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First Report on

Moravian Green Anti-fouling Paint -

The Inorganic Components

By

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WASHINGTON, D. C.

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Moravian Green Anti-fouling Paint - The Inorganic Components.

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ABSTRACT

This report, one of a series on the composition of Moravian green anti-fouling paint, concerns the analysis of the inorganic components of the paint. The analytical procedures are described and the probable errors are discussed.

(a) Authorization

1. This problem was authorized by Bureau of Construction and Repair letter, reference (a). Other correspondence pertinent to the problem is listed as reference (b).

Reference: (a) BuC&R ltr. EN7(Secret 274)(D) of 17 January 1935.
(b) BuEng. ltr. Restricted NP14(5-6-W8) of 12 July 1935.

(b) Statement of Problem

2. The general problem is to determine the composition of Moravian green anti-fouling paint as supplied by the Bureau of Construction and Repair of the Navy Department. The present report concerns the analysis of the inorganic components.

(c) Known Facts Bearing on the Problem

3. A Moravian green anti-fouling paint was analyzed by the National Bureau of Standards and the Edgewood Arsenal in 1922. A copy of their results is given in Appendix A.

(d) Theoretical Considerations

4. Lead, copper, arsenic, and mercury, contained in a paint which is difficult to digest, cannot be determined quantitatively with any degree of accuracy without difficulty. The chemical literature gives no methods for handling this kind of material. Many methods of analysis for the individual metals, if they exist alone, are given, but methods of separation and analysis become scarce when the four metals exist together. In fact, some controversial points arise which must be decided by trial. With this in mind, several master samples were prepared containing known weights of materials approximating the percentages found in the paint. Digestion of master samples was identical with that of the paint, although it usually required less time. After digestion, what appeared to be the most reliable methods of analysis for the metals found were attempted.

5. In the case of mercury the often used[1] hydrogen sulphide precipitation and subsequent separation by boiling in nitric acid was tried with no consistent results. This method cannot be used for mercury in the presence of copper according to Hillebrand and Lundell[2]. The ammonium sulphide precipitation suggested by Vollard[1] and also Seamon's Volumetric method[1] were tried but were unsatisfactory. Consistent results for mercury were obtained only by the volumetric thiocyanate method[3,4]. Using nitric and sulphuric acids in digestion, only 51% of mercury from a master sample was recovered. On two other samples 13.2% and 11%, respectively, were found for 16.4% mercury. The fault was largely one of loss during digestion. But if the master sample is carefully digested with potassium permanganate and sulphuric acid in a Kjeldahl flask on a steam bath, the

loss in digestion is prevented. A silver foil placed in a tube at the top of a Kjeldahl flask containing a paint sample failed to pick up mercury when digestion proceeded as indicated above, thus showing that there was a negligible loss of mercury by volatilization. Consistent analyses followed this method of digestion.

6. Lead was determined as lead sulphate. Unfortunately, arsenic interferes for some of it is precipitated with lead. Without carefully eliminating arsenic two master samples analyzed 7.48 and 7.82 per cent for a theoretical 6.7 per cent lead. Ashing two master samples in the muffle gave 5.28 and 5.3 per cent for 6.7 per cent lead, showing that lead had probably fused into the crucibles and could not be removed entirely. By repeated evaporations with sulphurous acid and hydrochloric acid mixtures, arsenic can be volatilized, but precipitation as the sulphide in strong potassium hydroxide solution was found to be reliable and more convenient. Double salts as sulphates must be avoided.

7. No difficulty is encountered with copper provided oxides of nitrogen are absent and the titration carried out as discussed in paragraph 15.

8. "The best method for the separation of arsenic from other elements lies in its distillation from a hydrochloric acid solution containing all of the arsenic in the trivalent state," write Hillebrand and Lundell[5]. This official method[6] was used. Distillations on Bureau of Standards arsenic trioxide analyzed 99.0%. With mercurous and mercuric chloride added the analysis was 98.0% for pure As_2O_3. A determination on cupric arsenite resulted in 31.0% arsenic for a theoretical 31.7%. These determinations are low pointing either to a slight loss in digestion or in the distillation. Arsenic when run as the sulphide only roughly approximated the percentage found by distillation.

METHODS OF DIGESTION AND ANALYSIS

(a) Preliminary Treatment

9. Qualitative analysis of Moravian green anti-fouling paint showed the presence of an appreciable amount of lead, mercury, arsenic, and copper, and traces of zinc and tin probably as impurities. For a quantitative analysis of this type of material containing these metals no procedure was found in the chemical literature. Methods of analysis, therefore, had to be devised in this laboratory from a consideration of the chemistry of the elements involved.

