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A METHOD FOR DETERMINING THE AMOUNT OF ZINC CHLORIDE IN TREATED WOOD

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The need of a reliable method for determining the amount of zinc chloride in treated wood has already been mentioned in *THIS JOURNAL*. It was clearly shown in a series of wood-impregnation experiments recently conducted by the Forest Service. In these experiments maple and red oak ties were treated in three ways: (1) With zinc chloride solution alone; (2) with zinc chloride solution and creosote in emulsion; (3) with zinc chloride and creosote injected separately. The analytical method used until that time had given

excellent results for the soft woods, chiefly hemlock and tamarack, but when applied to the hard woods, particularly oak, it did not give concordant results, and failed entirely in the analysis of hard woods treated with zinc chloride and creosote in emulsion.

The method of analysis described in this paper is one developed to overcome the difficulties encountered. So far as known, the complete method has not been described before, although, in its separate parts, it is formed from a selection of certain well-known methods modified for this particular work. The problem that confronted the Forest Service in its experimental treatments necessarily confronts also many commercial treating plants and users of treated timber.

SEPARATING INORGANIC SALTS FROM ORGANIC MATTER

A choice is offered of three possible methods of freeing inorganic salt in wood from the organic matter so that the usual inorganic methods of analysis may be carried out. These methods are:

I. Destruction of organic material by burning; estimating inorganic materials from the ash.

II. Removal of inorganic material by leaching or extraction with water, or dilute chemicals; analysis of the leaching solution.

III. Destruction of organic material by chemical means; analysis of the resulting solution.

I. DESTRUCTION OF ORGANIC MATERIAL BY BURNING

This is the most simple method because it requires no special apparatus, but it is limited to those inorganic materials which are nonvolatile even at comparatively high temperatures. A portion of the inorganic salt would be lost, of course, if the temperature reached the volatilization point of the material. In spite of this limitation, the method is the one most generally used, and it is suitable for many inorganic materials. It should be remembered that certain metals, which in themselves are nonvolatile in an ordinary Bunsen burner, are volatile when in the form of chlorides. Iron and aluminum are notable examples. These metals and all of their salts, except halogen salts, are nonvolatile. The salts of zinc behave in the same manner, and the metal itself is volatile at about 1000° C. It is obvious, therefore, that a method of destroying the organic materials by burning can not be used in the estimation of zinc chloride.

In spite of these facts the idea is somewhat prevalent that this method can be used, and the following test was therefore made: Known amounts of a standard zinc chloride solution were added to 5 grams of dry sawdust, the excess of moisture carefully evaporated in a drying oven, and the wood ashed at as low a temperature as possible. Table I gives the results of these tests.

It is seen that at least 10 per cent less zinc chloride was found in the ash than was added to the sawdust, and in one case the difference was as great as 55 per cent. Further, there is no uniformity in the results, so that a factor for compensating for this loss can not be obtained. Any method, therefore, which includes the ashing of the wood is not reliable for zinc chloride determinations.

TABLE I—LOSS OF ZINC CHLORIDE IN THE DESTRUCTION OF WOOD BY BURNING

1 cu. ft. of dry wood assumed to weigh 30 lbs.							
Test No.	Zinc chloride added to 5 grams sawdust		Zinc chloride found in ash		Loss		
	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Per cent
1.....	0.0417	0.2502	0.0354	0.213	0.0063	0.037	14.9
2.....	0.0417	0.2502	0.0186	0.112	0.0231	0.138	55.3
3.....	0.0834	0.5004	0.0616	0.369	0.0218	0.131	26.3
4.....	0.0834	0.5004	0.0736	0.442	0.0098	0.058	11.7
5.....	0.0834	0.5004	0.0673	0.404	0.0161	0.096	19.3

II. EXTRACTION OF ZINC CHLORIDE BY LEACHING

This method consists of extracting the zinc chloride by leaching with water (or dilute chemicals). For the following reasons no experiments were conducted in this method: (1) For complete extraction a considerable amount of expensive apparatus, such as Soxhlet extractors, would be required. (2) There is a possibility that all of the zinc could not be obtained even with prolonged extraction. (3) There would always be some soluble organic matter, such as tannins, sugars, etc., extracted with the zinc, which would have to be either removed or destroyed by chemical means. This operation could be performed on the original material as well as on the leached extract.

