Estimation of Composition of Ancient Metal Objects

Utility of Specific Gravity Measurements

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The composition of valuable ancient metal objects, especially those composed of alloys of gold or silver, often cannot be estimated by chemical methods because samples cannot be taken. The utility and reliability of specific gravity as an index of the composition of such objects are critically discussed with numerous examples. It is generally useful for qualitative purposes, especially for distinguishing objects composed of precious metals from those composed entirely of base metals. For estimating gold in gold objects it is reliable and sufficiently accurate when the proportion of gold is high, but increasingly less so as the proportion of gold becomes lower. It is reliable for estimating silver in silver objects only when the proportion of silver is very high. No quantitative significance can be attached to the specific gravity of ancient objects composed of alloys of base metals. In spite of limitations, specific gravity is a valuable index of the chemical composition of certain kinds of ancient metal objects.

ONE principal obstacle in the way of determining the composition of metal objects of great antiquarian value or archeological significance is that the chemist is very frequently not permitted to sample such objects, even to the extent of obtaining sufficient material for microanalysis. Hence only physical methods of measurement can be used. Of such methods the oldest, simplest, and quickest are those that depend upon the measurement of density or specific gravity. (The term specific gravity seems to be preferable here because of the customary use of this term in the literature of the subject and because most of the former measurements to which reference is made in this paper are recorded as specific gravities and not as true densities.) Though such methods have often been used in the past for estimating the composition of samples of modern alloys, especially those of the precious metals, and of objects composed of these alloys, and have been used occasionally for estimating the composition of ancient metal objects, especially gold objects, not much attention has been paid to the validity of the results. The present paper discusses critically the validity and utility of specific gravity measurements as a means of estimating the composition of all kinds of ancient metal objects.

EXPERIMENTAL METHODS

For the measurement of the specific gravity of ancient metal objects the well-known method of Archimedes is the one most generally useful. In measuring the specific gravity of very small objects by this method, it is important to reduce as far as possible the error caused by the adherence of the surface film of water to the suspension wire. The wire should be as fine as possible and the addition of a drop or two of a dilute aqueous solution of any of the common wetting agents to the surface of the water is very helpful. This addition makes no significant change in the density of the water. A method devised by the author (*2*) has been found useful for measuring the specific gravity of very small grains or fragments of metal. There is little point, of course, in measuring the specific gravity of corroded metal objects, or of objects coated with heavy protective films of lacquer, varnish, or wax. Where it is allowed, such films should be removed by treatment with the appropriate organic solvent or mixture of solvents before the specific gravity is taken.

MEASUREMENTS FOR QUALITATIVE PURPOSES

The specific gravity of an ancient metal object is often useful as an indication of its qualitative composition. It is especially useful in the detection of forgeries of ancient metal objects. A few examples are shown in Table I.

Table I. Examples of Use of Specific Gravity Measurements for Qualitative Purposes

No.	Description of Object	Prior Opinion as to Composition	Observed Specific Gravity	Conclusion from Appearance and Specific Gravity	Result of Chemical Tests
1	Medieval coin	White gold	8.37	Base silver or white metal alloy	....
2	Medieval medal	Gilded silver	12.07	Base gold alloy	....
3	Forgery or copy of ancient Greek silver coin	Base metal	11.00	Lead alloy	Pb (high) Sn (low)
4	Forgery or copy of ancient Greek silver coin	Base metal	7.06	Zinc	Zn

No. 1 is a type of coin usually composed of a very pale or white gold-silver alloy. The specific gravity of this specimen is much too low for either white gold or pure silver. It is even too low for any uncorroded silver-copper alloy, and the figure suggests a white alloy composed of base metals. Unfortunately, chemical tests could not be made. This coin may be a medieval forgery.

No. 2 is a specimen of a medal of a type that has always been described in numismatic literature as being composed of gilded silver. The very light color of the raised parts of the design of this specimen as contrasted to the medium gold color of the depressed parts appeared to indicate such a composition. However, the specific gravity is much too high for gilded silver, as the figure for this does not exceed 10.75 at the most. The specific gravity of 12.07 indicates that it is composed of a base gold alloy, the normal color of which appears on the raised parts of the design that have been subjected to wear. It seems likely that this cast medal was treated chemically at the time of manufacture so as to enrich its surface with gold and give it the appearance of being composed of gold of high quality.

No. 3 may be an ancient forgery, a modern forgery, or merely a copy made for the purpose of study. The specific gravity indicates that it is composed of about 95% lead.

No. 4 is in all probability a modern forgery or copy, as it is almost certain that metallic zinc was unknown when coins of this type were issued.

