5	.131	.131	.133	0.132	0.125	2.29	7.92	10	2896.9
G 7	.154	.152	.157	0.154	0.143	2.12	50.35	10	421.1
G 8	.049	.046	.045	0.047	0.044	0.52	25.75	10	201.9
G 9	.455	.454	.444	0.451	0.440	8.00	50.45	10	1585.7
G 10	.069	.068	.064	0.067	0.056	0.78	95.05	10	82.1
G 12	.061	.062	.061	0.061	0.054	0.97	9.02	5	537.7
G 14	.089	.087	.089	0.088	0.085	1.02	11.05	5	461.5
G 16	.042	.044	.044	0.043	0.032	0.46	30.30	10	151.8
G 17	.079	.074	.076	0.076	0.073	0.88	26.20	10	335.9
G 18	.105	.104	.103	0.104	0.101	1.21	27.35	10	442.4
G 19	.080	.078	.077	0.078	0.075	0.95	11.55	5	415.6
G 20	.050	.047	.049	0.049	0.046	0.55	11.53	5	238.5
G 22	.108	.105	.108	0.107	0.104	1.25	9.30	5	672.1

Table XIV, 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.)
G 23	.029	.029	.028	0.029	0.022	0.40	22.82	10	177.0
G 24	.136	.136	.132	0.135	0.132	1.62	9.22	5	878.5
G 26	.085	.082	.083	0.083	0.072	1.06	56.80	10	186.6
G 27	.061	.060	.056	0.059	0.048	0.69	51.20	10	134.8
G 28	.132	.131	.128	0.130	0.127	1.54	25.48	10	604.4
G 29	.070	.070	.070	0.070	0.067	0.82	27.00	10	303.7
G 30	.124	.126	.117	0.122	0.111	1.63	58.50	10	278.6
G 32	.205	.201	.196	0.201	0.190	2.95	56.00	10	526.8
G 33	.434	.433	.431	0.433	0.430	6.51	11.61	11	6168.0
G 35	.060	.064	.065	0.063	0.060	0.72	9.53	5	377.8
G 36	.097	.096	.096	0.096	0.085	1.25	95.21	10	131.3
G 37	.089	.087	.090	0.089	0.078	1.12	54.00	10	207.4
G 38	.056	.056	.058	0.057	0.046	0.67	54.25	10	123.5
G 39	.265	.273	.269	0.269	0.258	4.38	92.65	10	472.7
G 40	.060	.052	.059	0.057	0.046	0.67	94.92	10	70.6
G 41	.116	.118	.112	0.115	0.104	1.52	91.10	10	166.8
G 42	.072	.070	.072	0.071	0.060	0.86	55.00	10	156.4

Table XIV, 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.)
G 43	.020	.016	.014	0.017	0.010	0.13	23.42	10	76.9
G 44	.046	.041	.045	0.044	0.041	0.50	23.69	10	211.1
G 45	.030	.034	.034	0.033	0.026	0.47	27.76	10	170.6

1 - absorbances corrected for instrument drift.

2 - mean absorbance corrected for copper concentration in the hydrochloric acid-aqua regia blank.

Table XV. The copper concentration in the S native gold samples, as determined by atomic absorption.

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 1	.127	.126	.128	0.127	0.124	1.51	27.15	11	611.8
S 2	.130	.131	.128	0.130	0.127	1.56	9.50	5	821.1
S 3	.047	.045	.040	0.044	0.037	0.66	26.81	10	246.2
S 4	.135	.135	.132	0.134	0.131	1.61	24.04	10	669.7
S 7	.144	.148	.148	0.147	0.136	1.99	57.65	10	345.2
S 8	.019	.020	.017	0.019	0.012	0.21	7.54	5	139.3
S 9	.024	.027	.026	0.026	0.019	0.34	9.65	5	176.2
S 10	.053	.052	.051	0.052	0.045	0.80	26.31	10	304.1
S 11	.053	.052	.051	0.052	0.045	0.80	28.01	10	285.6

1 - Absorbances corrected for instrument drift.
2 - Mean absorbance corrected for copper concentration in hydrochloric acid-aqua regia blank.

Table XV 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 13	.050	.052	.051	0.051	0.044	0.80	29.24	10	273.6
S 15	.038	.038	.041	0.039	0.032	0.57	27.54	10	207.0
S 16	.114	.113	.112	0.113	0.110	1.32	26.90	10	490.8
S 17	.196	.194	.196	0.195	0.192	2.56	25.45	10	1005.0
S 19	.078	.072	.074	0.075	0.072	0.86	25.19	10	341.4
S 20	.057	.055	.053	0.055	0.048	0.88	30.32	10	290.2
S 21	.062	.064	.066	0.064	0.057	1.03	27.76	10	170.6
S 22	.136	.133	.132	0.134	0.131	1.60	24.75	10	646.5

1 - Absorbances corrected for instrument drift.
2 - Mean absorbance corrected for copper concentration in hydrochloric acid-aqua regia blank.

