after revision by a committee of physicians and pharmacists of the homeopathic school. Radium emanations just spoken of as being effective in such small doses remind me of being near akin to homeopathy.

Mr. W. Jay Schieffelin, Jr., of New York:—Referring to radium, it seems to me that when we are considering minute doses, that radium water, or emanation water, ought to be put in the homeopathic pharmacopoeia.

Mr. Gordon:—The use of radium in homeopathic hospitals is common. I know of one that has at least $50,000.00 worth.

Mr. Schieffelin:—I remember years ago hearing a receipt for homeopathic punch. You take a little rum, the less you take the better, drop it in the lakes of Wenner and of Wetter. You stir the mixture well, lest it prove inferior, and put one drop of it into Lake Superior. Stir again and then lest it makes you groggy, you place one drop of it into Lake Winnepesaukee, and then every other day you take a drop of that in water. That will make you well, or at least it ought to. (Laughter.)

When you take the mother tincture and make it up to a sixtieth or one hundred and twentieth potency, you actually dilute it as much as the punch. An atom of helium is very minute. An atom of helium is to a drop of water as is a walnut in size to the globe. So you can see what there is in small doses.

Mr Gordon:—I can beat that. One of the old tests as to the truth of Homeopathy was the following: Put one teaspoonful of whiskey into a bucket full of water and give an old sailor teaspoonful doses of the dilution until you got him drunk. I have seen it tried, but there was too much water to suit the sailor. (Laughter.) He takes his straight. But to be serious, I have had the privilege of studying a little into the doctrines of Hahnemann, and I am surprised how near he came to our own modern doctrines. We boast of our vaccines and prophylactic serums; what are they but an exemplification of Hahnemann's famous doctrine "Like cures like"? We give the same germs that caused the disease, to cure it. Take the theory of dilution of drugs. It is but the ionic theory in embryo. The homeopathic school does not teach that the weaker a drug is the more powerful it is, just the contrary. The basis of its teachings is that a drug in a finely divided state, dilutions or triturations, is more active than when in mass. Is not that the ionic theory? Does sodium chloride as NaCl exert any chemical action until it is disassociated by solution in water into sodium and chlorine ions?

Prof. L. E. Sayre, of Lawrence, Kansas:—How about those substances which do not ionize? Do they act?

Mr. Gordon:—Not to be ironical I answer yes, just as a flatiron does when applied to the head. How, I don't know from experience.

NOTES ON THE ANALYSIS OF SOME ESSENTIAL OILS.

FRANCIS D. DODGE.

1. *Detection of Pinene in Oil of Lemon.*

To demonstrate the presence of pinene among the terpenes of oil of lemon, or of similar oils, reliance is generally placed on the well-known nitroso-chloride reaction, the crystalline product being identified by its melting point, or the melting point of nitrolamine derivative. As a rule, however, a mixture of nitrosochlorides is obtained, and the recognition of the pinene derivative is attended with some uncertainty. We have found it convenient, for this purpose, to utilize the reaction of the nitroso-chloride with anilin.

Wallach (Ann. 252, 132) has shown that pinene nitroso-chloride, on heating with anilin, regenerates pinene, with formation of amido-azo-benzene:

$$(C_{10}H_{16}NOCl)_2+6C_6H_5NH_2=$$
$$2C_{10}H_{16}+2C_6H_5-N_2-C_6H_4NH_2+2C_6H_5NH_2HCl+2H_2O.$$

whereas limonene nitroso-chloride passes under similar conditions, into a nitrolanilide:

$$(C_{10}H_{16}NOCl)_2+4C_6H_5NH_2=$$
$$2C_{10}H_{15}NOH.NHC_6H_5+2C_6H_5NH_2HCl.$$

The reaction thus effects a most satisfactory separation of these terpenes, pinene being isolated as such, in convenient shape for further tests if necessary.