ESTIMATION OF GOLD

The determination of the fineness of gold objects by specific gravity measurements is one of the oldest methods of assay. In spite of the long time this method has been known and used, there is little evidence that much critical attention has been paid to its probable accuracy, and considerable evidence that some investigators have attributed to it an unwarranted degree of accuracy. For example, Giesecke (*5*) determined the specific gravities of a considerable number of ancient electrum coins and calculated their per cent gold content through two decimal places. It may easily be shown that no basis exists for expressing results to such an apparent degree of accuracy.

A primary difficulty in the determination of the composition of alloys of gold and silver, or of gold and copper, by specific gravity measurements is that the specific gravities of the pure metals themselves cannot be defined with any high degree of precision. Results of even very careful measurements of this so-called constant have varied considerably in accordance with the physical state of the specimens studied. Mellor (*12*) has ably summarized the discordant results obtained by different workers. Though the lack of agreement is less when only the most reliable results on massive specimens are considered, and still less when mechanically worked metal alone is considered, this being of more practical significance for objects assayed by the specific gravity method, there is nevertheless apparently no justification for expressing the specific gravities of the pure metals to more than a single decimal place for the purpose of computing the composition of their alloys.

This means that as a basis for determinations made at or close to 25° C. with reference to the density of water at 4° C. the specific gravity of gold should be taken as 19.3, that of silver as 10.5, and that of copper as 8.9. Hence it follows that for the determination of the composition of gold-silver alloys with a possible range of 0 to 100% for either component, there are actually available from the difference between the specific gravities of the two metals only 88 possible units in the scale of measurement, each a tenth of a unit in specific gravity. On the average, therefore, a little more than 1% is the closest approach that can possibly be attained in respect to the composition of such alloys by this method. Actually, if no contraction or expansion occurs on alloying, each tenth of a unit in specific gravity represents a little more than 0.5% change in composition near the top of the range in gold content and about 2% change near the bottom of the range. Likewise for gold-copper alloys there are only 104 possible units in the scale of measurement, and on the average slightly less than 1% is the closest possible approach to composition that can be attained, with approximately the same differences at the extremes. These differences at the extremes of the ranges necessarily follow from the nature of ideal proportional relationship between specific gravity and percentage composition by weight of such alloys. This relationship may be expressed by the following formula:

$$\% \text{ of } A = \frac{D_aD_x - D_aD_b}{D_aD_x - D_bD_x} \times 100$$

where, on the same temperature basis for each, D_a is the specific gravity of the major component A, D_b is the specific gravity of the minor component, and D_x is the specific gravity of a given alloy.

As the author (*3*) has shown, a comparison of ideal figures computed by the above formula with the best experimental figures obtained by various investigators (*6, 7, 11, 15*) on gold-silver and gold-copper alloys also indicates that the method is not more reliable than within about 1%. But when this method is used for estimating the gold content of actual objects of unknown composition, the error may often far exceed 1% for various reasons. The presence of foreign inclusions in the metal, or worse yet the presence of hidden cavities, may cause serious error. Another serious source of error may be a lack of knowledge of the particular metals alloyed with the gold. The presence of platinum or other heavy metals of the platinum group, for example, would lead to deceptively high results, though this cannot be considered a common source of error. More commonly, if the gold is alloyed with copper alone and it is assumed that it is alloyed with silver, or vice versa, or more commonly still, if it is alloyed with both in some unknown proportion and the assumption is made that it is alloyed with one or the other only, serious errors may arise in estimation of the gold content of the metal from the observed specific gravity. The possible extent of this error from this one important source alone is indicated by the differences in the computed ideal figures shown in Table II. This source of error is not very serious for alloys of very high gold content, but it becomes increasingly serious with decrease in gold content.

As a considerable number and variety of natural and artificial gold objects have been assayed or analyzed by standard dry or wet assay methods by previous investigators, who at the same time carefully measured the specific gravity of these objects, the degree of error from all sources likely to be encountered in actual practice may be approximated by an examination of their results. Only thirteen examples could be found where the investigator, himself, had estimated the gold content from the specific gravity and compared the result with the actual gold content found by analysis or assay. For most of the collected examples shown in Table III, the gold content has been computed from the specific gravity and compared with the actual gold content for the first time. All previous investigators who calculated the gold content from the observed specific gravity did so on the assumption that the gold was alloyed with silver alone. But it can be shown that this assumption does not provide the best general basis for estimating the gold content of objects in which the nature and proportion of the alloying metal or metals are unknown. It is true that in natural objects of very high gold content, or in objects fashioned from such native gold, silver is often the sole alloying

