THE TECHNICAL ANALYSIS OF SPIRITS OF TURPENTINE, WITH A NEW METHOD FOR THE DETECTION OF PETROLEUM ADULTERATIONS AND OF WOOD SPIRITS OF TURPENTINE.

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Received May 26, 1904.

AN ACT, passed by the last General Assembly of Georgia, provided for the appointment of an inspector of naval stores for this State, forbade the adulteration of pure spirits of turpentine, with petroleum, wood turpentine or other adulterants, and in case of dispute between the party charged with adulteration and the inspector, provides that a properly drawn and sealed sample be sent to the State chemist to decide the issue. In this way it has become my duty to study the existing methods for the analysis of turpentine and the detection of its adulteration. A good review of the previous literature on the subject is given by Worstall in his interesting article in the *Journal of the Society of Chemical Industry*, 23, 302 (1904), and, as stated by him, this literature is scanty, and the various tests given, including specific gravity, etc., somewhat unsatisfactory. The usual adulterants are petroleum oil, gasoline, rosin spirits, and recently there has been introduced another possible adulterant in the turpentine distilled from pine wood and old lightwood knots, and stumps, sometimes called stump turpentine or stump spirits. Realizing the necessity of personal experience with samples of undoubted purity and previous history, and being well situated for the purpose of obtaining such samples, I secured from different sections of the State a number of samples of genuine turpentine, representing the entire turpentine-producing area of the State. Also a number of samples of wood spirits of turpentine.

As a preliminary test, Dunwoody's 99 per cent. acetic acid test was tried, but without success in detecting known adulterations. The following figures for iodine absorption, specific gravity and flash test were next obtained. The iodine absorption determinations were carried out precisely in the manner prescribed by Worstall,[1] weighing carefully about 0.1 gram of each sample into glass stoppered flasks, using 40 cc. of Hübl solution, and allowing the action to proceed for eighteen hours in the dark, conducting care-

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[1] *Loc. cit.*

ful blanks at the same time. Flash tests were made in the Elliott closed cup in the manner prescribed for the test of illuminating oils in Georgia.

Nature of sample.	Specific gravity at 15.5° C.	Iodine numbers.		Flash-point. °F.
		(1)	(2)	
Pure spirits of turpentine, Ware Co., Ga	0.868	383	...	...
" " " " Calhoun Co., Ga	0.8653	388	388	...
" " " " Decatur " "	0.8695	380	375	...
" " " " (yellow), Telfair Co., Ga	0.8927	371	...	85
Pure spirits of turpentine, Wilcox Co., Ga.	0.8725	380	...	89
" " " " Emanuel Co., Ga	0.8668	397	...	...
Pure spirits of turpentine, Brooks Co.. Ga.	0.872	384	...	...
" " " " Marianna, Fla.	.....	364	...	87
" " " " Savannah, Ga	0.8655	394.9	...	...
Mixture, 96 per cent. of above and 4 per cent. kerosene	.....	383	...	...
Adulterated sample from city	0.863	373	...	83
" " " inspector, R No. 1	0.864	364	373	87
" " " " " " 2	0.8665	356	...	88
" " " " " " 3	0.8665	390.7	...	89
Wood spirits from Mobile	0.8625	282	...	...
" " " City Store	0.888	352	...	...
" " " Cordele	0.8605	351.9	...	...
" " " Waycross, steam process (H)	0.8725	331	...	...
Wood spirits, Waycross, steam process (R)	0.8805	298	...	...

Allen gives the specific gravity of genuine oil as ranging from 0.864 to 0.870; as is evident from an inspection of the above table, adulteration may exist and the specific gravity give no indication of it. Likewise with the flash tests; samples afterwards shown to be adulterated flashed at as high a temperature as the genuine oil. Doubtless spirits adulterated with gasoline or with kerosene flashing at a lower point than that permitted by the Georgia law (100° F. in the Elliott cup), would respond to this test. Although I had hoped for much more decisive evidence from the iodine absorption, it becomes evident from the variations in the figures for undoubtedly genuine oil, that the process cannot be relied on for detecting small percentages of adulteration with petroleum.

Turning next to the methods of Armstrong, as given by Allen in "Commercial Organic Analysis," second edition, Vol. II, I found the first method of distillation in a current of steam unsatisfactory and leaving the mind in doubt in case of small percentages of adulteration. I found his method for detection of petroleum naphtha, by polymerization with sulphuric acid followed by steam distillation, better, even for kerosene, but time-consuming and tedious, and permitting adulterations of 5 per cent. and under, of kerosene, to escape detection. I had no difficulty in detecting 10 per cent. adulteration by his method, but in the case of a 4 per cent. mixture I failed utterly to discover it. In this latter case the final volume of the distillate amounted to just 4 per cent., or entirely within the limits for genuine oil, as given by Allen for pure spirits in his description of the method. Moreover, the final product could not be positively identified, as the process had destroyed the characteristic fluorescence of the petroleum, even when dissolved in ether. At this point it occurred to me to test the refractive index of the oils resulting from the steam distillation and polymerization. Obtaining important results from this procedure, after much labor and experiment the following comparatively easy and rapid method of detecting petroleum was worked out:

Transfer 100 cc. of the oil to a 600 cc. flask, preferably of Jena glass, add 50 cc. of concentrated sulphuric acid from a graduate, a few cubic centimeters at a time, agitating the acid thoroughly with the oil and cooling in a current or basin of water, if the action is very violent, between each addition of acid. When all the acid has been added and there is no further rise of temperature on repeated agitation, add 25 cc. of water to the flask, connect the flask by means of a double-bored cork and a suitable bulb-tube with a Liebig condenser and also with a large flask containing water. A current of live steam is now sent through the mixed oils and acid in the flask at such a rate as not to project any of the dark oils into the bulb-tube intervening between the flask and condenser. Distil until the volume of distillate (mixed water and oil) reaches 100 cc., now separate the oil from the water and test with a few drops the refractive index, then measure the oil approximately, transfer to a small dry flask of 50 cc. capacity, glass-stoppered, and add as much fuming sulphuric acid as there was of oil, agitate violently, removing the stopper occasionally for the escape of sulphur gases. Pour the resulting mixture into cold water, separate the oil which floats, transfer it to a distilling flask and repeat the distillation in a current of steam. Distil to a volume of 100 cc., separate the oil from the water as before, take the refractive index, then polymerize the resulting oil for the third time with at least an equal volume or better, twice its volume of fuming sulphuric acid. The resulting mixture is again poured into cold water, the oil separated and washed with cold water, its volume noted and the refractive index again taken. The instrument used in taking the refractive indices was the "Zeiss butyro-refractometer," provided with a centesimal scale, ranging from N_D 1.42 to 1.49. For the sake of convenience and greater distinctiveness the results given below are expressed in terms of the centesimal scale of the butyro-refractometer. These may be translated into corresponding refractive indices by means of the table given on page 342, Volume III, of Wiley's "Principles and Practice of Agricultural Analysis." All readings were made at a temperature of 25° C. and by sodium light.

Nature of sample.	Oil from 1st polymerization.	Oil from 2nd poly. merization.	Oil from 3rd polymerization.	Final vol. cc.
Calhoun Co., turpentine	79	58	33.5	1.1
Decatur Co., "	74	48	32.0	1.2
Savannah pure spirits	82	58	35.0	0.7
Pure spirits with 1 per cent. kerosene	72	43	25.0	1.4
" " " 2 " " "	65	39	21.0	2.2
" " " 4 " " "	57	34	18.0	2.7
Adulterated samples from inspector R, No. 1	49	17	13.0	3.5
" " " " " " 2	70	45	20.0	2.1
" " " " " " 3	71	43	22.0	2.0
5 cc. of pure kerosene	18	..	12.0	2.9
Wood spirits, Cordele	80	66	43.0	2.0
" " crude	79	64	31.0	1.7
" " steam process	69	45	30.0	1.8
" " Mobile	78	64	37.0	2.0

In no case was I able to reduce the reading below 30 with genuine turpentines or wood spirits, but with adulterated spirits, containing even as little as 1 per cent. of kerosene, the reading fell as low as 25 on the third polymerization, and could be slowly reduced to 22 by continued treatment with fuming acid; the greater the percentage of adulteration the lower in the scale would the reading fall.

I have not succeeded yet in making the method quantitative, though the chemist would run but little risk in certifying the final volume to be the minimum percentage of petroleum, when the refractometer reading is as low as 22. Adulteration with naphtha or kerosene with low flash-point would show still lower readings than those obtained above. The kerosene sold in this state flashes at or above 100° F. in the Elliott cup; it is, therefore, to be expected that adulteration with kerosene of a lower flash-point would show a somewhat lower reading. Adulteration with rosin spirits may be shown by the Liebermann-Storch test.

Adulteration with wood spirits is unlikely, since there is but little difference in price between wood and genuine spirits. The crude wood spirits may be known by its odor, but with a highly refined article it would be different. Adulteration of this kind may be detected as follows: Kerosene or naphtha having been proved to be absent by the above process of polymerization, a distillation is carried out on 100 cc. of the sample in a flask made precisely according to the specifications of Engler for the distillation of illuminating oil.

The flame used must be small, the thermometer rise very slowly, and the first 0.5 cc. of distillate collected by itself, drop by drop, and the refractive index taken at 25° C. In the case of no genuine oil will this fall below 60, being usually 61 to 63. Several samples of wood spirits show readings as low as 59, 58 and even 57. When the wood spirits do not show a low initial reading, they nearly always show a high reading on the final portion of the distillate. I have adopted the 97th and 98th cc. of the distillate as being in practice the most convenient to collect separately for the purpose of taking the final refractive index. In the case of genuine spirits this reading will not exceed 77, usually much less, but with wood spirits will (especially if the initial reading be high) exceed 77 and may even reach 90. A further distinction between genuine and wood spirits may be observed during this distillation; in nearly all genuine spirits 95 per cent. will have distilled over by the time the temperature reaches 165° C., whereas, with wood spirits, when 95 per cent. have come over, the thermometer is much higher than 165°. It is possible that the methods described above may, with modifications, be applied to the detection of turpentine in the more costly essential oils. I have to thank Messrs. Williams and Burton, of this laboratory, for their indispensable aid and valuable suggestions during the progress of the work.

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