under different conditions, as showing the change in phosphate content through the increase of organic life.

The amount of phosphate and its variation seem to follow the same general line as the other mineral constituents which either accompany the polluting material or are produced by its decay, especially the nitrates and chlorides. It is not, however, so delicate an indicator as these. This correspondence is well shown in the samples in Table IV and also in samples 10 to 12 of Table III, where the increased pollution, as evidenced by the gradual increase in chlorine, is accompanied by increased phosphate.

The results obtained by the colorimetric method would seem to indicate that the limit of 0.5 part of phosphorus pentoxide in a million, as given by Hehner for unpolluted waters, is rather low. A safer amount would be 1.0 part, although the average would doubtless be lower than this.

The highest amount found was 13.3 parts, in sample 19 of Table III. The same rather surprising cases were found as noticed by Hehner in which the amount of phosphate is very much lower than would be expected from the source of the water and the other constituents determined, which may be due to the character of the soil through which the water has percolated. Even with all the drawbacks which are noted there can be no question, in view of the figures given above, that the presence of phosphates in a water in any quantity is significant of pollution, and the determination must be considered as another link (of which we have none too many, anyway) in the chain of circumstantial evidence by which we are often compelled to judge the purity of a water.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., March, 1902.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FIFTH PAPER.)

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 14, 1902.

IN this paper we describe a number of exceptions to the rule that the only halogen compounds which undergo any material conversion into isothiocyanate, by acting on potassium thiocyanate in benzene or alcoholic solutions, are those in which the halogen is in direct combination with a negative group, as in the case of the acyl halides.[1] This rule, until recently, was supposed to be general for all except the allyl halides. The formation of isothiocyanates by the latter had already been ascribed to the negative character of the allyl group.[2]

The view that a strong negative character favors the formation of isothiocyanates appears to be supported by the fact that 2,4-dinitrochlorbenzene gives a normal thiocyanate, $C_6H_3(NO_2)_2SCN$, while 2,4,6-trinitrobenzene gives an isothiocyanate, $C_6H_2(NO_2)_3NCS$.[3]

In the first paper[4] of this series it was shown that certain more or less negative halogen compounds, which were supposed to give isothiocyanates, in reality give nothing but normal thiocyanates. In the second[5] the combined influence of several negative groups together was considered, and it was found that when two hydrogen atoms in methyl bromide were replaced by two phenyl groups another exception to the above rule resulted. Diphenylmethyl bromide was found to give an isothiocyanate. The presence of three phenyl groups, on the other hand, and also of one, two, or three carboxyl groups, did not confer on the substituted methyl halide the property of forming isothiocyanate.

The third paper[6] dealt with dirhodanides, but no isothiocyanates were observed in these cases.

In the fourth[7] a series of tertiary halides were examined and here again no exceptions to the above rule were found.

From these results, especially those in the second paper, it would seem that the tendency to form isothiocyanate is not dependent on, or proportional to, the negative character of the halide, for it would seem probable that triphenylmethyl bromide is a more negative halide than diphenylmethyl bromide, and di- and tricarbethoxymethyl bromide more negative than the latter. This, as already pointed out, is indicated by comparing the affinity-

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[1] Dixon: *J. Chem. Soc.* (London), **75**, 390 (1899).

[2] Michael: *J. prakt. Chem.*, **37**, 509 (1888).

[3] Crocker: *J. Chem. Soc.* (London), **81**, 436 (1902).

[4] This Journal, **23**, 283 (1901).

[5] *Am. Chem. J.*, **26**, 345 (1901).

[6] This Journal, **24**, 439.

[7] *Ibid.*, **24**, 680.

constants of acids that contain these groups. It must be remarked, however, that Vorländer,[1] in his interesting paper "Ueber die Natur der Radicale," calls attention to the fact that this method of deciding negative character can not be relied upon.