Table II. Magnitude of Possible Error When Alloying Component Is Unknown

Observed Specific Gravity	Calculated Gold Content, %		
	Silver assumed sole alloying component	Copper assumed sole alloying component	Difference
19.20	99.4	99.6	0.2
19.00	98.1	98.6	0.5
18.80	96.8	97.7	0.9
18.60	95.5	96.8	1.3
18.40	94.2	95.8	1.6
18.20	92.8	94.8	2.0
18.00	91.4	93.8	2.4
17.80	89.9	92.8	2.9
17.60	88.5	91.7	3.2
17.40	87.0	90.7	3.7
17.20	85.4	89.6	4.2
17.00	83.9	88.4	4.5
16.80	82.2	87.3	5.1
16.60	80.6	86.1	5.5
16.40	78.9	84.9	6.0
16.20	77.2	83.6	6.4
16.00	75.4	82.4	7.0

Table III. Gold Content of Various Natural and Artificial Objects as Estimated from Specific Gravity and as Determined by Analysis

No.	Description	Specific Gravity	Gold Content from Specific Gravity on Given Basis, %			Gold Content by Analysis, %	Difference Error on Given Basis, %			Literature Reference
			A	B	C		A	B	C	
1	Nugget	19.10	98.8	99.1	99.0	99.0	−0.2	+0.1	0.0	(*16*)
2	Ancient ornament	19.10	98.8	99.1	98.0	98.0	+0.8	+1.1	+1.0	(*17*)
3	Nugget	18.67	96.0	97.1	96.6	94.2	+1.8	+2.9	+2.4	(*4*)
4	Ancient wires	18.59	95.4	96.7	96.2	96.9	−1.5	−0.2	−0.7	(*10*)
5	Native grains	18.31	93.6	95.4	94.6	94.7	−1.1	+0.7	−0.1	(*4*)
6	Ancient bar	18.05	91.7	94.1	93.1	90.7	+1.0	+3.4	+2.4	(*18*)
7	Nugget	17.96	91.1	93.6	92.6	91.4	−0.3	+2.2	+1.2	(*16*)
8	Nugget	17.84	90.2	93.0	91.9	93.5	−3.3	−0.5	−1.6	(*4*)
9	Nugget	17.59	88.4	91.7	90.3	90.8	−2.4	+0.9	−0.5	(*16*)
10	Nugget	17.48	87.5	91.1	89.6	89.4	−1.9	+1.7	+0.2	(*16*)
11	Nugget	17.40	87.0	90.7	89.1	87.4	−0.4	+3.3	+1.7	(*16*)
12	Ancient plate	17.33	86.4	90.3	88.7	88.7	−2.3	+1.6	0.0	(*10*)
13	Celtic ring money	16.90	83.1	87.8	85.9	85.6	−2.5	+2.2	+0.3	(*10*)
14	Nugget	16.87	82.9	87.7	85.7	86.8	−2.9	+0.9	−1.1	(*16*)
15	End of ancient bracelet	15.50	70.7	79.0	75.6	75.6	−4.9	+3.4	0.0	(*17*)
16	Ancient bosses	15.43	70.1	78.5	75.0	74.7	−4.6	+3.8	+0.3	(*17*)
17	Ancient coin	15.06	66.4	75.9	72.0	69.0	−2.6	+6.9	+3.0	(*1*)
18	Ancient bar	14.83	64.0	74.2	70.0	66.8	−2.8	+7.4	+3.2	(*18*)
19	Ancient coin	13.85	53.0	66.3	60.8	59.5	−6.5	+6.8	+1.3	(*1*)
20	Ancient coin	13.23	45.3	60.7	54.3	57.3	−12.0	+3.4	−3.0	(*18*)
21	Ancient coin	13.07	43.1	59.2	52.5	51.8	−8.7	+7.4	+0.7	(*18*)
22	Ancient coin	12.19	30.4	50.1	41.9	37.9	−7.5	+12.2	+4.0	(*1*)

metal, but in objects of lower gold content, especially those fashioned from artificial alloys, copper may also be present in a proportion similar to that of the silver, and sometimes the copper is in much higher proportion than the silver. For example, object 4 of Table III was found by the analyst to contain 2.49% silver and only a trace of copper, whereas object 15 was found to contain 13.03% silver and 11.61% copper, and object 16 to contain 6.22% silver and 19.09% copper. It is therefore important to make some allowance for the possible presence of copper in considerable proportion when computing the gold content of objects of low fineness from specific gravity measurements.