Table XVI. The iron concentrations in the G samples of native gold, as determined by atomic absorption.

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.)
G 1	.016	.014	.014	0.015	0.009	0.50	9.95	5	251.2
G 2	.038	.036	.037	0.037	0.031	2.40	10.35	5	1159.4
G 4	.058	.057	.060	0.058	0.055	6.30	93.60	10	673.1
G 5	.009	.011	.014	0.011	0.010	2.00	7.92	10	2525.3
G 7	.013	.012	.014	0.013	0.010	0.80	50.35	10	158.9
G 8	.023	.019	.018	0.020	0.014	0.80	25.75	10	310.7
G 9	.020	.016	.017	0.018	0.015	1.30	50.45	10	257.7
G 10	.015	.017	.014	0.015	0.012	1.00	95.05	10	105.2
G 12	.019	.020	.016	0.018	0.017	3.20	9.02	5	1773.8
G 14	.017	.017	.014	0.015	0.009	0.50	11.05	5	226.2
G 16	.014	.016	.014	0.015	0.012	1.00	30.30	10	330.0
G 17	.035	.031	.033	0.033	0.027	1.90	26.20	10	725.2
G 18	.017	.017	.018	0.017	0.011	0.60	27.25	10	219.4
G 19	.017	.014	.016	0.016	0.010	0.60	11.55	5	259.7
G 20	.022	.019	.021	0.021	0.015	0.90	11.53	5	390.2

Table XVI. 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.)
G 22	.025	.019	.024	0.023	0.017	1.05	9.30	5	564.5
G 23	.026	.022	.022	0.023	0.022	4.30	22.82	10	1917.4
G 24	.037	.035	.036	0.036	0.030	2.40	9.22	5	1301.5
G 26	.012	.012	.014	0.013	0.010	0.80	56.80	10	140.8
G 27	.015	.017	.016	0.016	0.013	1.10	51.20	10	214.8
G 28	.024	.020	.022	0.022	0.016	1.00	25.48	10	392.5
G 29	.017	.015	.017	0.016	0.010	0.55	27.00	10	203.7
G 30	.030	.026	.025	0.027	0.024	2.10	58.50	10	359.0
G 32	.010	.016	.018	0.015	0.012	1.00	56.00	10	178.6
G 34	.010	.012	.012	0.011	0.005	0.25	11.61	11	236.7
G 35	.019	.013	.012	0.015	0.009	0.50	9.53	5	262.3
G 36	.018	.015	.017	0.017	0.014	1.20	95.21	10	126.0
G 37	.014	.015	.015	0.015	0.012	1.00	54.00	10	185.2
G 38	.012	.015	.015	0.014	0.011	0.95	54.25	10	175.1
G 39	.090	.089	.089	0.089	0.086	16.25	92.65	10	1753.9
G 40	.017	.018	.018	0.018	0.015	1.30	94.92	10	137.0

Table XVI, 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.)
G 41	.014	.012	.011	0.012	0.009	0.75	91.10	10	82.3
G 42	.007	.008	.008	0.008	0.005	0.40	55.00	10	72.7
G 43	.011	.014	.017	0.014	0.013	2.50	23.42	10	1067.5
G 44	.015	.010	.010	0.012	0.006	0.30	23.69	10	126.6
G 45	.044	.044	.047	0.045	0.044	9.04	27.76	10	3261.1

1 - absorbances corrected for instrument drift.

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

Table XVII. The iron concentrations in the S samples of native gold, as determined by atomic absorption.

Sample	Corrected absorbance.			Mean absorbance	Corrected absorbance[2]	Concentration in solution (p.p.m.)	Weight (mgm.)	Volume (cc.)	Concentration in sample (p.p.m.)
S 1	.017	.015	.015	0.016	0.010	0.55	2[illegible]15	11	222.8
S 2	.016	.014	.014	0.015	0.009	0.50	9.50	5	263.2
S 3	.013	.017	.017	0.016	0.015	2.85	26.81	10	1063.0
S 4	.022	.017	.018	0.019	0.013	0.80	24.04	10	332.8
S 7	.021	.022	.023	0.022	0.019	1.60	57.55	10	277.5
S 8	.014	.012	.014	0.013	0.012	2.25	7.54	5	1492.0
S 9	.010	.010	.015	0.012	0.011	2.10	9.65	5	1088.1
S 10	.013	.017	.020	0.017	0.016	3.00	26.31	10	1140.3
S 11	.018	.023	.020	0.020	0.019	3.60	28.01	10	1285.3
S 13	.016	.016	.020	0.017	0.016	3,00	29.24	10	1026.0
S 15	.013	.015	.019	0.016	0.015	2.85	27.54	10	1034.9
S 16	.027	.028	.027	0.027	0.021	1.35	26.90	10	501.9
S 17	.035	.029	.029	0.031	0.025	1.75	25.45	10	687.6

1 - Absorbances corrected for instrument drift.

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