Unfortunately, the method, like all based on the nitroso-chloride reaction, has only a qualitative value, for the yield of nitroso-chloride depends largely on the rotation of the pinene, being greatest from the inactive variety, and little, if any, being obtainable from pinene of high rotation, whether dextro- or lævo; and in cases where turpentine oil may have been added to oil of lemon, it is reasonable to suppose that a highly dextro variety would be selected.

In many cases, however, we have obtained positive results by operating as follows:

100 cc. of oil are fractioned very slowly from a three-bulb Ladenburg flask, collecting the first 10 cc. This distillate is then mixed with 10 cc. glacial acetic acid and 10 cc. ethyl nitrite, in a freezing-mixture. 3 cc. 25% hydrocloric acid is now slowly added, and the mixture allowed to crystallize for several hours in the cold. The nitroso-chloride is then filtered off, washed with cold methyl alcohol, and dried. The crystals are now mixed with three times their weight of re-distilled, colorless aniline, and eight times their weight of 95% alcohol, in a small flask, and heated gently on the water-bath. A rather vigorous reaction generally ensues. In the absence of pinene, the solution remains light colored: with pinene, it darkens very noticeably.

After one half-hour, 25 cc. water are added, and steam is passed through the flask. Pinene, if present, distils with a little aniline: the latter is dissolved by addition of a little dilute acetic or hydrochloric acid, and the pinene remains as insoluble light oil, recognizable by its odor.

The limit of sensibility of this method, appears to be at about 10% turpentine in lemon or orange oil. By more careful fractionation of larger amounts of oil, the delicacy of the test could no doubt be increased.

2. *Detection of Chlorine in Benzaldehyde and Oil Bitter Almond.*

The occurrence of *minute* traces of chlorinated compounds in commercial benzaldehyde, can hardly be considered of much importance, but in the case of oil of bitter almond, natural or freed from hydrocyanic acid, the detection of *any* chlorine is *prima facie* evidence of the presence of artificial benzaldehyde Hence, any method of increasing the delicacy and certainty of the test becomes of interest.

We have obtained very satisfactory results by the following modification of the well known combustion process.

A circular filter paper, about four inches in diameter (as free from chlorides as possible), is placed in a suitable funnel, and washed completely chlorine-free with ditsilled water. 25 cc. of this filtrate are set aside as *Blank No. 1.* Fifteen drops of an oil, known to be chlorine-free, are then placed on a small, folded, chlorine-free filter, ignited (as in the U. S. P. method) and covered with the wet filter and funnel. The combustion is regulated by raising or lowering the funnel, as may be necessary.

When all the oil has been burnt, the funnel is inverted, and carefully washed with distilled water until about 25 cc. have run through.

This is *Blank No. 2.* The combustion is then repeated with the sample of oil in question, using the same filter and funnel, which then, on washing, yield 25 cc. of test filtrate. The three filtrates are then treated with five drops of n/10 silver nitrate, and the presence or absence of turbidity or opalescence noted.

By making two blank experiments in this way, a possible accidental contamination with chlorides, would be immediately noticed.

In doubtful cases, we have found that the delicacy of the reaction, is increased by exposing the tubes to direct sunlight, when the presence of a trace of chloride, is shown by a brown coloration. This is evidently due to a "photo-reduction" of the silver chloride by some organic product of combustion.

We have noticed that samples of benzaldehyde which show chlorine by the combustion test, will, also often, give indications of the chlorine *ion* by simple washing with water, and addition of silver nitrate to the clear aqueous extract. For example, a sample, supposed to be the natural oil, freed from hydrocyanic acid, (S. G. 1.0433 at 25°), showed chlorine on combustion, and by the sodium-reduction assay, contained 0.03% Cl.

25 cc. were washed with 25 cc. water; the latter, decanted, and warmed until clear, gave a decided opalescence with a few drop of silver solution.