As shown in Table III, the gold content of the various objects has been calculated from the observed specific gravities on three different bases in order to find out empirically the best single basis for such estimations. For basis A the assumption is that the gold was alloyed with silver alone, for basis B that it was alloyed with copper alone, and for basis C that it was alloyed with equal proportions of silver and copper, all computations being made in accordance with the ideal formula. A slight uncertainty exists in these computed results, because some of the investigators did not state the temperatures at which the specific gravities were measured, and others measured them at different stated room temperatures. However, as found by trial calculations, this lack of uniformity in the specific gravity figures can have little effect on the validity of the conclusions.

Table IV. Practical Conversion Table for Estimating Gold Content of Objects from Specific Gravity Measurements

Specific Gravity 25°/4°	Alloying Element		
	Silver	Copper	Silver and copper in equal proportions
	%	%	%
19.3	100	100	100
19.2	99	100	99
19.1	99	99	99
19.0	98	99	98
18.9	98	98	98
18.8	97	98	97
18.7	96	97	97
18.6	96	97	96
18.5	95	96	96
18.4	94	96	95
18.3	94	95	95
18.2	93	95	94
18.1	92	94	93
18.0	91	94	93
17.9	91	93	92
17.8	90	93	92
17.7	89	92	91
17.6	89	92	90
17.5	88	91	90
17.4	87	91	89
17.3	86	90	89
17.2	85	90	88
17.1	85	89	87
17.0	84	88	87
16.9	83	88	86
16.8	82	87	85
16.7	81	87	84
16.6	81	86	84
16.5	80	86	83
16.4	79	85	82
16.3	78	84	82
16.2	77	84	81
16.1	76	83	80
16.0	75	82	79
15.9	75	82	79
15.8	74	81	78
15.7	73	80	77
15.6	72	80	76
15.5	71	79	76
15.4	70	78	75
15.3	69	78	74
15.2	68	77	73
15.1	67	76	72
15.0	66	76	71
14.9	65	75	71
14.8	64	74	70
14.7	63	73	69
14.6	62	73	68
14.5	61	72	67
14.4	59	71	66
14.3	58	70	65
14.2	57	69	64
14.1	56	68	63
14.0	55	68	62
13.9	54	67	61
13.8	52	66	60
13.7	51	65	59
13.6	50	64	58
13.5	..	63	57
13.4	..	62	56
13.3	..	61	55
13.2	..	61	54
13.1	..	60	53
13.0	..	59	52
12.9	..	58	51
12.8	..	57	49
12.7	..	56	..
12.6	..	55	..
12.5	..	53	..
12.4	..	52	..
12.3	..	51	..
12.2	..	50	..

The actual figures for the gold content and the difference error on the three different bases are shown in Table III. When the gold content is very high, basis A yields the best results, but this same basis yields poor results on objects of low gold content. Basis B gives the poorest results when the gold content is high, and results that are nearly as poor as with basis A when the gold content is low. Basis C yields results on objects of very high gold content that are fairly good, and results on objects of lower gold content that are much better than those on either basis A or basis B. It is evident from all these figures that basis C is the best to use for objects of unknown composition. Of course, where the alloying metal is known from qualitative tests to be solely or predominantly silver or copper, basis A or basis B should be used. Still closer results on objects of unknown composition and of medium to high gold content might be obtained by selecting as a basis for computation an ideal alloy having a higher proportion of silver than copper, or by using basis A for objects of very high specific gravity and basis C for objects of lower specific gravity, but in view of the approximate nature of the results it is doubtful whether much would be gained by introducing such further refinements. Table IV provides a convenient means for converting the observed specific gravity to percentage of gold when estimating the gold content of objects by this method.

Table V. Estimations of Fineness of Gold Coins of Roman Empire

Ruler	Approximate Date of Coin, Years A.D.	Specific Gravity	Gold Content, %
Tiberius	14-15	19.2	99
Tiberius	16-21	19.2	99
Tiberius	21-25	19.2	99
Nero	64-68	19.2	99
Nero	64-68	19.2	99
Titus	74	19.1	99
Domitian	84	19.1	99
Trajan	100	19.2	99
Hadrian	117	19.0	98
Verus	163-164	19.1	99
Verus	163-164	19.1	99
Verus	163-164	19.2	99
Septimus Severus	193	19.0	99
Macrinus	217-218	19.1	99
Diocletian	287	19.1	99
Diocletian	290-292	19.0	98
Jovian	363-364	18.3	95
Valens	364-378	18.5	96
Valens	364-378	18.4	95
Valentinian III	425-455	18.8	97
Valentinian III	425-455	18.7	97
Julius Nepos	474-475	17.8	92

It is further evident from Table III that the method is reliable only for objects of high gold content. The average error for objects of high gold content is around 1% and the error for any given object may be around 2%. Because of the large errors that may occur with objects of low gold content, this method can be relied on only to give rough estimates of their true gold content.