10. Representative samples of the paint (about 5 grams) were dug from a 5-gallon bucket of paint, avoiding the dried crusts on the surface, and placed on weighed pieces of glass which were then reweighed and slid into Kjeldahl flasks. Enough acid to cover the paint was added and the flasks heated until organic matter was destroyed, fresh acid being added as necessary. The following reagents were tried as digesting media:

1. Concentrated nitric and sulphuric acid mixtures (2-1).
2. Aqua regia.
3. Nitric and perchloric acids (1-1 nitric and 60% perchloric).
4. Potassium permanganate and concentrated sulphuric acid.
5. Potassium chlorate and concentrated sulphuric acid.
6. Concentrated sulphuric acid and sodium sulphate.
7. Concentrated sulphuric acid and ammonium persulphate.
8. Fuming nitric acid, potassium nitrate, and concentrated sulphuric acid.
9. Fuming nitric acid.

11. It was found that numbers 1, 3, 4, and 9 were best suited for the digestion from a consideration of the analytical procedures that were to follow. The temperature at which digestion must take place varies with the metals to be determined. It was found that for mercury, digestion must be performed in permanganate-sulphuric acid solutions in Kjeldahl flasks at temperatures around 100°C. For arsenic, digestion using solutions 1, 3, 4 or 9 should be carried out on a steam bath although temperatures up to 200°C. entailed no apparent loss. For lead and copper, digestion over an open flame was expedient.

12. When solutions of the paint became clear, digestion was stopped. Because of the presence of organic acids of high molecular weight which proved to be difficult to destroy, digestion often proceeded for days. The reagents used and the time consumed in digestion will vary with the particular organic compounds present. Upon complete digestion of the paint samples, the Kjeldahl flasks were removed and their contents carefully washed into volumetric flasks of a liter capacity. Nitric acid was used in putting the white precipitates in solution. Aliquot portions were taken from the volumetric flasks for analysis of the individual metals.

13. Several samples of paint were ashed in porcelain crucibles in the muffle at 700 - 900°C. but analyses showed that this procedure gave reproducible results only in the case of copper.

(b) Analysis of Metals

14. Lead. The procedure of analysis for lead consisted of taking a 250 c.c. portion of a digested liter solution of known weight of paint, making strongly alkaline with potassium hydroxide, cooling, and bubbling in hydrogen sulphide to precipitate lead as lead sulphide[7]. This step separates arsenic from lead, as arsenic sulphide does not precipitate in strong potassium hydroxide solution when hydrogen sulphide is introduced. The solution is filtered through a Gooch crucible and the lead sulphide is removed to a 400 c.c. beaker and put into solution with nitric and hydrochloric acids. Sulphuric acid is added and the solution evaporated carefully on a hot plate to SO_3 fumes; the sides of the beaker are washed down carefully with distilled water and evaporation is resumed again to SO_3 fumes. Then after diluting with water, an equal volume of alcohol is added, and the solution allowed to stand over night. The

precipitated lead sulphate is then washed into a weighed Gooch crucible and dried at 500°C., cooled in a desiccator and weighed as lead sulphate[7,8].

15. Copper. Copper was determined by the potassium iodide method[9,10,11]. A 250 c.c. aliquot of a digested sample was evaporated to SO_3 fumes, bromine water was added and boiled off, and the clear solution was tested with a drop of permanganate to see that oxidation was complete. The solution was made alkaline with ammonia, then faintly acid with acetic acid, 10 c.c. of acetic acid being added in excess. To the cold solution 3 grams of potassium iodide were added. The liberated iodine was quickly titrated with 0.05 N sodium thiosulphate using starch as indicator just before the end point.

16. Mercury. A 200 c.c. aliquot from the stock solution of paint digested in solution No. 4 was diluted and a drop of permanganate solution added to see that no reducing agents were present. Oxalic acid crystals were used to destroy excess permanganate. Four c.c. of saturated ferric alum indicator were next added and the solution titrated to a faint pink with 0.1 N ammonium thiocyanate[1,2]. Copper does not interfere if kept in the cupric state[2].

17. Arsenic. A 200 c.c. aliquot from the stock solution was evaporated to drive off completely any nitric acid present. The solution was then transferred to an all Pyrex distillation apparatus, 3 or 4 grams of cuprous chloride in concentrated hydrochloric acid were added, and the arsenous chloride distilled over into ice water. This distillate was neutralized with ammonia, made slightly acid with HCl and then made alkaline with sodium bicarbonate. The solution was titrated with 0.1 N iodine using starch as an indicator. A blank was run using the same reagents - blanks usually used from 0.4 to 0.8 c.c. iodine while the ordinary determinations used 20 to 50 c.c. depending on the weight of the sample.