The washing was repeated until no further chlorine *ion* could be detected, but, by combustion, the oil still showed unmistakable traces of chlorine. It was thought that this water-soluble chlorine, might be due to traces of salt, derived possibly from sodium sulphate, used for drying the oil. This appeared, however, not to be the case, for, on washing the oil with water, and evaporating the latter to dryness, a very slight residue, apparently benzoic acid, was left, in which *no* chlorine *ion* could be detected.

A portion of the same oil, was then shaken with an excess of dilute caustic soda, and carefully distilled with steam. The distilled oil showed chlorine by combustion, but *not* by simple washing. It was allowed to stand for nine months, with an equal volume of water, in a closed bottle, exposed to diffused light. The aqueous solution showed now the presence of chlorine *ions*.

It is evident that the chlorinated derivatives, contaminating benzaldehyde made from benzyl or benzal chloride, undergo a gradual decomposition, with liberation of hydrochloric acid. A similar behavior has been observed with various benzyl ethers and esters, which are not readily obtained free from chlorine.

For the quantitative determination of chlorine, we have employed the sodium-reduction method, in the following form:

10 grams oil are dissolved in 50 cc. absolute alcohol, and 2.5 grams clean sodium added, in small pieces. When the mixture becomes pasty, 25 cc. more alcohol are gradually added. When all the sodium is dissolved 100 cc. water are added, and the mixture evaporated to about 50 cc. A slight excess of *pure* dilute sulphuric acid is run in, the solution chilled, filtered through a wet filter, and the crystalline residue washed free from chlorine. The combined filtrate and washings are now exactly neutralized with n/2 potassium hydroxide, noting the amount used and titrated with n/10 silver nitrate, applying a correction for chlorine in the potassium hydroxide, if necessary.

Examples. Sample A. S. G. 1.0433 @ 25°, 10.046 gms., req. 0.8 cc. $AgNO_3$ (0.03% Cl).
Sample B, S. G. 1.044 10.04 gms. req. 1.22 cc. $AgNO_3$ (0.04%).
Sample C, S. G. 1.043 10.03 gms. req. 0.53 cc. $AgNO_3$ (0.02%).
Sample D, S. G. 1.046 10.50 gms. req. 11.9 cc. $AgNO_3$ (0.39%).
Sample E, (Natural oil, freed from hydrocyanic acid, old). 10.00 gms. req. 0.1 cc. $AgNO_3$ (0.0035%).

This sample contained about 8% benzoic acid; the amount of chlorine found is probably within the limits of error of the method.

3. *Examination of Oil of Lavender.*

The determination of the amount of ester was early suggested as a means of valuation for this oil, though it is evident that linalyl acetate cannot be considered as the only valuable constituent. The method of quantitative saponification, however, gives us, really, only the amount of combined acid, which is assumed to be acetic acid in combination with linalool. Other esters, if present, would give quite erroneous results, and this fact has stimulated the ingenuity of some chemists to provide a variety of synthetic esters, for the express purpose of supplying a fictitious high ester-value to inferior oils. Of these products, the most frequently observed appear to have been glyceryl acetate, or acetin, and terpinyl acetate. The former is especially objectionable by reason of its high saponification value; one percent. of tri-acetin, for example, increases the apparent lialyl acetate content by 2.69%.

Esters of citric, succinic, tartaric, phthalic, salicylic acids, and the mixed esters derived from cocoa-nut oil, have also been found in sophisticated oils, and methods for the detection of some of these have been proposd by Schimmel and Co., and others.

As a rule, these esters are less volatile than lavender oil, and remain as residue, when the oil is redistilled with steam. This test is often useful, and is easily performed.

100 cc. oil are boiled with 150 cc. water in a 250 cc. Ladenburg flask, and the distillate is collected in a "cassia" flask, with the neck graduated for 10 cc. Good oils are readily volatile with this amount of water, and the yield is easily ascertained. The ester-content of the distilled oil should not be more than two percent. lower than that of the original oil, linalyl acetate being not appreciably hydrolyzed under these conditions. The residue can be examined for foreign acids.

