

pine gave 0.96, 0.66, 0.43, and 0.80 per cent; sugar pine gave 0.55 and 0.35 per cent of galactan. It is believed that the described procedure gave approximately correct results. A critical study of the whole galactan method is still much needed, however.

DISCUSSION OF RESULTS

It is believed that analyses of coniferous woods made by the methods described account for all important constituents of those woods. The sum is in every case slightly over 100 per cent but not more so than might be expected from the character of the methods employed. A variation of several tenths of a per cent between duplicate determinations is usual. The cellulose and lignin are probably always slightly overestimated on account of the practical impossibility of getting complete contact between all particles of the material and the attacking reagents. This difficulty could be partly overcome by better mechanical condition of the wood.

The possibility of overlapping of values due to certain constituents being included in more than one determination has received careful consideration throughout these investigations. It is believed that such double estimations have been largely avoided. Most of the proximate groups can be shown to be free from any of the constituents contained in the other groups. It has already been pointed out that this is true in the case of cellulose and lignin. Mannan and galactan determinations depend upon reactions too specific to admit of the inclusion of other constituents.

By improving the mechanical condition of the sample in respect to fineness, better results should be obtained in all the determinations. Some of the determinations, particularly that of galactan, could probably be made more accurate and reliable. These changes would no doubt give a considerably better summation and a consequently more satisfactory accounting of the constituents of the coniferous woods.

SUMMARY

1—An improved procedure is described for the summative analysis of coniferous woods. Methods are given for the estimation of the following constituents: loss on drying, benzene extract, alcohol extract, cellulose, lignin, soluble pentosans, mannan, and galactan.

2—By the omission of preliminary hydrolysis, more reliable results are obtained in the cellulose and lignin determinations than by methods previously used.

3—Soluble pentosans are determined in the chlorination liquors, mannan and galactan on separate portions of the original material. Improvements in the galactan determination are described.

4—Complete analyses of redwood, yellow pine, and sugar pine are carried out by these methods. A summation of slightly over 100 per cent is obtained in every case.

5—The results indicate that overlapping of the proximate groups, *i. e.*, partial inclusion of any constituent in more than one group, has been largely avoided.

6—Analyses by the proposed scheme probably

account for all important constituents of coniferous woods.

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THE DETECTION OF ARSENIC IN SULFUR

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Received October 23, 1919

A certain sample of sulfur was reported to contain arsenic. It had been tested by a method first devised by Schaeppi¹ and later accepted by many authorities.² We found that the sulfur contained no trace of arsenic, but that when it was tested by Schaeppi's method, a decided qualitative test for arsenic was obtained. On further investigation it was found that this method contains a fundamental error which makes it useless as a test for small quantities of arsenic.

The method as described by Schaeppi consists essentially in first digesting the sulfur with dilute nitric acid for the purpose of removing calcium chloride, sulfate, and sulfide. The sulfur washed free from acid is now treated with dilute ammonia solution for 15 min. at 70° to 80° C. Schaeppi assumes that any arsenic present in the sulfur must exist as sulfide, mainly arsenious sulfide, and will be dissolved by the ammonia. The arsenic is then estimated indirectly through determination of the amount of sulfide by precipitation with silver nitrate in neutral solution.

"For very rough estimations, it is sufficient to treat 10 g. of finely ground sulfur with nitric acid, to extract with ammonia, and to add silver nitrate. From the intensity of the color or the quantity of the precipitate of silver sulfide, it may be judged whether the sulfur is approximately free from arsenic or is strongly contaminated."³

Schaeppi endeavored to test the accuracy of his method by dissolving known amounts of pure arsenious sulfide in ammonia solution, carefully neutralizing with nitric acid, and titrating with decinormal silver nitrate using chromate as indicator. His results showed fairly good agreement between the quantities of arsenic taken and those found. However, his results would have

¹ *Chem. Ind.*, **4** (1881), 409.

² Crooks, "Select Methods of Chemical Analysis," 4th ed., 416; Lunge, "Technical Methods of Chemical Analysis," **1** (1908), 267; Lunge, "The Technical Chemist's Handbook," 1916, 107.

³ Crooks, *Loc. cit.*

been conclusive only if the arsenious sulfide had been added to the sulfur and the mixture tested by his method. Any other sulfide if present in the ammonia solution would also be precipitated by the silver nitrate. As a matter of fact, we found that sulfur continuously reacts with dilute ammonia at 70° to 80° C. to form sulfides, so that even arsenic-free sulfur will give a qualitative test for arsenic by this method.

EXPERIMENTAL

The sulfur used in these experiments was obtained from Texas deposits¹ and was found to be absolutely free from arsenic when tested by the Gutzeit method as described later in this paper.

