FOOD ANALYSIS

TYPICAL METHODS
AND
THE INTERPRETATION OF RESULTS

BY

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PREFACE TO THE THIRD EDITION

In this edition there has been practically no change in the plan of the book and no attempt to make it more comprehensive by the inclusion of more topics. Some of the methods have been changed to conform to the advances initiated by the referees of the Association of Official Agricultural Chemists and detailed in the *Journal* of the Association.

As in the second edition, the portions of the book relating specifically to alcoholic beverages have purposely been left untouched.

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CAMBRIDGE, MASS.
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PREFACE TO THE FIRST EDITION

This book has grown out of the courses given to the author's students in food analysis during the last few years. Experience with these classes, which have used as textbooks mainly Leach's "Food Analysis" and *Bulletin* 107 of the Bureau of Chemistry, has shown the need of a book which should cover distinctly less ground than either of these, but should give to the student a more detailed discussion of the analytical processes involved, their suitability and limitations. Further, an attempt has been made to lay greater emphasis on the interpretation of the analytical results. To the author's mind the principal asset to be gained by the student from any detailed consideration of the methods employed to detect adulteration in foods is the exercise of judgment and the training of the sense of discrimination, which is derived from a critical balancing of the data obtained in a food analysis. Substances are being examined which are usually capable of wide natural variations in composition, and an exceptional opportunity is afforded for a critical study of the analytical factors in order to determine whether or not they imply artificial manipulation of the product.

Because the primary intention has been to write a book of the character outlined no effort has been made to include a great variety of food materials, nor necessarily those of greatest economic importance or which are most widely used. Certain typical foods have been selected to illustrate important methods of attack or characteristic methods of food analysis. In a word, the book has been written and the material selected primarily for the undergraduate student of analytical chemistry rather than for the practicing chemist.

The fact that certain typical foods have been selected should not be considered as implying any intention to limit the student to the particular examples cited. Other products, similar in general character to those discussed, involving the same or different forms of adulteration, will readily suggest themselves. These

may be purchased, or sometimes more conveniently be prepared in the laboratory, and given to the student for analysis and intelligent interpretation.

Three of the most important groups of foods, fats and oils, carbohydrate foods, and alcoholic beverages, have been treated at some length, general methods common to the group being taken up first in each case, followed by a more detailed discussion of several typical examples. The detection and identification of artificial colors has been treated perhaps more fully than is warranted by the actual importance of the subject because this part of the work frequently causes the student some difficulty, and adequate discussions of it are hard to find. Moreover, it affords excellent training in the detection of minute quantities of material through a systematic procedure.

The standard texts on food analysis and related subjects have been freely consulted, especially those of Leach, Browne and Sherman, as well as Allen's "Commercial Organic Analysis," and much valuable material selected. Particularly helpful have been found the publications of the Bureau of Chemistry, especially the bulletins comprising the annual proceedings of the Association of Official Agricultural Chemists, these furnishing access to the best of present American work in food analysis. For these reasons the methods chosen follow most closely typical American practice, although an earnest endeavor has been made not to slight the work of European food chemists.

Acknowledgment is gratefully made to the author's many friends who have aided by encouragement and advice, and especially to Mr. G. W. Rolfe and Mr. A. L. Sullivan, who have read the chapters on Carbohydrate Foods and Alcoholic Beverages, respectively, and made many valuable suggestions.

A. G. WOODMAN.

BOSTON, MASS.
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FOOD ANALYSIS

CHAPTER I

GENERAL METHODS

Preparation of the Sample.—The material will often be in proper condition for analysis as received. The main points to be considered are whether the portion to be examined is of uniform composition and whether it is finely divided. Usually the first condition may be brought about by thorough mixing and sampling of the material; for the latter it may be ground in an ordinary food chopper or pulverized in a coffee or drug mill, or if small the sample may be ground in an ordinary porcelain mortar.

