tion, in drawing conclusions as to the addition of water, from the facts of low ash and solids.

The skilful adulteration of wine is extremely difficult to detect by chemical analyses, and these abnormally low results, obtained by analysis of perfectly pure and reliable samples, make such conclusions from these determinations all the more unsatisfactory.

It is of interest also to compare the composition of these samples with that of authentically pure California samples. Many such analyses have been made and reported by Prof. Hilgard,[1] and while they do not include determinations of glycerol, the contents of ash and solids are usually higher than those of European samples.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 3.]

## THE DETERMINATION OF SULPHUR IN ASPHALT.

BY E. H. HODGSON.

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THE numerous articles recently published on the analysis and chemistry of asphalts, and the wide range of opinion as to the relative values of the different methods in use for the determination of sulphur, have led me to make a comparison of results on some typical asphalts.

Dr. E. H. Miller, through the kindness of Mr. A. W. Dow, of Washington, was enabled to secure samples, the sources and natures of which were known. The samples were labeled Trinidad Lake, Trinidad Crude, Trinidad Lake Refined, Cuban Crude, Alcatraz Crude, and California Crude, and were described by Mr. Dow as follows:

*Trinidad Lake.*—Asphalt from the lake on the island of Trinidad, imported by Barber Asphalt Co. for paving.

*Trinidad Crude.*—Crude asphalt from Hadley's Diggings, about one mile from Trinidad Lake. It is known as "iron pitch," being the hardest asphalt found in Trinidad.

*Trinidad Lake Refined.* This is crude Trinidad Lake asphalt, melted up to drive out the water.

*Alcatraz Crude.*—From Ventura Co., California, used by

[1] Bulletin 13, Division of Chemistry, U. S. Department of Agriculture.

the Alcatraz Asphalt Co. for paving, after the addition of liquid asphalt.

*California Crude.*—From Kern Co., California, used by the Standard California Asphalt Co. for paving, after the addition of liquid asphalt.

Sample "Trinidad Lake" was found to lose water very rapidly, so it was heated to about 60° C. (not sufficient to melt it) and then remained constant.

The samples were ground as fine as possible in a mortar, and then placed in glass bottles, fitted with tight corks. From these bottles average samples were taken and kept in test-tubes for use.

### HEATING WITH STRONG NITRIC ACID IN A SEALED TUBE—CARIUS' METHOD.

The tubes were made in the usual way from heavy glass tubing. Two determinations were made on each sample. One on one-half gram and one on three-fourths gram. A general description of the method is as follows: One-half gram of asphalt is introduced into the bottom of the tube, and fifteen cc. of fuming nitric acid (1.60 sp. gr.) is poured upon it. The open end of the tube is then drawn out into a thick-walled fine-caliber tube, but not sealed. The tube is then heated, for about six hours, in a water-bath kept at 80°–90° C. Then five cc. more acid are added, the tube is sealed, and heated in a guarded furnace at a temperature of about 150° C. for from four to five hours. Allow the tube to cool, then open and reseal, and reheat for from two to four hours at a temperature of 180°–200° C. Cool, open, and remove the liquid and residue into a No. 2 beaker. Dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of solid sodium hydroxide. The nitric acid is driven out by repeated evaporation of the solution, with the addition of hydrochloric acid, and the silica dehydrated in an air-bath at 110°–115° C. Cool the dehydrated mass, add two to three cc. of hydrochloric acid and 100 cc. of water, stir well, filter, and wash well with hot water. Dilute the filtrate to about 200 cc., heat to boiling and while boiling add twenty cc. of barium chloride (twenty per cent. solution), drop by drop, from a burette, at the rate of

about a drop a second. Stir all the time. Boil the solution about ten minutes, and allow it to stand twenty-four hours. Filter, wash with hot water, and ignite. Treat with sulphuric acid and reignite. Then cool and weigh the barium sulphate. A pure white product was obtained, and the precipitate did not run through the filter.

*The residue* from the sealed tube, if not thoroughly oxidized, is fused with six grams of mixed carbonates and one gram of potassium nitrate. The fusion is dissolved in water and hydrochloric acid. The nitrates are destroyed by evaporating with the addition of hydrochloric acid, and the silica dehydrated as before. Filter off the silica and wash. Then determine the sulphuric acid in the filtrate as before described.

When three-fourths gram of asphalt was used, twenty-five cc. of fuming nitric acid were employed instead of twenty cc.

