

the solution is much more dilute than the one proposed, still twenty minutes is ample time to completely oxidize the glycerin.

We tried checking our results by means of the specific gravity method and found that it may be feasible with certain cautions. First, there seems to be a surprising lack of complete glycerin specific gravity tables, and in those we have, there is a question concerning the accuracy of the expansion factor for dilute solution. On the other hand, if concentrated glycerin solutions are used, temperature becomes very important, an error of 0.1° in reading causing an error of nearly 0.15 *per cent.* in the amount of glycerin. But using a solution of from 60 to 80 *per cent.* glycerin and being very careful in reading the temperature a reasonably accurate check may be obtained for the oxidation method.

The following results give a fair comparison of the two methods, showing how they may be used as comparative methods.

SPECIFIC GRAVITY METHOD.				
WATER	COMMERCIAL GLYCERIN	TEMPERATURE	CORRECTED SP. GR.	PERCENT OF GLYCERIN
14.8920 gms.	23.7315 gms.	80° F.	1.1526	95.08
20.1857 gms.	19.2522 gms.	82° F.	1.1194	95.14
20.0300 gms.	10.2064 gms.	82.7° F.	1.0809	95.02
.....	31.113 gms.	85.1° F.	1.2537	95.20
Average.....				95.11

DICHROMATE METHOD.		
N/10 THIO. CORRECTED	N/10 DICHROMATE	PERCENT OF GLYCERIN
19.58 cc.	49.40 cc.	95.36
19.56 cc.	49.40 cc.	95.39
19.60+ cc.	49.40 cc.	95.23
19.53 cc.	49.40 cc.	95.49
Average		95.37%

DISCUSSION.

MR. VORISK:—I would like to ask the second speaker about the titration of that liquid after the oxidation has taken place,—What indicator is used?

MR. BRADT:—Simply use potassium iodide and the iodine liberated is titrated with thiosulphate, using starch as indicator. The color changes from blue to green.

THE NECESSITY OF A METHOD OF ESTIMATING THE INTRINSIC VALUE OR ESSENTIAL QUALITIES OF COFFEE.

L. E. SAYRE.



It has always seemed to the writer that the references in formularies, such as our National Formulary, in specifying the commercial or geographical brand of coffee, are made with a definiteness which is rather superfluous. To say, for example, that a coffee must come from Java and Mocha is a rather excessive discrimination. This will appear when it is shown that there are other brands than Java and Mocha (usually specified) which will give to coffee preparations equally fine flavor peculiar to the roasted berry. It is true that Mocha and Java coffees have a fine flavor widely esteemed, but Santos coffees for example, are immensely popular among American consumers and are

said to be fast supplanting the milder growths of other countries, the finer grades being invariably smooth and pleasing in liquor and flavor, possessing all the essentials of fine coffee. In point of quantity, it is stated by coffee dealers that Brazil heads the list of coffee producing countries, its annual product ranging from 7,000,000 bags to 8,000,000 bags of 130 pounds each, 75 *per cent.* of which is exported to the United States.

To give some idea of the brands or grades of coffee which are distributed in the Middle West, we give the following tabulated statement of one of the largest coffee distributors in that section.

PRINCIPAL BRANDS AND VARIETIES OF COFFEES SOLD IN WESTERN MARKET.

<i>Commercial Classification.</i>	<i>Variety or Grades.</i>
Mandheling	33
Java	24
Mocha	Many
Buckaramanga	20
Bogota	20
Maracaibo	20
Guatemala	20
African Java	10
Peaberry from Mexican Rio and Santos	Number almost indefinite
Santos, Bourbon	Number almost indefinite
Rio	Many grades
Victoria	5

Botanically speaking, the genus known as *Coffea* is divided by botanists into some sixty species, of which fifteen are referred to Africa, seven to Asia and about twenty-two to America; but there is abundant reason for supposing that the majority of these so-called species are but mere varieties, a single genus, due to different conditions of soil, climate and cultivation.

