so-called albuminoid ammonia, a series of waters were analyzed with and without the addition of sulphuric acid. The results of the analyses of nine typical Illinois waters as given in Table III show that the sulphuric acid has no appreciable effect on the amount of ammonia obtained. While the results are not identical, the variations are within the limits of experimental error.

URBANA, ILL.

THE COMPOSITION OF SOME GREEK VASES.

BY WILLIAM FOSTER.
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The purpose of this article is to give an account of some chemical tests made in order to determine the nature and composition of the black glaze of the black-figured and red-figured Attic styles and the red glaze of the Mycenaean style of vases.

This investigation was undertaken at the request of my colleague, Dr. O. S. Tonks, who is interested in Greek pottery from the standpoint of an archaeologist.

Guided by the results of these chemical tests, Tonks has confirmed some of the observations by synthesis, a partial account of which has already been published.[1]

1. Experiments with the Black Glaze.

(1) *Historical Introduction.*—The nature and composition of the fine black glaze on Greek pottery has been a subject of discussion and more or less speculation for many years. As far back as 1761 Caylus,[2] as a result of his investigations, claimed that the glaze was made up of a ferruginous earth, which he classified as manganese. He claimed that this substance baked red, but could be rendered black by an admixture of color, or other earths.

According to Blümner,[3] some later investigators have advanced theories that the materials of the glaze might be graphite and magnesia, that the glaze is made up of an earth but not a metal, and that a combination of the oxides of iron and manganese may have produced the black. Blümner claimed, however, that the real nature of the black color had not been finally determined.

Of the earlier experiments carried out with a view to discover the composition of the glaze, perhaps those of Salvétat,[4] at the Sèvres potteries, are the most worthy of consideration. While Salvétat, in reporting

[1] Tonks, *Am. J. Archaeology*, **12**, 417 (1908).

[2] *Recueil d' Antiquités*, **1**, 86–7.

[3] "Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern, II, pp. 74ff. The work done up to 1879 is here summarized.

[4] Brongniart, "Traité des Arts Ceramiques," I, pp. 549–52.

his analysis, did not give any *percentage* of manganese, he claimed that the oxide of manganese is an indispensable component of the composition, and this view is shared in by Brongniart.[1] This the writer hopes to disprove.

Among the later writers, H. B. Walters[2] believes that the problem is still unsolved. He distinguishes between a glaze which was applied. to the surface before the application of what he terms the black varnish and the black varnish itself. Birch, Blümner and Brongniart hold views that are somewhat similar. They consider that the glaze and black are different from each other.

Fürtwangler and Reichhold[3] are of the opinion that the black glaze is apparently made up of two parts, namely, a thin, reddish, shining, flowing material and some substance, which, by firing, gives the black. This I do not believe to be likely.

"The nature of the glaze which is to be seen on the finished vase in both the black- and red-figured styles, and the methods of its application, raise puzzling questions about which there is as yet no general agreement."[4]

It is hoped that the following experiments will aid somewhat in solving the puzzle as to the composition of the glaze.

(2) *Experimental.*—Experiments were conducted, in the first place, to find out whether manganese is present as an essential constituent of the glaze, as claimed by Salvétat, or whether its presence is accidental.

Experiment 1.—A fragment of a Greek vase[5] covered with fine black glaze and weighing about 51 grams was placed in a large silver crucible and fused with potassium hydroxide until all the glaze was removed from the clay.[6] The melt thus obtained had a faint greenish tinge, suggestive of a very small quantity of manganese. This melt was treated by the usual methods for the separation of silica and iron, and then hydrogen sulphide was conducted into the ammoniacal filtrate to precipitate any manganese that might be present. A *very* small dirty precipitate was obtained, which, when treated with a borax bead, gave no indication whatever of manganese. This test was confirmed by various other tests. The occurrence of manganese in the glaze must have been *accidental*, therefore, and not an *essential* component of it.

[1] *Rev. Archéologique,* **18,** 101 (1891).

[2] "History of Ancient Pottery," I, pp. 214 and 220.

[3] "Griechische Vasenmalerei," Series I, Text p. 19.

[4] Fowler and Wheeler, "Greek Archaeology," p. 429 (1909).

[5] From the American excavations at the Heraeum.

[6] NOTE.—A considerable quantity of the *body* of the vase was necessarily removed at the same time. The writer has tried different methods for removing the glaze, such as chipping it off, and scratching the surface with a fine diamond point; but in all cases the mass of the clay removed from the body of the vase was always much greater than that of the glaze itself. For this reason, since the glaze is exceedingly thin, it was impossible to get enough of the latter for chemical analysis.

Experiment 2.—In the second place, tests were made to find out the amounts of manganese in the black glaze and in the *body* of the vase.