The following results were obtained :

TRINIDAD LAKE.

| | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| One-half gram | 0.1526 | 4.192 |
| Residue | 0.0051 | 0.140 |
| | | 4.332 |
| Three-fourths gram | 0.2238 | 4.10 |
| Residue | 0.0068 | 0.18 |
| | | 4.28 |

TRINIDAD CRUDE.

| | | |
|---|---|---|
| One-half gram | 0.1249 | 3.400 |
| Residue | 0.0034 | 0.086 |
| | | 3.486 |
| Three-fourths gram | 0.1720 | 3.148 |
| Residue | 0.0106 | 0.19 |
| | | 3.338 |

TRINIDAD LAKE REFINED.

| | | |
|---|---|---|
| One-half gram | 0.1585 | 4 35 |
| Residue | .... | .... |
| | | 4.35 |

| | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| Three-fourths gram | 0.2160 | 4.21 |
| Residue | 0.0137 | 0.25 |
| | | 4.46 |
| CUBAN CRUDE. | | |
| One-half gram | 0.1315 | 3.61 |
| Residue | .... | .... |
| | | 3.61 |
| Three-fourths gram | No results. | |
| ALCATRAZ CRUDE. | | |
| One-half gram | 0.1839 | 5.05 |
| Residue | 0.0195 | 0.54 |
| | | 5.59 |
| Three-fourths gram | 0.2749 | 5.12 |
| Residue | 0.0294 | 0.46 |
| | | 5.58 |
| CALIFORNIA CRUDE. | | |
| One-half gram | 0.2589 | 7.11 |
| Residue | 0.0145 | 0.398 |
| Three-fourths gram | No results. | |

DEFLAGRATION METHOD—S. F. AND H. E. PECKHAM.

A porcelain crucible is heated to a dull red heat, and *small* amounts of a mixture of one gram finely ground asphalt, eight grams of potassium nitrate, and eight grams of mixed sodium and potassium carbonates, added from time to time, just keeping the material in the crucible melted. When all of the mixture has been added, heat to perfect fusion with a blast-lamp, and cool. Dissolve the fusion in twenty cc. hydrochloric acid and forty cc. of water, and wash the crucible well with hot water. The solution is evaporated down to dryness, dehydrated at 110°–115°, the silica filtered off, and the sulphuric acid determined in the filtrate as before. The results are as follows:

TRINIDAD LAKE.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2770 | 3.804 |
| 2 | 0.2689 | 3.68 |

TRINIDAD CRUDE.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2443 | 3.37 |
| 2 | 0.2359 | 3.24 |
| TRINIDAD LAKE REFINED. | | |
| 1 | 0.2634 | 3.62 |
| 2 | .... | .... |
| CUBAN CRUDE. | | |
| 1 | 0.2009 | 2.76 |
| 2 | 0.2052 | 2.82 |
| ALCATRAZ CRUDE. | | |
| 1 | 0.3054 | 4.19 |
| 2 | 0.2773 | 3.81 |
| CALIFORNIA CRUDE. | | |
| 1 | 0.4376 | 6.50 |
| 2 | .... | .... |

SODIUM PEROXIDE METHOD.

Place one gram of the fine asphalt in the bottom of a large nickel crucible. Cover with a layer of about four grams of mixed carbonates and about one gram of solid sodium hydroxide. Cover the crucible and heat gently until the gases are driven off. Then raise the heat and add small amounts of sodium peroxide, from time to time, until no further action is noticed on the addition of fresh $Na_2O_2$. Then, with the blast-lamp, heat to perfect fusion. This takes but a few minutes. Pour as much of the fusion as possible upon the cover of the crucible and cool slowly. Place the fusion, crucible, and cover in a casserole containing fifty cc. hot water, and after thorough digestion on the water-bath, filter off the residue, and wash well with hot water. The filtrate is made acid with hydrochloric acid, and evaporated down to dryness, dehydrated at 110°–115° C., the silica filtered off, and the sulphuric acid determined in the filtrate as already described. Results by this method:

TRINIDAD LAKE.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2687 | 3.69 |
| 2 | 0.2744 | 3.77 |

TRINIDAD CRUDE.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2426 | 3.33 |
| 2 | 0.2360 | 3.25 |
| TRINIDAD LAKE REFINED. | | |
| 1 | 0.2962 | 4.07 |
| 2 | 0.2929 | 4.02 |
| CUBAN CRUDE. | | |
| 1 | 0.2256 | 3.10 |
| 2 | 0.2230 | 3.06 |
| ALCATRAZ CRUDE. | | |
| 1 | 0.2887 | 3.97 |
| 2 | 0.2880 | 3.96 |
| CALIFORNIA CRUDE. | | |
| 1 | 0.4557 | 6.26 |
| 2 | 0.4481 | 6.15 |

IGNITION WITH CALCINED MAGNESIA—ESCHKA'S METHOD.