Specific Gravity.—In food analysis this determination has reference almost invariably to liquids. Where only a fair degree of accuracy is desired the determination can be made conveniently and quickly by means of the Westphal balance. In principle this device is based upon the well-known law of physics that a body immersed in a liquid is buoyed up by a force equal to the weight of liquid displaced. The apparatus, shown in Fig. 1, consists of a beam balanced on a knife edge X and having a plummet or sinker Y suspended from one end and counterpoised by a fixed brass weight Z at the other. The distance between X and the point of support W is divided by notches into 10 equal parts. The sinker, which is made of glass and provided with a thermometer, is made of such a size that it will displace exactly 5 grams of water at 15°C. or 15.5°C. The plummet and the

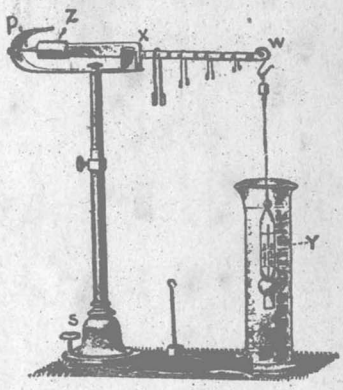

FIG. 1.—Westphal balance.

hook from which it is suspended are made of a definite weight, usually 15 grams, so that they are interchangeable in different instruments.

In using the balance it is first adjusted by means of the leveling screw *S* until the pointer *P* on the arm is exactly opposite the reference point. If now the sinker be entirely immersed in distilled water at the standard temperature, it will require a weight of 5 grams at *W* to make it balance again. For liquids heavier than water a greater weight will be needed and for liquids lighter than water one correspondingly less. For reading the decimals of a unit of specific gravity, use is made of the notched divisions on the beam. Thus if the 5-gram weight placed directly over the plummet shows a specific gravity of 1.0000, the same weight placed 0.3 of the distance on the beam would correspond to a gravity of 0.3000. The second decimal is obtained by means of a 0.5-gram weight, the third by a 0.05-gram weight and the fourth by a 0.005-gram weight. Typical examples of the method of reading the instrument are shown in Fig. 2.

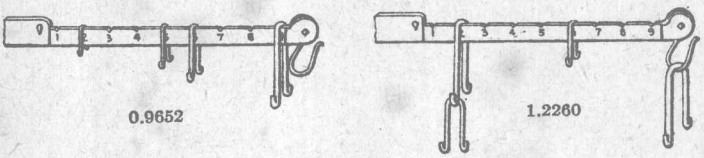

FIG. 2.—Reading the Westphal balance.

For more exact determinations of specific gravity some form of pyknometer should be used. Reduced to its lowest terms this apparatus consists of a light container for weighing equal volumes of liquids measured accurately at a definite temperature. Two common forms are the Sprengel-Ostwald tube (Fig. 3) and the specific gravity bottle (Fig. 4).

The Sprengel Tube.—This is especially useful when only a small amount of liquid is available for the determination; or when the determination is to be made at a temperature quite different from room temperature. The best form is the one suggested by Ostwald and shown in the figure, one arm being a capillary tube while the other holds the bulk of the liquid. In using it the end *B* should be dipped into the liquid, which has been cooled to several degrees below the desired temperature, and the

tube filled by applying suction through a rubber tube attached to the tip *A*. The pyknometer is then suspended in a narrow beaker filled with water at the desired temperature and when its contents have attained this temperature, as shown by the meniscus in the capillary remaining stationary, by touching the tip *A* with the edge of a filter paper the meniscus can be brought to the reference mark *C*. The pyknometer is then carefully wiped dry, suspended from the hook over the balance pan and weighed. It is necessary also to calibrate the pyknometer, which is done by weighing it empty and dry, then weighing it filled with recently boiled distilled water in the manner just described.

The Specific Gravity Bottle.—These can be procured of various sizes, most conveniently of 25- or 50-cc. capacity, provided with a thermometer stopper as shown, extending to 40°C. One should be chosen with as large a cap to the side tube as possible and it is best to have a very small hole drilled or blown in the extremity of the cap so that the liquid may expand into the cap during the weighing without forcing it up and causing leakage. The thermometers are not always accurate and for careful work should be tested by comparison with one of known accuracy.

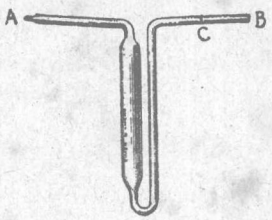

FIG. 3.—Sprengel-Ostwald tube.

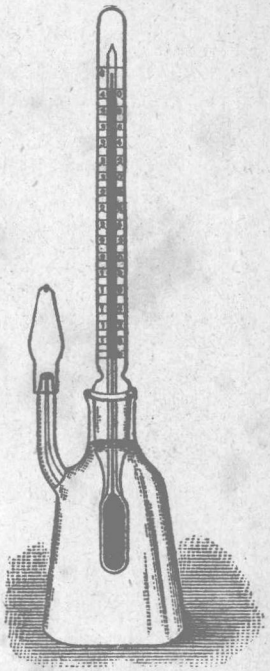

FIG. 4.—Specific gravity bottle—Geissler form.