For the estimation of acetin, this process is unsatisfactory, acetic acid being found in the distillate, although the greater part remains in the aqueous residue.

We have found that acetin can be determined very conveniently, and with accuracy sufficient for technical purposes, by direct titration in aqueous solution, as follows:

3 grams oil are shaken with 75 cc. water, in a 100 cc. flask. The free acid is then titrated with aqueous n/2 KOH, and phenolphthalein. 0.5 cc. more alkali is added, and the flask is heated at about 80°, with frequent shaking. If the color disappears, another 0.5 cc. is added, and the heating continued, with similar addition of alkali, if necessary, until the solution is permanently alkaline, after one hour's heating. The flask is then cooled, and titrated back with n/2 acid. The alkali used for saponification is calculated over to acetin (1 cc. n/2 KOH = 0.0363 tri-acetin).

Most oils will show a slight amount of water-soluble ester, up to about 0.3%; calculated as acetin, which may be considered as the allowable limit for this method.

No process appears to be available for the determination of terpinyl acetate. Schimmel and Co.'s test (Berichte, Oct., 1911) based on the relatively slow saponification of this ester, seems, however, to be a fairly reliable indication of its presence. In our experience, good oils should not show a difference greater than

0.75% between the ester-values obtained by half hour, and one and one half-hour saponifications.

Fractional distillation with steam, is often of value, the solubility and rotation of the sections being noted. The first 20% fraction should be soluble in three volumes of 70% alcohol; if not, an excess of terpenes is indicated. The rotation will generally increase steadily throughout.

The Specific Gravity of good lavender oil ranges from 0.882 to .892 at 25°, and the rotation from —4° to —7°.

A few examples, from a large number examined, may be of interest.

Sample A. S. G. .8913 @ 25° O. R. —3.20°.
Ester, (½ hour sapon.) 22.90%.
" (1 hour sapon.) 23.10%.
" (1½ hour sapon.) 23.40%.
Distillation test.
10 cc. yielded 9.8 cc., containing 22.1% ester.
Acetin titration, 0.4%.
Fractional distillation:
Section 1. 20%. O. R. — .88°.
2. 20%. O. R. —2.35.
3. 20%. O. R. —2.95.
4. 20%. O. R. —2.95.
5. 15%. O. R. —4.70.

The first section contained about 30% cineol, indicating the presence of oil of spike.

Sample B. S. G. 9893 @ 25° O. R.—5.55°.
Ester, (½ hour sapon.) 28.3%.
Ester, (1½ hour sapon.) 29.9%.
Acetin titration, 0.6%.
Fractions:
1. 20% O. R. —4.80° (insoluble in 70% alcohol).
2. 20% O. R. —5.35.
3. 20% O. R. —6.20.
4. 20% O. R. —6.60.
5. 17% O. R. —6.07.

The saponifications indicate the presence of terpinyl acetate: the insolubility of the first section points to excess of terpenes, probably from some other source.

Sample C. S. G. 0.9094 @ 25° O. R. — 3.30°.
Ester, (½ hour sapon). 29.4%.
Ester, (1½ hour sapon). 30.2%.
Acetin titration, 3.9%.
Distillation test:
10 cc. yielded 9.4 cc., containing 21.2% ester.
Fractions:
1. 20% O. R. —5.15° (insoluble).
2. 20% O. R. —2.43.
3. 20% O. R. —1.91.
4. 20% O. R. —2.64.
5. 15% O. R. —4.75.

The drop in ester, in the distilled oil, and the variation in rotation are significant.

Sample D. S. G. 0.9069 @ 25°, O. R. — 3.96°.
Ester, (½ hour sapon.) 23.6%.
Ester, (1½ hour sapon.) 28.4%.
Acetin titration, 0.4%.
Distillation test:
10 cc. yielded 9.8 cc., containing 26.8% ester.

The high Specific Gravity, and the variation in saponification, are decided indications of the presence of terpinyl acetate.

Laboratory of the Dodge and Olcott Co.