

SULFUR IN ROMAN BRASS

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In a previous paper (Caley, 1955) it was shown that the proportion of zinc in Roman coinage brass decreases progressively with time, and that this change is accompanied by an increase not only in the proportion of copper, but also in the proportions of tin and lead. A possible explanation of the chronological changes in the proportions of these metals was suggested.

The present investigation was undertaken to find out whether the proportion of sulfur in Roman coinage brass varies in any regular way with time. The possibility that it may do so is indicated by the results of some analyses of Bibra (1869), who found determinable amounts of this nonmetallic impurity in three coins struck in the second century A.D., but only traces or none at all in a few earlier coins. However, Bibra did not describe his analytical procedure in any detail, and there is at least one indication that it may have been defective.

Seventeen Roman brass coins of known date covering almost the entire period of issue of such coins were taken for analysis. The samples for analysis were prepared by filing away all exterior corrosion products from the coins and cutting out sectors of clean metal that weighed about a gram. The procedure used for the detection or determination of sulfur was especially devised for the purpose. Though based on established principles, it differs considerably from the usual procedures used for the determination of sulfur in modern copper alloys. For this reason, and because no detailed procedure for the determination of sulfur in any kind of ancient copper alloy appears ever to have been published, it is given here as a complete working procedure.

ANALYTICAL PROCEDURE

Accurately weigh a clean sample amounting to about 1 g. Place this in a 250-ml beaker, add 20 ml of concentrated nitric acid and cover at once with a watch glass. When action has ceased, place the beaker on a steam plate or low temperature hot plate and digest until all spray has been washed from the watch glass and sides of the beaker. Then place glass hooks under the watch glass and evaporate to 10 ml. Add water to bring the volume to 50 ml and digest on the steam plate or hot plate for about an hour. Macerate a quarter of a quantitative filter paper in water by shaking in a test tube, and add the mixture to the solution. Filter through a double quantitative paper of fine texture and wash the precipitate and filter at least 10 times with hot 1% nitric acid. Catch the filtrate and washings in a 250-ml beaker, add 10 ml of concentrated hydrochloric acid, cover with a watch glass supported by glass hooks and evaporate nearly to dryness on a hot plate. Add another 10 ml of concentrated hydrochloric acid and again evaporate nearly to dryness. Dilute with 50 ml of water. If the solution is not entirely clear, filter through quantitative paper, wash with small portions of water until the paper is colorless, and catch the filtrate and washings in a 250-ml beaker. Add dilute ammonium hydroxide solution cautiously until a small precipitate of copper hydroxide persists, and add dilute hydrochloric acid solution (1:4) cautiously until this precipitate just dissolves, then 5 drops more. Heat the solution nearly to boiling and add 10 ml of 1% barium chloride solution drop by drop over a period of 10 min while stirring. Cover the beaker with a watch glass and allow to stand at least 12 hr. The appearance of a white turbidity or precipitate indicates the presence of sulfur.

To determine the amount, heat the mixture nearly to boiling for about an hour

and filter through a weighed porcelain filter crucible. Wash with successive small portions of warm water until the washings become entirely colorless. Ignite at 500°C in a muffle for an hour. If the ignited precipitate is entirely white, cool and weigh to determine the weight of the barium sulfate. If it is discolored, cool the crucible and place it in a suction filtering apparatus arranged so that filtrate and washings may be caught in a 250-ml beaker containing 75 ml of water. Then, without turning on the aspirator, add with a pipet 1.0 ml of concentrated sulfuric acid drop by drop to the precipitate in the crucible. After the precipitate has dissolved turn on the aspirator and draw the solution through the crucible. Turn off the aspirator and add 0.5 ml of concentrated sulfuric acid to the crucible. After about half a min draw this wash acid through the crucible. Repeat with another 0.5 ml portion of acid. Wash the crucible rapidly with several small portions of water. Heat the filtrate containing the reprecipitated barium sulfate nearly to boiling and digest until the precipitate settles readily. Filter through a weighed porcelain filter crucible, wash with several small portions of water, ignite at 500°C in a muffle for about an hour, cool, and weigh. Multiply the weight of the precipitate by 0.1374 to obtain the weight of sulfur.