Calibration of the Pyknometer.—This is done by weighing the pyknometer empty and dry and then filling it with recently boiled distilled water at a temperature one or two degrees below that at which the determination is to be made. The pyknometer should

be filled nearly full with the water so that when the thermometer is inserted the water shall overflow through the capillary. The bottle is then placed in a bath of water kept at the desired temperature, and as soon as its contents have reached that temperature, as shown by the thermometer, the excess of water is carefully wiped from the tip of the capillary, the cap placed on, and the bottle wiped dry and weighed. Subtracting the weight of the pyknometer gives the water content of the bottle at the temperature used, which is most conveniently 20°C., although 15.6°C. is often employed. The determination should be repeated and the mean of two closely agreeing values recorded for use.

To determine the specific gravity of a liquid, the pyknometer thus calibrated is rinsed several times with the liquid with which it is to be filled, or it may be rinsed with alcohol and then with ether and dried in an oven at 100°C. (If this is done care should be taken that the thermometer is not put into the oven also, since this, registering to only 40°, will be broken.) The pyknometer is then filled with the liquid, using the same precautions as regards temperature as with distilled water, and weighed. The weight of the liquid contained, divided by the water content, is the specific gravity.

In stating the specific gravity of a liquid it is advisable to record the temperature at which the determination was made, as well as the temperature of the water with which it is compared. This is done in the form of a fraction thus, $\frac{20°}{20°}$, meaning the specific gravity at 20°C. referred to water at 20°C.

In order to determine the specific gravity at a given temperature $t°$, referred to water at its maximum density 4°C., the value determined at $\frac{t°}{t°}$ should be multiplied by the density of water at $t°$, taken from Table 1, page 6.

Thus the value for $\frac{20°}{20°}$ must be multiplied by 0.998234 to obtain the value at $\frac{20°}{4°}$.

Index of Refraction.—When a beam of light passes obliquely from one medium to another of different optical density it is bent

out of its course or *refracted.* For two given media the amount of this refraction is a constant for any definite temperature and can be stated mathematically by the expression $\frac{\sin i}{\sin r} = n$, where i is the *angle of incidence* made by the incident ray with the perpendicular to the dividing surface and r is the *angle of refraction* made by the refracted ray with the perpendicular; n is called the index of refraction. For example, in Fig. 5 let AB be the surface of separation between two media, of which the upper is the rarer, and let a beam of light pass through in the direction RO. The angle RON, which the incident ray makes with the perpendicular, is the angle of incidence; and the angle ION' made by

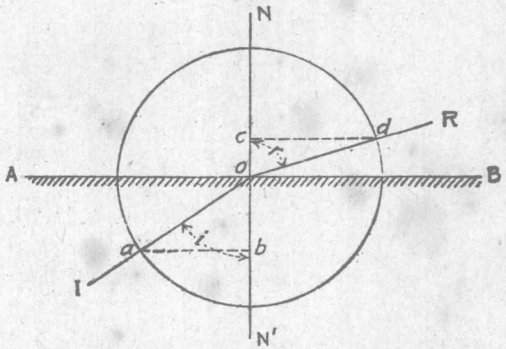

FIG. 5.—Illustrating the law of refraction.

the refracted ray with the perpendicular is the angle of refraction. The index of refraction would be represented in the figure by the ratio $\frac{cd}{ab}$.

Ordinarily the index of refraction of a substance is taken as the ratio of the angles formed when light passes from *air* to the substance and is referred to the *D*-ray of the spectrum as the standard wave length of light, so that for a temperature of 20°C. n would be written $n_D{}^{20}$.