On the basis of all these considerations there is no point, therefore, in determining the specific gravity of objects to more than the first decimal place in per cent for the purpose of estimating their gold content by this method, nor is there any point in expressing the results closer than the nearest whole number in per cent. Furthermore, the method should be restricted to objects of a high degree of fineness.

As an example of the proper application of this method and its utility where other methods are not applicable, there are shown in

Table V results obtained by the author on some gold coins of the Roman Empire. These illustrative and typical results are taken from a longer series of such determinations published elsewhere (*3*). An independent, though indirect and random, check on the essential correctness of these results is given by some figures published by Rauch (*14*) on the percentages of gold in a few Roman coins as obtained by fire assay. He reports that a coin of Nero contained 99.3% gold, which is close to the two results of 99% here found by specific gravity. For a coin of Titus he gives 99.6%, which is in fair agreement with the 99% found here, and for one of Verus he gives 99.0%, which agrees with the three results of 99% here obtained for coins of this emperor. It seems likely, therefore, that a considerable degree of confidence may be placed on the percentage figures shown in Table V.

ESTIMATION OF SILVER

The estimation of the fineness of silver objects, and in practice this means objects composed of silver-copper alloys, by means of specific gravity measurements is also a very old method, but it has been used to a much smaller extent than for gold objects, in part because of the lesser value of silver objects and the consequent smaller need for such a method, and in part because of the small difference between the specific gravity of silver and that of copper, which makes the method inherently less accurate. If the specific gravity of silver is taken as 10.5 and that of copper as 8.9, there are only 16 units in the scale of measurement for the entire range of composition from 0 to 100% for either component. However, the experiments of Karmarsch (*9*) on the relationship between specific gravity and composition in a series of silver-copper alloys indicate the possibility of obtaining less approximate results. Typical figures from his experiments are given in Table VI.

For the purpose of calculating the ideal values, the specific gravity of silver was taken as 10.50 and that of copper as 8.90. The agreement between the ideal values and the actual values throughout this series is fairly good. The average error is only 0.5% and the largest single error is only 1.9%. However, his experiments were made on coinage alloys prepared under carefully controlled conditions; it does not seem probable that anything like this accuracy could be obtained on ancient objects, especially those of varied physical history. On the other hand, because coins are the kind of object for which this method would be most useful in practice, and these have nearly always been produced from worked metal under similar conditions, it seemed worth while to investigate the actual accuracy of the method when applied to the determination of the fineness of ancient silver coins. The only previous data that could be located on the relationship between specific gravity and composition in a series of ancient silver coins are those of Brüel (*8*), and these data were obtained from coins evidently corroded to various degrees. Most of his results are given in Table VII, along with the ideal figures computed on the same basis as for Table VI. Obviously, the agreement between the ideal figures and the actual figures is very poor, except for the two highest results. The high proportion of silver chloride in Nos. 7, 9, and 10 helps to account for the very poor results on these coins, but it is difficult to understand why the results for Nos. 4, 5, and 6 are so poor, especially as the proportion of silver chloride is about the same as that in Nos. 1 and 2. Some other factor other than the presence of this corrosion product must account for the poor results.

Table VI. Comparison between Actual Silver Content of Silver-Copper Alloys and Silver Content Calculated from Specific Gravities

Specific Gravity	Silver Content from Specific Gravity	Actual Silver Content	Difference
	%	%	%
10.36	92.5	92.0	+0.5
10.30	89.0	89.8	−0.8
10.30	89.0	89.4	−0.4
10.25	86.5	87.2	−0.7
10.20	83.5	82.8	+0.7
10.17	82.0	81.7	+0.3
10.17	82.0	81.0	+1.0
10.16	81.5	81.0	+0.5
10.05	75.0	75.0	0.0
10.05	75.0	74.7	+0.3
9.97	70.5	69.0	+1.5
9.97	70.5	68.8	+1.7
9.87	64.5	62.6	+1.9
9.76	58.0	56.4	+1.6
9.76	58.0	56.3	+1.7
9.69	53.5	52.1	+1.4
9.65	51.0	49.7	+1.3
9.63	49.5	50.0	−0.5

Table VII. Silver Content of Corroded Ancient Coins Estimated from Specific Gravity and as Determined by Analysis