The work done in this laboratory has also shown that of the twenty possible halides which can be formed by substituting the three groups, $-CH_3$, $-C_6H_5$, and $-CO_2C_2H_5$, for hydrogen in methyl bromide, only one of these, namely, diphenylmethyl bromide, gives an isothiocyanate. It appears now that this unique behavior is general in the case of those substituted methyl bromides which contain two aromatic radicals.

We have found that phenyl-α-naphthylmethyl and di-α-naphthylmethyl bromides give isothiocyanates. Phenylparatolylmethyl bromide, $C_6H_5CHBrC_6H_4CH_3$, from the carbinol and hydrogen bromide, also gives an isothiocyanate, while, on the other hand, the isomeric halide, parabenzyl-1′-bromtoluene, $C_6H_5CH_2C_6H_4CH_2Br$, forms a normal thiocyanate.

That the rhodanides are isothiocyanates follows from the fact that they react at ordinary temperature with amines yielding thioureas, and also, from their action with thioacetic and thiobenzoic acids, when carbon disulphide is evolved and substituted amides are formed.

The fact that the above bromides react with potassium thiocyanate, and the ease with which the isothiocyanates react with amines (especially β-naphthylamine) to form difficultly soluble ureas, afford an easy test for the position of halogens in the homologues and analogues of diphenylmethane. For example, on brominating *p*-benzyltoluene at 130°-135°, and converting the product into rhodanide, it was easy by means of β-naphthylamine to show that phenylparatolylmethyl bromide had been formed, or in other words, that hydrogen in the CH_2 group had been substituted. According to Senff[2] the corresponding metabenzyltoluene is attacked only in the CH_3 group.

Again, if, as formerly considered, the bromxanthenes, bromdinaphtoxanthene, etc., have the structure represented by Formula I, it might be expected that they would yield isothiocyanates, while

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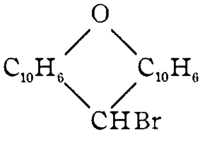
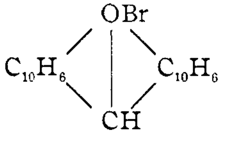
[1] *Ann. Chem.* (Liebig), **320**, 99 (1902).

[2] *Ibid.*, **220**, 240 (1883).

according to the latest representation,[1] II, they probably would not.



I.

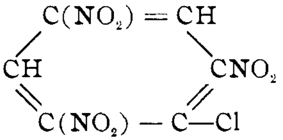


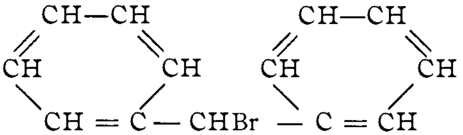
II.

A qualitative test with β-naphthylamine, in fact, after boiling the bromide in chloroform with potassium thiocyanate, failed to give any evidence of the formation of an isothiocyanate.

If the aryl groups are given Kekulé's formula, then the alkyl halides which have thus far been found to give isothiocyanates have one common property. There is either a double bond or at least an unsaturated condition in the 2,3-position:

$$CH_2 = CH - CH_2I,$$





A similar condition, nevertheless, exists in 2,4-dinitrochlorbenzene and in 1'-bromethylbenzene, in brommalonic ester and in the α-halogen acid derivatives, $ClCH_2CO.R$, in general; but none of these halides gives isothiocyanate. This would seem to indicate that a sufficiently negative character as well as an unsaturated condition is required for the formation of isothiocyanates. In how far this idea is applicable and what other influences are at work, cannot be judged from the few data at hand.

EXPERIMENTAL PART.

Phenylparatolylmethylbromide, $C_6H_5CHBrC_6H_4CH_3$.—Phenylparatolyl carbinol was heated to 100° in a stream of dry hydrogen bromide, whereupon water was evolved and the required increase in weight took place. The product, a thin red oil, was then dried in a vacuum at 100° for analysis. A bromine determination gave:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	30.40

This bromide refused to solidify in a freezing-mixture or on

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[1] Werner: *Ber. d. chem. Ges.*, **34**, 3503 (1901); Fosse: *Compt. rend.*, **133**, 101 (1901); **134**, 64 (1902).

standing exposed to the air for over three weeks. No attempt was made to distil the oil since diphenylmethyl bromide is decomposed by this treatment even in a vacuum.