III. DESTRUCTION OF ORGANIC MATERIAL BY CHEMICAL MEANS

METHOD PREVIOUSLY USED BY THE FOREST SERVICE—

This method separated the zinc chloride from the wood through destruction of organic materials by chemicals. It consisted of the following steps: 5–10 grams of finely ground treated wood were digested in a Kjeldahl flask with 10 cc. of equal parts by volume of concentrated sulfuric and nitric acids. At the start, only a small flame was used under the flask, but as the foaming of the material subsided, the flame was gradually increased until the digestive mixture could be kept boiling constantly. From time to time, as the material became charred, more nitric acid was added until the solution remained water-white or pale yellow on boiling to sulfuric acid. With soft woods this point was reached in from 2–3 hrs., but with such woods as maple and oak the time was usually doubled, and frequently 8–10 hrs. were required for digestion. When creosote was present the solution sometimes failed to clear to a light yellow even after two days of digestion. Furthermore, in the subsequent analysis, it was frequently impossible to throw out with ammonium hydroxide the traces of iron which were always present; thus high results were obtained. The reason for the failure to digest creosoted material is not apparent, but it seems possible that, at times, conditions in the digestion flask were such that quinones and nitro bodies of anthracene and its homologues were formed which were not completely destroyed by sulfuric and nitric acids. An explanation of the failure of ammonium hydroxide to throw down iron in the dilute solution is equally hard to find, but it is supposed that sometime during the digestion one or more organic acids were formed. Iron compounds of these acids form double salts with ammonia which are soluble in

ammonium hydroxide. Whatever the reason, the fact is, that at times organic matter was present, and small quantities of iron remained in solution; hence the method was unreliable for the estimation of zinc. A further objection to the method is the extremely large amount of breakage of digestion flasks due to the severe treatment with boiling sulfuric acid. Furthermore, all the flasks tried by this method were attacked by the reagents, and either zinc, manganese, or some other interfering metal was dissolved, making it necessary to use a comparatively high correction to compensate for the flask. All kinds of glass are liable to this correction, but it is more nearly constant and smaller in amount when shorter methods of digestion are used.

IMPROVED METHOD—The details of the digestion method finally adopted are as follows: 5 grams of finely ground wood or sawdust are weighed into a 500 cc. short-neck, round-bottom Jena boiling flask; 50 cc. of a previously prepared saturated solution of potassium chlorate in concentrated nitric acid are then added in the cold and mixed with the sawdust by a vigorous shake. A violent reaction, accompanied by the evolution of considerable heat, immediately takes place, but subsides after a few minutes, leaving a wine-colored solution in which particles of partly digested wood are floating. When the solution has cooled somewhat, 10 cc. of concentrated sulfuric acid (sp. gr. 1.8) are carefully added and the solution again shaken. When this second reaction is complete the wood substance is all dissolved and the solution is of a dark red color. The solution is then boiled. At first the color becomes much lighter, but finally darkens to a brown. At this point more of the potassium chlorate-nitric acid solution is added and the solution kept boiling until no further charring occurs on evaporation to sulfuric acid. This boiling usually takes 1–1.5 hrs. after the digestion in the cold is started. In the course of 200–300 determinations, this treatment has not failed to give a clear solution free from organic matter and from which iron can be precipitated, if desired.

ESTIMATION OF ZINC IN THE DIGESTION SOLUTION

CHOICE OF METHODS—The material having been digested to a form suitable for analysis, it was necessary to find some simple method of analysis with a fairly high degree of accuracy. The determination of zinc gravimetrically gives results more nearly correct than any volumetric method, but this method was not undertaken because, even in the hands of a trained chemist, it requires a large amount of delicate manipulation and is somewhat tedious and time-consuming. It was believed, moreover, that the extra time required for extreme accuracy would not be justified. Of the volumetric methods, those using potassium ferrocyanide as the titrating reagent are generally considered the best. Two methods using this reagent were tried, and were found to be about equally accurate. They differed from each other in the indicator used to determine the end point of the titration and in the preparation of the digestion solution for analysis.

METHOD USING URANIUM ACETATE AS INDICATOR—This method was the one commonly used. It is described in Sutton's "Volumetric Analysis" as "Fahlburg's" method, and consists of a titration with potassium ferrocyanide in hydrochloric acid solution, using uranium acetate as an outside indicator. This titration, to give the best results, must be carried out under reducing conditions; all nitrates, nitrites, and chlorates must be destroyed and iron must be removed.