Coin No.	Specific Gravity	Silver Content from Specific Gravity	Silver Content by Analysis	Difference	AgCl Present
		%	%	%	%
1	10.45	97.5	98.2	− 0.7	0.49
2	10.43	96.5	98.1	− 1.5	0.31
3	10.12	79.0	92.5	−13.5	0.76
4	9.85	63.5	83.5	−20.0	0.54
5	9.74	56.5	79.9	−23.4	0.40
6	9.63	49.5	90.0	−40.5	0.63
7	9.57	46.0	87.6	−41.6	5.77
8	9.52	42.5	85.9	−43.4	1.86
9	9.50	41.5	76.5	−35.0	6.21
10	9.02	8.5	76.3	−67.8	13.04

Table VIII. Silver Content of Mechanically Cleaned Coins Estimated from Specific Gravity and as Determined by Analysis

Coin No.	Specific Gravity	Silver Content from Specific Gravity	Silver Content by Analysis	Difference
		%	%	%
1	10.49	99.5	98.7	+ 0.8
2	10.29	88.5	94.2	− 5.7
3	10.28	88.0	94.5	− 6.5
4	10.28	88.0	96.4	− 8.4
5	10.09	77.5	90.6	−13.1
6	10.05	75.0	87.5	−12.5
7	9.95	69.5	92.9	−23.4
8	9.92	67.5	73.4	− 5.9
9	9.84	62.5	76.9	−14.4
10	9.66	51.5	74.3	−22.8
11	9.59	47.0	67.9	−20.9
12	9.34	31.0	52.2	−21.2
			Av.	−12.8

Table IX. Silver Content of Blanks of Mechanically Cleaned Coins Estimated from Specific Gravity and as Determined by Analysis

Blank No.	Specific Gravity	Silver Content from Specific Gravity	Silver Content by Analysis	Difference
		%	%	%
1	10.51	100.5	98.7	+1.8
2	10.35	92.0	94.2	−2.2
3	10.37	93.0	94.5	−1.5
4	10.28	88.0	96.4	−8.4
5	10.18	82.5	90.6	−8.1
6	10.19	83.0	87.5	−4.5
7	10.14	80.5	92.9	−12.4
8	10.09	77.5	73.3	+4.2
9	10.05	75.0	76.9	−1.9
10	10.06	75.5	74.3	+1.2
11	9.85	63.5	67.9	−4.4
12	9.63	49.5	52.2	−2.7
			Av.	−3.2

Results obtained in the author's laboratory on a series of ancient silver coins are shown in Table VIII. These coins had been cleaned mechanically, and only traces of dirt and corrosion products were visible on their surfaces. It is evident that in this series also the agreement between the ideal figures and the actual figures for the silver content is generally poor. The only satisfactory result is for No. 1, where the silver content is very high. For the purposes for which this information is useful, the results for Nos. 2, 3, and 8 might also be acceptable, but the other results are much too poor and invariably too low. To determine whether some condition of the metal on the surfaces of the coins, such as porosity and consequent low apparent density, could account for these low results, the designs were completely filed off, the edges were also filed smooth, and the specific gravities of the clean blanks were determined. The results are shown in Table IX, where the blanks are in the same serial order as the corresponding coins in Table VIII. It is evident that the agreement between the ideal figures and the actual figures is generally much better, both individually and on the average.

Table X. Silver Content of Electrolytically Cleaned Coins Estimated from Specific Gravity and as Determined by Analysis

Coin No.	Specific Gravity	Silver Content from Specific Gravity	Silver Content by Analysis	Difference
		%	%	%
1	9.91	67.0	69.8	−2.8
2	9.73	56.0	58.2	−2.2
3	9.53	43.5	51.0	−7.5
4	9.48	40.0	47.3	−7.3
5	9.38	33.5	43.1	−9.6
6	9.42	36.0	41.8	−5.8
			Av.	−5.9