Some fragments of a vase covered with black glaze were treated with a mixture of sulphuric and hydrofluoric acids until all the glaze was removed · and disintegrated. After expelling the excess of hydrofluoric acid by repeated evaporations with sulphuric acid, the residue was dissolved in water and nitric acid, and the manganese determined by the colorimetric method of Walters,[1] *i. e.*, by oxidizing the manganese to permanganic acid by means of ammonium persulphate and then diluting in a Nessler cylinder to the mark. The amount of manganese calculated as the oxide (MnO) was 0.06 per cent.

The experiment was repeated with a similar sample taken from the body of the vase. The percentage of manganese was identical (0.06).

The experiment was repeated with a different sample of vase, in this case a diamond point being used to remove the glaze, and 0.04 per cent. of MnO was found in the glaze and also in the body of the vase.

These experiments go to show that the amount of manganese in the glaze is the same as that in the body of the vase. This small amount of the element (average 0.05 per cent.) might very well be *accidental*, for it is well known that ordinary clays and rocks containing iron usually contain more or less manganese.

Experiment 3.—It was suspected by the writer that the black glaze might be due primarily to ferrous silicate, therefore the following experiments were carried out to test this hypothesis.

(1) Three grams of a fragment of a vase covered with glaze (the sample was not ground up) were placed in a platinum crucible and treated with a mixture of sulphuric and hydrofluoric acids, great care being exercised to exclude all air. The solution thus obtained was evaporated to dryness, the residue taken up with dilute sulphuric acid, and the ferrous iron determined by means of dilute potassium permanganate. 0.6 cc. of the permanganate were required. The same test was applied to an equal amount of the vase without the glaze. In this case 0.2 cc. of the permanganate was required to oxidize the ferrous iron.

(2) Two grams of a fragment of a vase covered with glaze were crushed to a powder and treated as in (1), the final titration being made with $N/50$ potassium permanganate. Amount of ferrous oxide (FeO) present, 0.50 per cent.

Two grams of the body of the vase were next treated in a similar way. Amount of FeO present, 0.30 per cent.

Several other tests were made, and invariably more ferrous iron was found in the glaze than in the body of the vase.

[1] *Chem. News*, **84**, 239 (1901); *Proc. Eng. Soc. West. Pa.*, **17**, 257 (1901); Hillebrand *Bulletin* **422** (U. S. G. S.), pp. 116–8.

Owing to the fact that it was impossible to get the glaze anything like free from the clay, it was not possible to determine the absolute amount of iron in the ferrous condition in the former; but enough evidence was obtained to indicate that *ferrous iron* (probably as ferrous silicate) is responsible for at least a part of the fine black color of the decorating medium of some of the Greek pottery.[1]

II. Experiments with the Red Glaze of the Mycenaean Style.

If the Greeks employed compounds of iron in the ferrous condition for the production of black glaze, it is reasonable to assume that they employed compounds of the element in the ferric condition to obtain the red glaze, and I dare say that it has been quite generally believed by writers on the subject that iron in the ferric condition had much to do with the production of the red glaze. If this be the case, one would expect to find more ferric iron in the glaze than in the body of the pottery, and less ferrous iron in the glaze than in the body. To test this hypothesis the following experiments were conducted:

Experiment 4.—(1) A fragment of a Mycenaean[2] vase covered with red glaze was found by the analytical method already described to contain 0.44 per cent. of iron calculated as ferrous oxide (FeO). An equal weight of the body of the vase gave 0.56 per cent. of FeO.

A second sample, from another vase, gave 0.35 per cent. FeO in the glaze and 0.43 per cent. in the body, and a third and still different sample gave 0.17 per cent. in the glaze and 0.25 per cent. in the body of the vase.

From these experiments it would appear that the body of the pottery covered with red glaze contains more ferrous iron than the glaze—just the opposite of the observation made in the case of the black glaze.

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[1] Tonks has succeeded, it appears, in confirming these observations by synthesis. He says: "Not to be tedious by enumerating the number of trials I made before getting the desired result, I may say that it proved eventually that a combination of eight parts of nitrate of soda to one of clay, fritted together, and then mixed in the proportions of two parts of frit to one of ferrous oxide, produced a glaze identical with that on Greek vases" (*Amer. J. Archaeology*, XII, 1908, p. 424). Tonks used pipe clay and he claims that if it had been a more fusible variety, the amount of sodium nitrate could have been much less.

It might be objected by some that the Greeks knew nothing about ferrous oxide, inasmuch as the pure compound is a modern preparation of the chemical laboratory. Compounds containing ferrous oxide or iron in the ferrous condition are abundant enough in nature, however, *e. g.*, magnetic oxide of iron, or ferroso-ferric oxide, and ferrous carbonate. Tonks informs me that he has recently succeeded in reproducing the black glaze by the use of the magnetic oxide of iron in place of pure ferrous oxide, but he has not as yet completed his experiments.

[2] Picked up by Tonks at Mycenae. Mycenaean vases were manufactured by the Greeks as far back as 1200–1300 B. C. The other specimens of vases with red glaze experimented on by the author were of the Mycenaean style, but from the Heraeum.