Phenylparatolylmethylisothiocyanate, $C_6H_5CH(NCS)C_6H_4CH_3$, was obtained by heating a benzene solution of the bromide with potassium thiocyanate for two days. The product was a thin reddish colored oil, the vapor of which, especially when warmed, had an irritating action on the eyes. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}NS$.	Found.
Nitrogen	5.85	5.72

Phenylparatolylmethylacetamide, $C_6H_5(CH_3C_6H_4)CHNHCOCH_3$.—Two grams of the isothiocyanate, 1.5 grams of thioacetic acid and 2 volumes of benzene were heated somewhat over two hours on the steam-bath. On evaporating the benzene, carbon disulphide was found in quantity, and the residue taken up in ether, washed with alkali and water, gave colorless, flat, rectangular prisms, on evaporating the solvent. This amide is soluble in hot water but on cooling it separates as an oil. For analysis it was crystallized from ether, whereupon it melted at 129.5°-131°, and a nitrogen determination of the sulphur-free material gave:

	Calculated for $C_{16}H_{17}ON$.	Found.
Nitrogen	5.85	6.12

Phenylparatolylmethylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNH_2$, was obtained by dissolving the isothiocyanate in alcoholic ammonia. It separated from alcohol in clusters or balls of colorless needles which melted at 162°-163° and gave the following result on analysis:

	Calculated for $C_{15}H_{16}N_2S$.	Found.
Nitrogen	10.93	11.13

Phenylparatolylmethylphenylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_6H_5$.—The isothiocyanate reacted immediately with aniline. The product formed colorless, flat prisms from alcohol, which melted at 159°. A nitrogen determination gave:

	Calculated for $C_{21}H_{20}N_2S$.	Found.
Nitrogen	8.4	8.5

Phenylparatolylmethyl-β-naphthylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_{10}H_7$, forms as a precipitate when alcoholic solutions of the rhodanide and β-naphthylamine are mixed. It crystallizes from alcohol in bunches of slender, colorless needles melting at 170°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.73	7.70

The Bromination of Parabenzyltoluene.—The hydrocarbon was brominated at 130°-135° and the product was distilled at 11 mm. pressure, whereupon it boiled quite constantly at 179°-180°. It formed a heavy, pale yellow oil. The amount of replaceable bromine was determined by means of sodium ethylate:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	27.74

The brominated material was heated with potassium thiocyanate in benzene solution for two days. An oil was thus obtained which responded to the reduction test for a normal thiocyanate. A nitrogen determination gave 5.18 per cent. nitrogen instead of 5.85 per cent. An alcoholic solution was allowed to stand with β-naphthylamine, and one with ammonia. In both cases a small amount of crystals was obtained which were identical with the corresponding ureas described above from phenylparatolylisothiocyanate prepared from the carbinol. This shows that on brominating benzyltoluene a portion of the bromine enters the CH_2 group.

Phenyl-α-naphthylmethylbromide, $C_6H_5(C_{10}H_7)CHBr$.—Miquel[1] obtained this bromide by brominating α-benzylnaphthalene, either hot or cold or in carbon disulphide solution. He found that it was a syrup. Our material was prepared by brominating the hydrocarbon at 140°-150°, under the same conditions as the crystalline diphenylmethyl bromide is obtained.[2] The product formed a dark red oil which was dried over potash for analysis. The amount of replaceable bromine was then determined by warming a sample with sodium ethylate:

	Calculated for $C_{17}H_{13}Br$.	Found.
Bromine	26.9	24.6

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[1] *Bull. Soc. Chim.* [2], **26**, 4 (1876).

[2] Friedel, Balsohn: *Bull. Soc. Chim.*, **33**, 339.