Results obtained in the author's laboratory on a series of ancient silver coins that had been cleaned by electrolytic reduction are shown in Table X. Here the results are much better than on the mechanically cleaned coins of Table VIII, especially when the comparison is made between coins of about the same actual silver content in the two series. However, here again the figures for the silver content on the basis of specific gravity are low. Results obtained on the blanks of these electrolytically cleaned coins are shown in Table XI. As with the blanks of the mechanically cleaned coins, the results are better than on the whole coins, but they are invariably too high in contrast to the invariably low results on the coins themselves. These high results may be explained from the composition of the coinage alloys. As may be seen from the analyses by the author shown in Table XII, the alloys contain small proportions of gold and lead, and the proportions of these metals of high density are sufficient to account for the high results for the silver content on the basis of specific gravity, as the assumption was made in the calculations that copper was the sole alloying element. For both the mechanically cleaned coins and the electrolytically cleaned coins it is clear that the low results on the whole coins as compared to those on the blanks must be attributed to metal of lower density on the surface than in the body of the coins. From the weights and specific gravities of the coins and the blanks, the actual figures for the average specific gravity of the layer of surface metal that was removed by filing may be computed. Also the average depth of the metal removed by filing may be easily estimated from the diameters of the coins and the data on weights and specific gravities, at least for coins of closely circular shape. The results of such calculations for the six electrolytically cleaned coins of Table X are shown in Table XIII. The specific gravity of the layer of metal on the surface is invariably lower than that of the blank and the ratio of the specific gravity of this layer to that of the blank, as shown in the last column of the table, increases in a general way with the increase in the thickness of the layer that was removed. This indicates that the specific gravity of this layer of metal increases with depth, or in other words, that its porosity decreases with depth. The existence of such porosity has been confirmed by microscopic examination. It seems to be the result of intergranular corrosion followed by the leaching out of soluble corrosion products. Calculations of this sort should obviously be of value for determining the depth of metal that should be removed from corroded ancient silver objects in order to obtain for analysis samples of metal truly representative of the composition of the original alloy.

Table XI. Silver Content of Blanks of Electrolytically Cleaned Coins Estimated from Specific Gravity and as Determined by Analysis

Coin No.	Specific Gravity	Silver Content from Specific Gravity	Silver Content by Analysis	Difference
		%	%	%
1	9.97	70.5	69.8	+0.7
2	9.86	64.0	58.2	+5.8
3	9.78	59.0	51.0	+8.0
4	9.64	50.5	47.3	+3.2
5	9.57	46.0	43.1	+2.9
6	9.52	42.5	41.8	+0.7
			Av.	+3.6

Table XII. Chemical Analyses of Blanks of Electrolytically Cleaned Coins

Coin No.	Ag	Au	Cu	Sn	Pb	Fe	Ni	Zn	Total
	%	%	%	%	%	%	%	%	%
1	69.77	0.42	27.74	0.75	1.15	0.02	0.02	0.10	99.97
2	58.19	0.53	37.29	1.26	2.65	0.02	0.03	None	99.97
3	50.97	0.35	43.97	2.35	2.34	0.03	0.02	None	100.03
4	47.29	0.43	49.10	1.83	1.41	Trace	0.03	None	100.09
5	43.10	0.33	52.26	2.64	1.51	0.05	0.04	None	99.93
6	41.84	0.34	51.92	3.44	2.48	0.04	0.02	None	100.08

Table XIII. Specific Gravity of Metal on Surface of Electrolytically Cleaned Coins

Av. Depth of Metal Removed, Mm.	Specific Gravity			Spec. Grav. of Metal
	Coin	Blank	Metal	Spec. Grav. of Blank
0.23	9.38	9.57	9.09	0.950
0.27	9.53	9.78	9.23	0.944
0.28	9.48	9.64	9.29	0.964
0.29	9.73	9.86	9.58	0.972
0.29	9.91	9.97	9.83	0.986
0.35	9.42	9.52	9.34	0.981
			Av.	0.966

Table XIV. Specific Gravity and Silver Content of Coins of Low Fineness and Blanks of Such Coins

Specimen	Specific Gravity of Whole Coin	Specific Gravity of Blank	Silver Content by Analysis, %
1	8.86	9.23	24.4
2	8.83	9.23	41.9
3	8.48	9.10	39.8
4	8.10	8.77	15.5
5	7.89	8.60	28.6
6	7.66	8.02	48.6
7	7.34	7.86	42.4
8	6.12	6.30	55.8
9	5.65	8.21	51.0
10	5.59	6.77	22.5

Table XV. Lack of Relationship between Specific Gravity and Composition in Ancient Objects Composed of Copper Alloys

Specific Gravity	Cu	Sn	Pb	Zn
	%	%	%	%
8.72	94.26	5.51	...	...
8.71	90.42	9.48	...	...
8.59	85.31	11.15	2.86	...
8.09	83.71	10.82	3.21	...
8.64	62.13	7.69	29.36	...
8.64	79.05	8.02	12.84	...
8.52	82.39	...	...	17.36
8.53	70.95	6.78	22.01	...

The present experiments indicate that ancient silver objects that are cleaned by electrolytic reduction have in general a higher specific gravity than similar untreated objects, or those cleaned mechanically. The reason for this appears to be that some of the voids in the body of the object are filled or partly filled with metal derived from the reduction of corrosion products on the surface.