One gram of finely ground asphalt is intimately mixed with one gram of calcined magnesia and about one-half gram of dry mixed carbonates is added. Mix well and place in a platinum or porcelain crucible. With the crucible in an inclined position, heat at a dull red heat, stirring every few minutes until the ash is a dull yellow. Cool and add about one gram of finely ground ammonium nitrate and mix thoroughly. Heat slowly to a dull red, and continue the heating until the ammonium nitrate is entirely decomposed. Cool, extract the mass thoroughly with water (hot water preferred), filter, and wash well. Acidulate the filtrate with hydrochloric acid, and precipitate the sulphuric acid as before described. The results are as follows:

TRINIDAD LAKE.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2660 | 3.65 |
| 2 | 0.2791 | 3.83 |
| TRINIDAD CRUDE. | | |
| 1 | 0.2608 | 3.58 |
| 2 | 0.2567 | 3.53 |

TRINIDAD LAKE REFINED.

| No. | Weight of barium sulphate. Gram. | Sulphur. Per cent. |
|---|---|---|
| 1 | 0.2744 | 3.77 |
| 2 | 0.2650 | 3.64 |

CUBAN CRUDE.

| | | |
|---|---|---|
| 1 | 0.2020 | 2.77 |
| 2 | 0.1941 | 2.66 |

ALCATRAZ CRUDE.

| | | |
|---|---|---|
| 1 | 0.3054 | 4.19 |
| 2 | 0.3021 | 4.16 |

CALIFORNIA CRUDE.

| | | |
|---|---|---|
| 1 | 0.5011 | 6.88 |
| 2 | 0.5109 | 7.01 |

The relative accuracy of the different methods is best shown by tabulating the results, as follows:

| | Trinidad Lake. | Trinidad Crude. | Trinidad Lake Refined. | Cuban Crude. | Alcatraz Crude. | California Crude. |
|---|---|---|---|---|---|---|
| Sealed tube | 4.33 | 3.49 | 4.35 | 3.61 | 5.59 | 7.51 |
| | 4.28 | 3.34 | 4.46 | ... | 5.57 | ... |
| Deflagration | 3.80 | 3.37 | 3.62 | 2.82 | 4.19 | 6.50 |
| | 3.68 | 3.24 | ... | 2.76 | 3.81 | ... |
| Peroxide | 3.69 | 3.33 | 4.07 | 3.10 | 3.97 | 6.26 |
| | 3.77 | 3.25 | 4.02 | 3.06 | 3.96 | 6.15 |
| Eschka's | 3.65 | 3.58 | 3.77 | 2.77 | 4.19 | 6.88 |
| | 3.83 | 3.53 | 3.64 | 2.66 | 4.16 | 7.01 |

It would appear, therefore, that the "sealed tube" gives the most accurate results, but on account of the explosion of the tubes and the time required for a determination, it would probably be barred out.

The deflagration method apparently gives low results. It is much shorter than the sealed tube, but longer than either the peroxide or Eschka's method.

Of the latter two, the Eschka's method is perhaps the better, as it requires less time and attention to carry out, and gives about as good results.

The peroxide method is shorter than the deflagration method and about as accurate.

The reagents employed were first tested for sulphur.

| | Sulphur. Per cent. |
|---|---|
| The sodium and potassium carbonate contained..... | 0.005 |
| The sodium peroxide contained..... | 0.003 |

The rest of the reagents were sulphur free or contained but the merest trace.

## NOTE.

*Testing for a Yellow Azo-Color in Fats, Etc.*—In this Journal, **20**, 110, Joseph F. Geissler describes a delicate test for the detection of a yellow azo-dye used in coloring fats. The test has proved of the greatest service to me, and I make use of it constantly. While experimenting upon the subject, I have noted another simple test for this azo-color that seems fully as delicate as Geissler's. To a few cubic centimeters of the pure filtered fat in a large test-tube are added an equal volume of a mixture of one part strong sulphuric acid, and four parts glacial acetic acid. The contents of the tube are then heated almost to boiling, and thoroughly mixed by violently agitating the bottom of the tube. When now allowed to stand and separate, the lower layer of mixed acids will be strongly colored wine-red if the azo-color be present. Pure butter-fat imparts no color, or at most only a very faint brownish tinge to the acids. Strong hydrochloric acid may replace the sulphuric in the above mixture, or a mixture of one part strong sulphuric acid, and three parts water may be used, but I have obtained the best results in the manner described. ALBERT H. LOW.

DENVER, COLORADO, August 27, 1898.

## NEW BOOKS.

A BRIEF COURSE IN QUALITATIVE ANALYSIS. BY ERNEST A. CONGDON, PH.B., F.C.S. New York: Henry Holt & Co. 1898. iv + 62 pp. Price 60 cents.

Professor Congdon has given us a very satisfactory little text-book. While brief, the course, so far as it goes, is quite thorough.