Phenyl-α-naphthylmethylisothiocyanate, $C_6H_5(C_{10}H_7)CHNCS$.—A benzene solution of the bromide was heated for forty-eight hours with potassium thiocyanate. On filtering and evaporating the benzene a thick red oil was obtained which deposited nothing solid on cooling. An attempt to purify a portion by distilling under reduced pressure resulted in complete decomposition of the material, some naphthylphenylmethane being obtained. A portion was treated with alcohol and sodium, whereupon it was found that sodium cyanide and thiocyanate were formed. This indicates the presence of normal thiocyanate. The crude oil was dried in a vacuum for analysis and a nitrogen determination then gave:

	Calculated for $C_{18}H_{13}NS$.	Found.
Nitrogen	5.09	4.27

When a portion of this oil was allowed to stand for about six months it solidified. It then formed small plates, from petroleum ether, melting at 76°-77°.

Phenyl-α-naphthylmethylacetamide, $C_6H_5(C_{10}H_7)CHNHCOCH_3$.—Ten grams of the crude isothiocyanate, in benzene solution, were mixed with 2.8 grams of thioacetic acid and heated upon the steam-bath for three hours. Carbon disulphide was evolved and the acetamide separated on cooling the solution. When crystallized from toluene and some alcohol, small needles were obtained which melted at about 210°. A nitrogen determination gave:

	Calculated for $C_{19}H_{17}ON$.	Found.
Nitrogen	5.09	5.23

Phenyl-α-naphthylmethylbenzamide, $C_6H_5(C_{10}H_7)CHNHCOC_6H_5$.—Ten grams of the rhodanide were heated for an hour with the calculated amount of thiobenzoic acid. On evaporating the benzene, carbon disulphide was found in quantity by the xanthate test. The benzamide was crystallized from alcohol; it then melted at 158° and a nitrogen determination in the sulphur-free material gave:

	Calculated for $C_{24}H_{19}ON$.	Found.
Nitrogen	4.15	4.11

Phenyl-α naphthylmethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNH_2$.—A solution of the isothiocyanate in alcoholic ammonia was obtained and in a half hour, radiating masses of flat rectangular prisms separated. They were crystallized from alcohol and melted at 197°-198°. A nitrogen determination gave:

	Calculated for $C_{18}H_{16}N_2S$.	Found.
Nitrogen	9.58	9.59

This thiourea is insoluble in water and very difficultly soluble in 20 per cent. sodium hydroxide.

Phenyl-α-naphthylmethylmethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHCH_3$.—Three grams of the isothiocyanate were dissolved in alcohol and an excess of a 33 per cent. solution of methylamine was added. After standing some time small prisms arranged in clusters separated. They were crystallized from alcohol and melted at 175°-176°. A nitrogen determination gave:

	Calculated for $C_{19}H_{18}N_2S$.	Found.
Nitrogen	9.1	8.8

Phenyl-α-naphthylmethyldiethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_2H_5)_2$, from the isothiocyanate and diethylamine, formed clusters of flat prisms or a sandy powder. It melted at 112°-113° and a nitrogen determination gave:

	Calculated for $C_{22}H_{24}N_2S$.	Found.
Nitrogen	8.04	8.00

Phenyl-α-naphthylmethyldiisobutylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_4H_9)_2$, formed clusters of slender radiating crystals from alcohol melting at 142°-143°. A nitrogen determination gave:

	Calculated for $C_{26}H_{32}N_2S$.	Found.
Nitrogen	6.93	7.22

Phenyl-α-naphthylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_5$, formed a difficultly soluble precipitate when the constituents were mixed in benzene. It was crystallized from a mixture of toluene and ethyl benzoate, whereupon colorless prisms melting at 185° were obtained. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}N_2S$.	Found.
Nitrogen	7.60	7.64

Phenyl-α-naphthylmethylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(CH_3)C_6H_5$, formed a fine, white crystalline powder which, on crystallizing from toluene, melted at 182°-183°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.32	7.35

Phenyl-α-naphthylmethylmetachlorphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4Cl$, formed colorless, needle-like prisms from alcohol, melting at 172°-173°. A nitrogen determination gave:

	Calculated for $C_{24}H_{19}N_2ClS$.	Found.
Nitrogen	6.95	6.93

Phenyl-α-naphthylmethylmetanitrophenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4NO_2$, was difficultly soluble in alcohol from which it crystallized in the form of light yellow prisms. It melted at 191°, and a nitrogen determination gave:

	Calculated for $C_{24}H_{19}O_2N_3S$.	Found.
Nitrogen	10.17	10.10

Phenyl-α-naphthylmethyl-β-naphthylthiourea, $C_6H_5(C_{10}H_7)CH{-}NHCSNHC_{10}H_7$, gave colorless needles from toluene melting at 195°. A nitrogen determination gave:

	Calculated for $C_{28}H_{22}N_2S$.	Found.
Nitrogen	6.69	6.52

Phenyl-α-naphthylmethylphenylthiosemicarbazide was obtained from the isothiocyanate and phenylhydrazine in an alcoholic solution. Thus obtained, it melted at about 154°, solidified, and melted then at 174°-175°, with decomposition and effervescence. A recrystallization from alcohol gave needles which melted at 178°-179°. Evidently we have to deal here with a molecular rearrangement similar to that observed by Busch and Holzmann:[1]

$$C_6H_5(C_{10}H_7)CHNHCS(C_6H_5)N{-}NH_2 \longrightarrow$$

Melting-point 154°.

$$C_6H_5(C_{10}H_7)CHNHCSNH{-}NHC_6H_5.$$

Melting-point 178°-179°.

An analysis of the material crystallized from alcohol gave:

	Calculated for $C_{24}H_{21}N_3S$.	Found.
Nitrogen	11.32	11.30

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[1] *Ber. d. chem. Ges.*, **34**, 320 (1901).

Di-α-naphthylmethane, $(C_{10}H_7)_2CH_2$.—The onlymethod given in Beilstein's "Handbuch" for the preparation of this hydrocarbon is that of Grabowski.[1] This method, according to our experience, gives a very poor yield (4 to 6 per cent.). By far the largest portion of the naphthalene in this process is converted into a difficultly soluble substance, the nature of which we did not stop to determine.

By means of the following method we have obtained yields over twice as great as by the above and with much less trouble.

Twenty-three grams of chlormethylacetate, CH_3COOCH_2Cl, 60 grams of naphthalene and 15 grams of fused zinc chloride (powdered) were mixed and heated on the steam-bath until the evolution of hydrogen chloride practically ceased. This required about three hours. The product was then washed with water, taken up with ether, and dried over calcium chloride. The ether was removed and all that came over below 300° was discarded. From this point the distillation was carried on as long as possible. The product above 300° was then distilled at 14 mm. pressure, whereupon most of the material boiled at 270°-272°. It had a strong blue fluorescence by reflected light and on standing a few hours it solidified. On crystallizing from alcohol 7 grams of the hydrocarbon were obtained melting at 99°-100°.

Di-α-naphthylmethylbromide, $(C_{10}H_7)_2CHBr$, was prepared from the hydrocarbon, obtained by both of the above methods, by brominating at 135°-145°. The bromide crystallized from benzene in needle-like prisms which melted at 181°-182°. It was very soluble in chloroform and sparingly soluble in ligroïn. A bromine determination gave:

	Calculated for $C_{21}H_{15}Br$.	Found.
Bromine	23.0	22.9

Di-α-naphthylmethylisothiocyanate, $(C_{10}H_7)_2CHNCS$. — The bromide was boiled in benzene with potassium thiocyanate for three days. The product, an oil, solidified on standing. It was then crystallized from alcohol and obtained in the form of colorless rectangular prisms, which melted at 124°-125°. A nitrogen determination gave:

	Calculated for $C_{22}H_{15}NS$.	Found.
Nitrogen	4.30	4.30

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[1] *Ber. d. chem. Ges.*, 7, 1605.