When an attempt is made to estimate the silver content of ancient objects of base silver by means of specific gravity measurements, the results are usually very low, and in fact the observed specific gravity is often below that of copper, so that the indication is that no silver is present. Some objects of this sort have an apparent specific gravity that is surprisingly low, and so does the metal in the interior of the objects. Some typical results obtained on coins of low fineness and on the blanks of such coins are shown in Table XIV. In such objects intergranular corrosion has extended throughout the mass of the metal, and the leaching out of soluble corrosion products of base metals has left behind metal of spongy structure. The existence of this structure is apparent not only on microscopic examination but also from the ease with which such metal absorbs liquids. For example, in one experiment a piece of macroscopically clean and solid metal weighing 7.047 grams was found to weigh 7.384 grams after immersion in water under reduced pressure; the increase of 0.337 gram, or 4.78% of the weight of the dry metal, was obviously due to the water absorbed in the pores. Though specific gravity measurements are of no value for estimating the silver content of such objects, they may be of some value as a measure of the extent of intergranular corrosion.

In general, these experiments indicate that specific gravity as an index of the silver content of untreated silver objects is reliable and useful only when the specific gravity is very high—that is, in excess of 10.30. For electrolytically cleaned objects it may be reliable and useful when the specific gravity is much lower, but the exact safe lower limit can be established only after many more data are obtained. As with gold objects, there is no point in expressing results closer than the nearest whole number in per cent.

ESTIMATION OF BASE METALS

Specific gravity measurements appear to be of no value for estimating the quantitative composition of ancient objects composed of base metals or their alloys. Typical results for copper alloys are shown in Table XV, which was constructed from data published by Phillips (*13*). Objects of the same specific gravity often have a very different composition, and those of similar composition may have very different specific gravities. Such discrepancies are in large measure caused by the different extent of intergranular corrosion in the metal of the objects.

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Action of Celites on Carotene and Lutein

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Celites, widely used as inert filter aids in chromatographic analyses, have been examined for destructive action toward carotene and lutein. Isomerization and oxidation of carotene by Celites are demonstrated; lutein is altered even more readily. The effect of moisture, temperature, presence of acetone, and ammonia is measured. Suitable adjustment of these factors prevents loss of carotene. Lutein is not recovered in completely unaltered form by similar adjustments.

THE use of Celites in the analysis of carotenoids is general (*2-8*). Many finely powdered adsorbents with unsuitable filtration rates are rendered useful when mixed with these filter aids. In this laboratory, the useful range of selection of commercially available limes for analysis of carotene isomers has been extended by use of Celites. However, because carotenoids may be in contact with the Celite-adsorbent mixture for as long as 45 minutes, it is essential that the Celite exercise no action on the pigments.

Under certain conditions, Celites, such as Hyflo Super-Cel and Celite 535, are very destructive toward carotenoids. Most investigators have not been cognizant of this effect, which could lead to serious error in the interpretation of results. When solutions of carotene or lutein in Skellysolve B are left in contact with Celite, major losses of the pigments may occur, the extent depending on such factors as time of contact, temperature, presence of acetone, surface moisture, and pretreatment of the Celites. The purpose of this investigation is to define these losses and to establish conditions whereby Celites may be safely used in chromatographic separations of carotenoids.

EXPERIMENTAL PROCEDURE

Absorbancy measurements for determining loss or changes in the characteristics of carotenoids were made with a Beckman Model DU spectrophotometer. Beta-carotene and lutein were obtained from the American Chlorophyll Co.

The carotene was further purified by passing a solution in Skellysolve F through a column of magnesium carbonate and adding ethyl alcohol to the eluate to precipitate the crystals. Several further recrystallizations from Skellysolve F by addition of alcohol gave a preparation with $E_{1\text{ cm.}}^{1\%}$ 450 mμ = 2580 in Skellysolve B, which is similar to that obtained by Bickoff *et al.* and other workers (*1*) for pure all-*trans*-β-carotene. Lutein was recrystallized several times from methanol by addition of Skellysolve F until the resulting precipitate showed a constant melting point 177–178° C. (uncorrected). Absorption ratios for this preparation of lutein at 430, 450, and 480 mμ were 74, 100, and 81, respectively (*7*).

Skellysolve was purified by repeated extractions with sulfuric acid to remove unsaturated compounds followed by extraction with 9% potassium dichromate in sulfuric acid (technical 93%, 1 volume added to 2 volumes of water). The remaining chromic acid was removed by washing with 10% solution of sodium hydroxide, and several times with water. The Skellysolve was then distilled from sodium hydroxide pellets. Acetone, c.p. grade, was used without purification. Hyflo Super-Cel and Celite 535 were obtained from Johns-Manville. The Celites

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