DATA OBTAINED

18. Lead. Following the procedure outlined under paragraph 14, analyses on four digested samples gave the following percentages for lead: 6.29; 5.89; 6.21; 6.17; average 6.14. Avoiding the sulphide precipitation and distilling off the arsenic with sulphurous and hydrochloric acids, then precipitating lead sulphate, gave 6.06; 6.38; 6.24; 6.09; average 6.19. Other treatments gave 5.68; 5.3% lead. Analyses of samples ashed in the muffle ran from 5 - 10% calculated as lead; some lead fused in the crucibles while arsenic was precipitated along with the lead sulphate. Best average, 6.2% lead.

19. Arsenic. The following percentages were found for arsenic by the distillation method on different samples of paint: 14.1; 14.1; 14.6; 14.4; 14.5; and 13.9, 13.4, 13.8 on one sample. Average, 14.2% arsenic.

20. Copper. The following results were obtained for copper: 2.66; 2.63; 2.62; 2.63. On ashed samples 2.60; 2.65 per cent. Average, 2.63% copper.

21. Mercury. On carefully digested samples following the procedure given in paragraph 11, results for mercury were: 4.46; 4.26; 4.50; 4.48 per cent. Best average, 4.5% mercury. From nitric-perchloric acid digestion on a steam bath, 3.18; 3.21; 3.28; 3.21 (aliquot parts from one sample). When nitric-sulphuric acid digestion is carried out for over a month on a steam bath there was found 1.85; 1.33 per cent mercury. Digestion in concentrated hydrochloric acid, then precipitation as the sulphide gave 4.42%. When the paint was extracted with ether and the ether layer discarded, the remainder was digested in permanganate and sulphuric acid. Analysis showed 4.0; 2.1 per cent mercury.

22. Summarizing the best averages for the individual metals in Moravian green anti-fouling paint:

Lead	6.2 per cent
Copper	2.63 " "
Arsenic	14.2 " "
Mercury	4.5 " "
Total metals	27.5 " "

23. In connection with the reliability of the analyses contained in this report of the metals in Moravian green anti-fouling paint, it is safe to say that exact duplicate analysis is impossible. Different batches of paint from the same bucket will vary a small amount in composition due to difficulties in mixing. Furthermore, it is quite probable that the manufacturers of this paint over a period of time will vary its composition to some extent. This may in part explain the discrepancy between analyses given in the appendix. Finally, the difficulty of digestion and analysis of the metals, combined with the personal error of any analyst may introduce uncertainties. The table below contains analyses on master samples digested and analyzed according to the procedures given in this report. It is believed that the accuracy in the analysis as given of this paint is commensurate with the accuracy shown below in the analysis of master samples.

NRL Master Samples - Composition

	Per Cent Put In	Salt Used	Per Cent Found
Mercury	5.48	Oxide	5.38
Copper	18.05	Oxide	18.18
Arsenic	15.54	Oxide	15.10
Lead	8.47	Nitrate	8.25

Rosin to make 100 per cent.

The determinations given under the column "Per Cent Found" are the mean of two or more determinations. The materials put in were individually analyzed for purity at this Laboratory.

SUMMARY

24. In this report is given the analysis of the inorganic constituents of the Moravian green anti-fouling paint.

APPENDIX

It is interesting for purposes of comparison to tabulate the results of analysis on the metals in this paint by the Bureau of Standards Test No. Tcp 34663 (1922) and the Chemical Warfare Service at Edgewood Arsenal.

	NRL	Bureau of Standards	Chemical Warfare
Lead	6.2	7.7	6.68
Copper	2.63	2.5	3.26
Arsenic	14.2	5.7	7.14
Mercury	4.5	8.1	2.90
Total metals	27.5	24.0	19.98

The wide variance in percentages of some of the metals suggests the difficulties that analysts encounter with material of this type. Standard methods of analysis cannot be used indiscriminately.

From work practically completed in this Laboratory, a further report will discuss the organic constituents of the paint, and discuss the isolation of the individual compounds.

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3. A.H. Low, Chemist Analyst 29, 13 (1919).

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5. Hillebrand and Lundell, "Applied Inorganic Analysis," p. 209.

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11. Foote and Vance, Ind. and Eng. Chem., Analytical Edition 8, 119, (1936); ibid, 8, 9 (1936).