Di-α-naphthylmethylphenylthiourea, $(C_{10}H_7)_2CH—NHCSNHC_6H_5$, from the above rhodanide and aniline, when crystallized from ethyl benzoate, gave colorless needles melting at 225°-226°. It was only sparingly soluble in toluene and amyl acetate. A nitrogen determination gave:

	Calculated for $C_{28}H_{22}N_2S$.	Found.
Nitrogen..........................	6.69	6.53

Di-α-naphthylmethylmethylphenylthiourea, $(C_{10}H_7)_2CH—NHCSN(CH_3)C_6H_5$, from the isothiocyanate and methyl aniline, crystallized from toluene in fine colorless needles melting at 210°-211°. A nitrogen determination gave:

	Calculated for $C_{29}H_{24}N_2S$.	Found.
Nitrogen...	6.48	6.59

Di-α-naphthylmethyl-β-naphthylthiourea, $(C_{10}H_7)_2CH—NHCSNHC_{10}H_7$, separated in balls of needles from the alcoholic solution of its constituents. It crystallized from amyl acetate and melted at 218°-219°. A nitrogen determination gave:

	Calculated for $C_{32}H_{24}N_2S$.	Found.
Nitrogen..........................	5.98	6.11

The following rhodanides were examined in order to complete the list of twenty compounds mentioned in the introduction.

1'-Thiocyanethylbenzene and Thioacetic Acid.—This thiocyanate, which may be viewed as methylphenylmethyl rhodanide, $CH_3(C_6H_5)CHSCN$, reacted smoothly with thioacetic acid and the product crystallized from alcohol, in which it was very soluble, in slender yellow prisms. It melted at 99°-100° and was soluble in alkali from which solutions acids precipitated the material unaltered. These properties and the following nitrogen determination show that this substance is an acetyldithiourethane, namely, $CH_3CONHCS.SCH(CH_3)C_6H_5$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen..........................	5.85	6.16

Isopropyl Thiocyanate and Thiobenzoic Acid.—Four grams of isopropyl thiocyanate and 5.4 grams of the acid were dissolved in 2 volumes of benzene and heated several hours on the steam-bath. On cooling, brilliant yellow plates separated. They were recrystallized from alcohol and melted at 74°-75°. The material was soluble in alkali and was reprecipitated unaltered by acids. A nitrogen determination agreed with the calculated for *benzoyldithioisopropyl carbamate,* $C_6H_5CONHCS.SC_3H_7$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	6.11	6.08

These latter rhodanides are therefore both normal thiocyanates.

NEW HAVEN, CONN.,
April 12, 1902

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY U. S. DEPARTMENT OF AGRICULTURE, NO. 45. SENT BY H. W. WILEY.]

REFRACTIVE INDICES OF SALAD OILS—CORRECTION FOR TEMPERATURE.

BY L. M. TOLMAN AND L. S. MUNSON.

Received April 28, 1902.

IT IS almost always difficult to obtain exactly a definite temperature at which to make readings of refractive indices. A method and factor for making exact correction for this variation and also for making possible recalculations of determinations made at different temperatures is desirable.

Two factors are ordinarily used in this country to make this correction. One, 0.000176[1] for 1° C. for instruments reading index of refraction directly, and 0.55 scale division for 1° C. for the Zeiss butyrorefractometer, which has an empirical scale. As will be seen later, the former is considerably too small, and the latter was determined for butter-fat and is not correct for oils which have higher refractive indices.

As the butyrorefractometer is very largely used in this country, special attention should be called to a satisfactory method for correcting its readings for temperature. It must be remembered, however, that this discussion is limited to oils, and to the very limited number of oils given in Table III. Other substances and oils vary, and require different corrections for temperature. This instrument on account of its simplicity, ease of manipulation, and water jacket has acquired a very wide use but its empirical scale with division of varying value in refractive indices makes correction for temperature difficult and not exact unless, as is shown

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[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 354.