

Two determinations gave the following results:

I. 25.64 grams of oil gave 0.464 gram of paracholesterol.

II. 15.792 grams of oil gave 0.3474 gram of paracholesterol.

	I.	Per cent.	II.
Calculated for paracholesterol.....	1.8		2.2

Although the paracholesterol was obtained in a comparatively pure form by this method, considerable difficulty was experienced in evaporating to dryness, several hours being required. It was also observed, that when more than the above-mentioned amount of nitric acid was used, the quantity of paracholesterol was diminished. Thus with double the quantities of nitric acid and mercury only four-tenths per cent., and with three times the quantity of acid and mercury only a trace, of the paracholesterol was obtained. Just why this diminution in the quantity of paracholesterol should occur, is not definitely known. The probabilities are, however, that it forms, with the excess of nitric acid, a nitrolic acid according to the common reaction.

THE ESTIMATION OF ARSENIC IN PARIS GREEN.

BY THORN SMITH.

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IN selecting a method for the analysis of the common insecticide, Paris green, some difficulty was encountered in finding one suitable to the ordinary requirements of rapidity and corresponding accuracy. In fact the only methods of which record was found are as follows:

First, by direct precipitation of the arsenic as magnesium pyroarsenite by means of magnesia mixture or what would be embodied in the same method, a first separation of the sulphides of arsenic and copper, by means of hydrogen sulphide, and a consequent tedious separation of the arsenic from the copper by means of ammonium sulphide, followed by the precipitation of the arsenic as at first. This latter modification is given in the majority of text-books, which mention the subject at all. Its objection is the large amount of time consumed in the operation and the danger of loss in separating the arsenic from the copper.

The second method known as the "Pearce" or "McCay" method is perhaps just as difficult with the added objection that such small amounts of the material are permitted in the pro-

cess, that errors are sure to creep in. The Paris green is fused with sodium carbonate and potassium nitrate, extracted with water, and the sodium arsenite in the water solution oxidized to the arsenate by nitric acid. The arsenate is then precipitated by silver nitrate, volumetrically. The amount of silver precipitated is to the arsenic as 108 is to 25. This method is undoubtedly well adapted to material containing but small amounts of arsenic, but where from forty to sixty per cent. is arsenic not more than two-tenths of a gram can be handled, and even then the precipitate is so bulky that inconvenience is caused. A large amount of the silver solution is also required. Either of the above will undoubtedly give exact results in the hands of an experienced analyst, but when the attempt is made by the ordinary student, woeful results generally follow and discouragement naturally attends.

In presenting the following method I may have nothing new; in fact it may be a well-known method but at least none of the text-books at my command nor any of the standard authorities mention it. I have taken advantage of well-known reactions, and in part have used volumetric methods given by Sutton. Owing to the variable composition of Paris green, one reaction does not fit all cases but the composition and degree of oxidation of the essential elements are the same. If a copper salt be boiled with a slight excess of sodium hydroxide, in the presence of a reducing agent, cuprous oxide is formed. Therefore, if the arsenite of copper be boiled with sodium hydroxide, cuprous oxide is formed by the reducing action of the arsenite and at the same time a portion of the arsenite is oxidized to the arsenate, in this case, sodium arsenate. The latter being soluble can be filtered from the precipitated cuprous oxide, and this solution being alkaline, can be concentrated without loss. If this concentrated solution be strongly acidified with hydrochloric acid and, while still warm, an excess of potassium iodide be added, the arsenate is wholly reduced to the arsenite. The reaction is complete in a few minutes. The acid solution now contains a large amount of free iodine which can be consumed by carefully adding a dilute solution of sodium hyposulphite, followed by the addition of sodium carbonate until the solution is neutral. An excess of the bicarbonate is then added and the

solution titrated against tenth-normal iodine, using starch as an indicator.

As finally adopted the following method is used in this laboratory :

Two grams of the Paris green are weighed out, about 100 cc. of water added, and two grams of sodium hydroxide. The solution is brought to a boil and boiling continued for a few minutes. It is then allowed to cool to room temperature and the solution made up to 250 cc. The well-shaken liquid is filtered through a dry filter and fifty cc. taken for the analysis. This portion equal to four-tenths gram is concentrated to about one-half its volume and allowed to cool to about 80° C. An equal volume of strong hydrochloric acid is then added accompanied by three grams of potassium iodide and the whole allowed to stand for ten minutes (longer is not necessary). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide and a dilute solution of sodium hyposulphite added until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth-normal iodine is dropped in and the end-reaction noted by starch solution.

I have found it easier in calculating results to use a solution of iodine such that one cc. equals 0.005 gram of arsenic trioxide, instead of the exactly tenth-normal solution, one cc. of which equals 0.00495 gram. The number of cubic centimeters of such a solution multiplied by one and one-fourth equals the per cent. of arsenic trioxide in the Paris green. Two grams are taken for the assay and four-tenths taken for the operation, owing to the fact that generally but slightly less than fifty cc. are required for the titration and thus a second filling of the burette is avoided, which would be necessary were five-tenths gram taken. Working by this method an analysis can be made in less than one hour whereas by the other methods several hours or days are required. If desired, the copper as cuprous oxide can be dissolved and titrated against potassium cyanide by standard methods. The end-reaction in the arsenic titration is sometimes difficult owing to the large amounts of foreign salts in the solution. A deep red color is produced as the titration

proceeds but the unmistakable blue can easily be seen after a few trials.

Working by this method I have obtained duplicates within 0.05 per cent. which is certainly accurate enough for all practical purposes. My results have also checked the gravimetric methods very closely.

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THE DETERMINATION OF SULPHUR IN BITUMENS.¹

BY S. F. AND H. E. PECKHAM.

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THE paper read by Mr. E. H. Hodgson, which appeared in the November (1898) number of this Journal, was read by us with great interest. It is evidently intended to be a description of a fair comparative test of the value of the several methods used for the determination of sulphur in the different varieties of bitumen examined.

We wish to call attention to a number of unrecognized, or at any rate unmentioned conditions, which, in our opinion, rendered the results, given by Mr. Hodgson, variable, and to some extent unreliable.

Of the specimens selected for analysis, it is to be said, that the two specimens called "Trinidad Lake" and "Trinidad Lake refined" are very peculiar substances. They, in common with all other Trinidad pitch, consist of a mixture of bitumen, mineral matter, organic matter that is not bitumen, and a considerable proportion of ferric and aluminic oxides, that are combined with organic radicals to form complex salts. There are sound reasons for believing that some of the sulphur is free, some of it in combination with iron as pyrites, in an extremely minute state of division, and some of it in combination as thio-salts, in which it performs a linking rather than saturating function.

There can be no question that the action of nitric acid on this complex mixture of various substances results in the formation, not only of sulphuric oxide, but of other oxides of alumina and iron, that will almost certainly form double barium salts with sulphuric acid, that are nearly or quite as insoluble as pure ba-

¹ Read at the June Meeting of the New York Section.