Experiment 5.—The total iron as ferric oxide (Fe_2O_3) was next determined, both in the red glaze and in the body of the clay. The surface of a fragment of vase covered with red glaze was scratched thoroughly with a diamond point and the powder analyzed. Total Fe_2O_3 present, 8.16 per cent. A sample of the same vase without the red glaze contained 7.36 per cent. total iron as Fe_2O_3. After allowing for the ferrous iron, the glaze was found to contain considerably more ferric iron than the body of the clay. A second experiment, on a different fragment of vase, confirmed this observation.[1]

III. Analyses of Mycenaean Vases.

So far as the writer knows, no analyses of Mycenaean pottery have been published. It was thought worth while, therefore, to make a complete analysis of a fragment of a vase of the Mycenaean style, and a partial analysis of another fragment. These results will be given below, and, for the purpose of comparison, the average *approximate* results of the analysis of four fragments of Attic pottery (with black glaze) made in the Harvard University laboratory under the direction of Professor Richards[2] will be given, and also the mean of Salvétat's[3] analyses:

ANALYSES OF ANCIENT POTTERY.

	Fragments of Mycenaean vase. Foster.		Fragments of jars and vases (Attic). Widtsoe & Lyon (Harvard Univ.).	Campanian pottery. Salvétat.
Silica (SiO_2)	40.60	47.51	56.10	55.88
Aluminium oxide (Al_2O_3)	17.07	20.40	17.25	18.88
Ferric oxide (Fe_2O_3)	6.93	8.89[4]	8.95	15.80
Ferrous oxide (FeO)	0.56	...	...	...
Calcium oxide (CaO)	19.80	13.82	5.52	7.48
Magnesium oxide (MgO)	4.42	4.41	5.00	1.63
Potassium oxide (K_2O)	2.96	...	3.26	...
Sodium oxide (Na_2O)	0.21	...	2.35	...
Carbon dioxide (CO_2)	5.40	} 2.78	...	...
Water (H_2O)	2.95		2.20	...
	100.90		100.63	

By a comparison of the figures in the different columns, it may be observed that the Mycenaean pottery contains considerably less silica than the Attic and the Campanian. They all contain about the same amount of alumina. The Mycenaean and the Attic appear to contain approximately the same amounts of ferric iron, but the Campanian ware contains

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[1] Tonks has been conducting some experiments to confirm these analyses synthetically, and he has already met with considerable encouragement.

[2] Robinson, "Cat. of Greek and Roman Vases," Museum of Fine Arts, Boston, 1893, p. 35.

[3] Brongniart, *op. cit.*, I, p. 550.

[4] Total iron.

about twice as much of this substance. The Mycenaean pottery is *much* higher in lime than the other varieties, and also contains (*i. e.*, the samples analyzed) considerable carbon dioxide. The amounts of magnesia in the Mycenaean and the Attic varieties are nearly equal, but it is considerably less in the Campanian. The potassium oxide is approximately the same in the samples analyzed at Harvard and in the one sample of Mycenaean pottery in which this constituent was determined. While the former contained over 2 per cent. of sodium oxide, the latter contained but a small amount (0.21 per cent.).[1] Owing to the fact that the Mycenaean clay analyzed is low in silica and comparatively high in lime, it should be more fusible. It was observed that in determining the loss of this variety of clay by ignition in a platinum crucible, it melted quite completely.

CHEMICAL LABORATORY,
PRINCETON UNIVERSITY.

CONDITIONS AFFECTING THE ELECTROLYTIC DETERMINATION OF COPPER.

BY W. C. BLASDALE AND W. CRUESS.

Although the electrolytic method for the determination of copper has been in use since 1864, and the literature of the subject is now voluminous, the application of the method to the analysis of ores and metallurgical products often presents difficulties, which are either ignored or but vaguely suggested in the current descriptions of the process. The frequent failures made by students in this laboratory in attempting to use the process have served to emphasize these difficulties, and have led to the series of experiments, the results of which are recorded below. In carrying out these experiments the needs and resources of the practical analyst have been kept constantly in mind.

Effect of Different Forms of Electrodes upon the Rate of Deposition and the Character of the Deposit.

The results obtained with the use of mechanical stirring devices during the last seven years have emphasized the desirability of maintaining a rapid circulation of the electrolyte during electrolysis. It has not been so generally recognized that the circulation of the electrolyte may be increased by taking advantage of the convection currents produced by the gases liberated at the anode or cathode, and by the substitution of Winkler gauze electrodes for those of the Mansfield type.[2] It seems probable that the relative efficiencies of the different forms of stationary electrodes depend almost entirely upon the extent to which they favor

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[1] Chemical analyses of the different varieties of clay used by the ancient Greeks are still too inadequate to throw much light on the manufactures of different localities.

[2] See, however, the Benner article, p. 1231.—EDITOR.