NOTES ON PROCEDURE

1. To avoid danger of loss from too violent action, the sample should be in the form of one or two large pieces rather than in the form of drillings.
2. If tin is absent as shown by the lack of a residue after concentration and dilution of the nitric acid solution, the hydrochloric acid may be added without the prior filtration. However, some tin is usually present in small amount.
3. The purpose of the double hydrochloric acid treatment is to destroy nitric acid, for erroneous results are obtained on precipitating barium sulfate in nitrate solution.
4. The hydrochloric acid solution should not be evaporated to dryness because it may be difficult to redissolve the salts completely without treatment with an excessive amount of acid.
5. Any turbidity or cloudiness in the solution after hydrochloric acid treatment is usually due to silver which is sometimes present in small amount. The silver chloride must be removed by filtration. Lead is usually present but not in sufficient amount to precipitate as chloride. However, if the amount is large enough, lead chloride will be precipitated at this point and must also be removed by filtration.
6. Usually the barium sulfate is contaminated by adsorbed copper and iron ions; hence the need for reprecipitation.
7. Barium sulfate is soluble in cold concentrated sulfuric acid due to the formation of a complex, whereas ferric oxide and to some extent cupric oxide are not. Addition of the barium sulfate solution to water causes an immediate reprecipitation of the barium sulfate.
8. The solution of the barium sulfate precipitate in the first portion of sulfuric acid must be washed through the crucible with additional portions of acid since immediate washing with water might cause reprecipitation of barium sulfate in the pores of the filter plate. However, the total volume of sulfuric acid must be restricted in the solution from which the barium sulfate is reprecipitated.
9. Since the barium sulfate is reprecipitated in a very finely divided state, the solution containing it must be heated near the boiling point for at least an hour so as to obtain a filterable precipitate.
10. The freedom of the reagents from sulfate should be tested by means of a blank determination. If any is found, this must be applied as a correction to the results obtained on samples. However, it is more preferable to select reagents that are free from detectable amounts of sulfate.

RESULTS AND CONCLUSIONS

The results are shown in table I. Duplicate tests or determinations were made when sufficient uncorroded alloy was available. The satisfactory agreement of the results of these tests and determinations is evident. It will be seen that sulfur was found to be absent from all coins struck before the beginning of the second century A.D., and that it was present in all but one of the coins struck in this century. However, this is the earliest second century coin investigated. Sulfur was found to be present in another coin of the same emperor struck a few years later, but the proportion is the lowest that was found in any of the coins. It will be seen that the latest coins contained the highest proportions of sulfur. Though the number of coins investigated is perhaps too few to warrant final detailed conclusions, the pattern of the results obtained from these representative examples is so definite that some valid general conclusions seem possible.

The only likely sources of sulfur in Roman coinage brass are the sulfide ores of copper, zinc, or both. Certain considerations indicate, however, that the principal or sole source was a sulfide ore or ores of zinc. Sulfur has not been found to occur except in traces in Roman copper coins, even in those of the second

TABLE I
Results chronologically arranged

Emperor	Date	Sample A Sulfur, %	Sample B Sulfur, %
Augustus	22 B.C.	none	none
Tiberius	22- 23 A.D.	none	none
Caligula	37- 38 " "	none	none
"	39- 40 " "	none	—
"	39- 40 " "	none	none
Claudius	41 " "	none	none
"	41 " "	none	none
Nero	64- 66 " "	none	none
Nerva	96- 98 " "	none	—
Trajan	112-114 " "	none	—
"	116-117 " "	0.08	—
Antonius Pius	141 " "	0.12	0.13
" "	154-155 " "	0.17	—
" "	154-155 " "	0.21	—
Marcus Aurelius	161-162 " "	0.17	—
" "	162-163 " "	0.28	0.28
Commodus	179 " "	0.31	0.33

century A.D., which indicates that the copper used in the manufacture of Roman coinage was obtained from oxidized ores such as cuprite or malachite. Since metallic zinc was unknown to the Romans or perhaps isolated rarely only by accident, Roman brass must have been manufactured by the cementation process, that is by stirring a mixture of zinc ore and some reducing agent, probably charcoal, into molten copper. If an oxidized ore was used, such as the carbonate, smithsonite, then the resulting brass would be free from sulfur, but if a sulfide ore, such as sphalerite, was used either alone or in admixture with an oxidized ore, then the brass would contain more or less sulfur. The above analytical results therefore indicate that only an oxidized zinc ore, probably the carbonate, was used in the manufacture of Roman coinage brass prior to about the beginning of the second century A.D., and that a sulfide ore, probably sphalerite, was admixed with the oxidized ore in increasing proportion during this century. This order of the usage of the two types of ores is what might be expected to occur generally in

the exploitation of ore bodies by ancient miners and metallurgists. The first ores used would be the more easily obtained and smelted oxidized ores near the surface of deposits, and only later would use be made of the deeper and less easily smelted sulfide ores. The fact that the percentage of zinc in Roman coinage brass decreases rapidly from about the beginning of the second century A.D. indicates either a progressive depletion of the known zinc ore deposits or a progressive depletion of the type of ore in these deposits that could be successfully smelted by the Romans. Furthermore, the fact that Roman coinage in brass ceased entirely near the end of this century indicates either the exhaustion of the known zinc ore deposits or the exhaustion of the type of ore that could be successfully smelted.

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