Ten grams of a representative sample, powdered to pass a 160-mesh, were digested with 25 cc. of hot water, to which 0.4 cc. concentrated nitric acid was added. It was then washed free from acid and sulfides and digested with 25 cc. water and 0.5 cc. ammonium hydroxide (sp. gr. 0.90) at a temperature of 70° to 80° C. for 15 min.

The filtrate was somewhat tinged with a bright yellow color and gave a heavy dark brown precipitate on the addition of silver nitrate. The sulfur was now washed clean from alkali and sulfides and the extraction repeated with ammonia solution as before. Again the filtrate gave a heavy precipitate on the addition of silver nitrate.

The extraction was repeated a third and a fourth time, washing the sulfur clean from alkali and sulfur in each case and the same results were obtained. The precipitate with silver nitrate in the last extract seemed as heavy as that in the first.

A sample of flowers of sulfur was tested in the same way, the extraction with dilute ammonium hydroxide being repeated three times. The results were the same as in the case of the crude sulfur.

To determine whether the ammonium hydroxide solution really contained arsenic or not, the first extract from 10 g. of crude sulfur was acidified with hydrochloric acid, a crystal of potassium chlorate added, and the solution boiled until all the chlorate was decomposed. This solution was now tested by Gutzeit's method for arsenic and none was detected.

Further, 8 g. of crude sulfur were extracted with dilute ammonia at 70° to 80° C. The extract was acidified with strong nitric acid and evaporated to dryness on a water bath. A few cc. of concentrated nitric acid were added and was again evaporated to dryness. The residue was dissolved in water and tested by Gutzeit's method for arsenic with negative results. In a check test, 0.00004 g. of arsenic under similar conditions in the Gutzeit apparatus gave a well-marked arsenic stain.

These experiments indicate that sulfur reacts with dilute ammonium hydroxide at 70° to 80° C. to form ammonium sulfides. This is substantiated by the well-known fact that sulfur readily dissolves in hot solutions of the strong alkalis to form polysulfides.

A sample of arsenic-free sulfur would, therefore, continue indefinitely to give a test for arsenic by Schaeppi's method.

TESTING THE SULFUR FOR ARSENIC BY GUTZEIT'S METHOD

To prepare the solution for the test, Scott¹ recommends the following procedure:

Ten grams of the material (brimstone) are treated with 30 cc. of carbon tetrachloride mixture (3 parts CCl_4 + 2 parts Br) and after standing for 10 min. 25 cc. strong nitric acid are added in small portions (a watch glass covering the beaker during the intervals of addition). The mixture is taken to dryness on a steam bath, water is added, and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit method for arsenic.

In our experience 25 cc. of strong nitric acid were insufficient to oxidize the sulfur bromide even when added drop by drop from a pipette; 10 to 15 cc. more were needed, depending on the length of time the solution was allowed to stand on the water bath. It was found advisable to warm the sulfur bromide slightly before adding the nitric acid from a dropping pipette. The final evaporations were carried out directly over a flame, instead of on a water bath, until sulfur trioxide fumes appeared.

By the action of the bromine and nitric acid the sulfur is completely oxidized to sulfuric acid. The carbon tetrachloride is added to moderate the violence of the reaction and to prevent the precipitation of sulfur. Any excess of these reagents is expelled by the final evaporations. The acid solution remaining in the flask was now tested for arsenic by Gutzeit's method, details of which may be found in any standard textbook on chemical analyses.

The crude sulfur used in the work on Schaeppi's method was tested in this way with the following results:

1—Ten g. of sulfur gave no test for arsenic. At the completion of the test 1 cc. of 0.001 N As_2O_3 solution (0.00004 g. As) was added to the solution remaining in the Gutzeit apparatus and a strong test for arsenic was obtained in a few minutes. This proved that no substance was present which would prevent the arsenic test from showing, had arsenic been present.

2—Ten g. of crude sulfur to which 0.00004 g. As were added gave a distinct test for arsenic, quite comparable with the stain obtained when a solution containing an equal quantity of arsenic was tested directly in the Gutzeit apparatus.

SUMMARY

I—It has been found that sulfur reacts somewhat with dilute ammonium hydroxide at 70° to 80° C. to form sulfides.

II—Schaeppi's method of testing for arsenic in sulfur has been shown to contain a fundamental error due to this interaction of sulfur with dilute ammonium hydroxide.

III—The method of testing for arsenic in sulfur which consists in oxidizing the sulfur with bromine and nitric acid and testing the residue by Gutzeit's method for arsenic has been proved to be reliable.

¹ From the recently developed deposits of the Texas Gulf Sulfur Co., at Gulf, Matagorda Co., Texas. The three great deposits of sulfur which are being worked commercially in the country (Union Sulfur Co., Freeport Sulphur Co., Texas Gulf Sulfur Co.) are all free from arsenic.

¹ Loc. cit., 415.