The Critical Angle and Total Reflection.—Referring again to Fig. 5 it will be seen that if the light pass in the opposite direction, from the denser to the rarer medium, the angle of refraction RON will be greater than the angle of incidence ION'. If the

TABLE 1.—DENSITY OF PURE WATER FREE FROM AIR

(Under standard pressure, 76 cm., at every tenth part of a degree of the international hydrogen scale from 0° to 40°C., in grams per milliliter*)

Degrees Centigrades	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
0	0.999 868	874	881	887	893	899	905	910	916	921
1	926	931	936	940	945	949	953	957	961	964
2	967	971	974	976	979	982	984	986	988	990
3	992	993	995	996	997	998	998	999	999	†000
4	1.000 000	†999	†999	†999	†998	†997	†997	†996	†994	†993
5	0.999 991	990	988	986	984	981	979	976	974	971
6	968	965	961	958	954	950	946	942	938	934
7	929	924	920	915	910	904	899	893	888	882
8	876	870	864	857	851	844	837	830	823	816
9	809	801	794	786	778	770	762	753	745	736
10	728	719	710	701	692	682	672	663	653	643
11	633	622	612	602	591	580	569	558	547	536
12	524	513	501	489	478	466	453	441	429	416
13	404	391	378	365	352	339	325	312	298	285
14	271	257	243	228	214	200	185	171	156	141
15	126	111	096	080	065	049	034	018	002	986
16	0.998 970	954	937	921	904	888	871	854	837	820
17	802	785	768	750	732	715	697	679	661	642
18	624	605	587	568	549	530	511	492	473	454
19	434	415	395	375	355	335	315	295	275	254
20	234	213	193	172	151	130	109	087	066	044
21	023	001	†979	†958	†935	†913	†891	†869	†847	†824
22	0.997 801	779	756	733	710	687	664	640	617	593
23	570	546	522	498	474	450	426	402	377	353
24	328	303	279	254	229	204	178	153	128	102
25	077	051	025	†999	†973	†947	†921	†895	†868	†842
26	0.996 815	789	762	735	708	681	654	627	600	572
27	545	517	489	462	434	406	378	350	321	293
28	265	236	208	179	150	121	092	063	034	005
29	0.995 976	946	917	887	857	828	798	768	738	708
30	678	647	617	586	556	525	495	464	433	402
31	371	340	308	277	246	214	183	151	119	088
32	056	024	†992	†959	†927	†895	†863	†830	†797	†765
33	0.994 732	699	666	633	600	567	534	501	467	434
34	400	367	333	299	265	231	197	163	129	095
35	061	026	†992	†957	†923	†888	†853	†818	†783	†748
36	0.993 713	678	643	607	572	536	501	465	430	394
37	358	322	286	250	214	178	141	105	069	032
38	0.992 996	959	922	885	849	812	775	738	700	663
39	626	589	551	514	476	438	401	363	325	287
40	249	211	173	135	097	058	020	†981	†943	†904

* According to P. Chappuis, Bureau international des Poids et Mésures, *Travaux et Mémoires*, XIII, **1907.**

† The dagger indicates a diminution of one in the third-place decimal.

angle of incidence be increased, then, at a certain angle of incidence, the angle of refraction will become 90°, *i.e.*, the refracted ray will coincide with the dividing surface. For incident rays striking the surface at a greater angle than this, the beam of light will be *totally reflected* and there will be no refracted ray. The angle of incidence at which this occurs is known as the *critical angle.*

Then since

$$n = \frac{\sin i}{\sin r},$$

at the critical angle

$$n = \frac{\sin i}{\sin 90°} = \frac{\sin i}{1} = \sin i.$$

That is, in passing from a denser to a rarer medium, the index of refraction is equal to the sine of the angle of incidence for the border line of total reflection.

The forms of refractometer most commonly employed in food analysis are based upon this principle of measuring the angle of incidence for total reflection.

Abbe Refractometer.—In this instrument the refractive index of a liquid is determined by measuring the critical angle for light passing into it from a glass prism of higher refractive index. The sine of this angle is the index of refraction of the liquid referred to glass and this, multiplied by the refractive index of the glass, gives the index of refraction of the liquid, referred to air.

The apparatus (Fig. 6) consists essentially of three parts:

a. Two prisms *A* and *B* of flint glass, having a refractive index of 1.75, mounted so that they can be separated and a few drops of the liquid to be examined placed between, forming a thin layer when the prisms are joined again. The prisms can be rotated by means of a movable arm or alidade *C* which carries the reading magnifier *M*.

b. A telescope *T* provided with cross-hairs by which the position of the border line of total reflection can be observed.

c. The sector *S* divided proportionally to the sines of the various angles of incidence for the border line of total reflection, and therefore representing indices of refraction.

An important part of the apparatus is the compensator, placed in the tube of the telescope at *P* and composed of two similar