The details of the method used in connection with the new digestion method are as follows: When the digested material remains clear after boiling for a few minutes to sulfuric acid, approximately 0.5 gram of solid sodium sulfite is dropped into the solution and the boiling continued for 5 minutes. This destroys all nitrates, nitrites, and chlorates, and also reduces any iron to ferrous compounds. The solution is then cooled and diluted with 100 cc. of cold water. The iron must now be reoxidized to the ferric condition by the addition of 25 cc. of bromine water and the solution boiled until all the excess of bromine is expelled. After cooling, and before filtering, the solution is made alkaline with ammonium hydroxide and set on the steam bath for about 1 hour to allow any iron present to settle. The filtered solution and the washing from the iron precipitate are neutralized with hydrochloric acid, and 5 cc. of concentrated acid in excess is added. The total volume is then made up to 175 cc. and the solution heated to 80° C. before titration. As a safeguard to make certain that the titration is carried out in a reducing solution, 25 cc. of saturated hydrogen sulfide water are added immediately before titration. Blanks on the complete method should be run, using dry, untreated sawdust or filter paper, and the correction for end point and the digestion flask should be subtracted from the readings in the analysis proper. It is usually not necessary to run more than duplicate or four blanks for even a large number of determinations, if the same standard solution is used; but blanks should always be run when the new standard solution is made up, unless it is exactly the same as the solution previously used.

METHOD USING ACETIC ACID AND FERRIC CITRATE AS INDICATOR—This method of analysis is a slight modification of the one used in the Sheffield Scientific School, Yale University. Potassium ferrocyanide is used as a standard solution, but the titration is carried out while the solution to be titrated is ammoniacal. Neither iron nor nitrates show any interference, but are added to the solution as an indicator; the necessity of removing them from the digested solution is, therefore, obviated and the titration can be carried out in the digestion flask. The end point of the titration is rather complex in theory, but very simple in practice. It depends upon the fact that ferric iron, in the presence of citric acid, is not precipitated by ammonia, but that a soluble salt, ammonium ferric citrate, is formed. The iron from this compound is not precipitated by potassium ferrocyanide in ammoniacal solution but is immediately thrown down when the solution is acid.

The details of the method are as follows: An outside indicator is first prepared of equal parts by

volume of glycerine and glacial acetic acid. The digestion mixture is then diluted with 100 cc. of water. Ten cc. of a 2 per cent ferric chloride solution and 10 cc. of dilute nitric acid and one gram of solid citric acid are then added and the solution allowed to cool; it is neutralized with ammonia and left slightly alkaline, and is then ready for titration. On account of the heat of neutralization of the acid with ammonia it is rarely necessary to heat the solution. It should, however, be about 80° C. at the beginning of the titration and its volume should be 200 cc. The end of the titration is reached when a drop of the solution placed in the center of a small portion of the glycerine acetic acid mixture appears as a blue or greenish blue circle. Blanks should be run as in the previous method.

COMPARISON OF THE TWO METHODS OF TITRATION—The accuracy of these two methods of titration is about the same, but the time required by the first method is twice as great as by the second. The second method can be used when phosphates are present with iron, a condition which frequently occurs in railroad ties which have been in service. For such a condition the first method would be unreliable, because the iron could not be removed by precipitation with ammonia, and part of it, at least, would be estimated as zinc. The second method has the further advantage of requiring no filtration, thus eliminating the chance for loss involved in this operation, especially in the hands of an untrained man. The results shown in Table II are as accurate as is required for routine testing of this nature, the error being not greater than 0.005 pound per cubic foot.

ACCURACY OF THE COMPLETE METHOD—In the tests in Table II, known amounts of zinc chloride were added to 5 grams of dry sawdust. The material was

TABLE II—TESTS TO ASCERTAIN ACCURACY OF NEW METHOD FOR ZINC CHLORIDE IN TREATED WOOD

Test No.	Zinc chloride added to 5 grams sawdust		Zinc chloride found		Average		Average error		
	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Gram	Lbs. per cu. ft.	Per cent
1.....	0.0417	0.2502	0.0418	0.251	0.0412	0.247	0.0005	0.003	1.3
2.....	0.0417	0.2502	0.0406	0.244					
3.....	0.06255	0.3753	0.0619	0.370	0.06235	0.373	0.0002	0.002	0.7
4.....	0.06255	0.3753	0.0628	0.377					
5.....	0.0834	0.5004	0.0820	0.492	0.0827	0.496	0.0007	0.004	0.9
6.....	0.0834	0.5004	0.0834	0.500					
7.....	0.1043	0.6258	0.1034	0.6204	0.1038	0.623	0.0005	0.003	0.5
8.....	0.1043	0.6258	0.1043	0.6258					
Average error									0.85

analyzed by the last method described above and the results calculated as in Table I. The results obtained were in all cases a trifle too low. The maximum error, shown in these analyses, is 1.3 per cent and the average less than 0.9 per cent. This error certainly is no greater than that likely to occur in any method of preparing the sample for analysis from a piece of treated wood.