According to some botanists, there is but one genus and species of the coffee plant, *Coffea Arabica*. Others again contend that there are two separate and distinct species, classed as *Coffea Orientalis* and *Coffea Occidentalis*. While admitting but one genus, the difference in size, appearance and product being attributed by them to a variation in the soil, climate, and method of cultivation. There are three principal varieties, however, readily distinguished and recognized by those who have much to do with it and are known to commerce as *Coffea Arabica*, *Coffea Liberica* and *Coffea Maragogipe*, lately discovered in Brazil, all of which, or their transplants, furnish the coffee of the market.*

It happens to fall to the lot of the Drug Laboratory of the University of Kansas, to examine, for the state, samples of coffees sent in by inspectors. No attempt is made to report on the quality, such as flavor, or commercial value, because of the entire absence of reliable tests, such as would stand in the courts, but enough experience has been gained to make the statement that there are a great number of brands and blends which furnish as fine a flavored preparation as that of Java and Mocha. For example, we have received during the past year an invoice from the Jamaica coffees which are grown in the upland and those which are grown in the lowland. Those from the upland, when properly roasted

* Coffee, Its History, Classification and Description: Walsh, page 37.

are of as elegant a flavor as that from Java or Mocha. The same may be said of the best brands of Santos coffee. Theoretically, therefore, it is unnecessary to confine, for pharmaceutical purposes, coffees to those of the definite geographical origin usually stated.

The quality of coffee, i. e., the "æsthetic" quality, which we find in the flavor or aroma, is not due to the caffeine or the caffeeo-tannic acid content, and, indeed, to no one of the principles which are usually included in the so-called official analyses.

Most any one who is familiar with the different brands of coffee acknowledge that Mocha and Java have very agreeable and "fine" flavors as above stated, but an analyst would be brave who would go before the courts and attempt to prove that they were worthy of this distinction, from the results of the "cup test," for example. That is to say, there is no scientific data which may be regarded worthy of the attribute "accuracy" which can be offered as evidence or proof of relative qualities,—"good," "better," "best," or "poor," "fair" or "fine."

Those who have followed the literature upon this subject no doubt are familiar with the fact that the so-called aromatic or æsthetic properties were contained in the volatile principles which may be recovered by sublimation or distillation.

One report upon this, made some years ago (Merck's Report, 1907, page 61), stated as follows regarding a sublimation test: Operating upon 500 grams, it was stated that "only a few drops of a colorless liquid were obtained in a second receiver. This product suggested an odor akin to capronic acid, mixed with a trace of valeric acid. It was acid in reaction, very powerful and penetrating, diffusing very rapidly in the air, and when thus very highly diluted, gave the pronounced odor of coffee. The condensed liquid, in the first receiver was of a yellowish brown color and had a rather acrid and ammoniacal odor; it also, when diffused, suggested the odor of coffee." It was then stated that the characteristic aroma developed in the roasting of coffee is due possibly to a mixture of organic acids and compounds of phenolic origin. Erdmann, in the *Berichte der Deutschen Chemischen Gesellschaft*, 1904, refers to the oil of coffee which has been obtained by treating roasted coffee with steam. The yield from 150 kilos of roasted and ground Santos coffee was 83.5 grams or 0.0557 per cent. of an oil of brown color, of a specific gravity of 1.0844, and strong odor of coffee. On distillation of the oil, the greater portion passed over between 150° and 190° C. in the form of a light colored oil. This contained furfural alcohol and much valeric acid.

In connection with the process of roasting, it is worthy of note,—First, the effect of roasting of coffee produces, by partial carbonization and partial caramelization, a number of insoluble constituents and an equal number, perhaps, of soluble ones, which have a definite relation to the flavor of the coffee. But the quantitative relationship of the æsthetic qualities seems impossible to make, partly because of the very minute quantity of the aroma-containing constituent; the so-called caffeeol, which is produced by roasting, does not often exceed .06% and thus far we have no easy means for estimating this quantitatively. From an ordinary infusion or decoction, this aromatic principle can be washed out by means of chloroform. On the evaporation of the chloroform, the caffeine crystallizes out and the chloroformic residue, when washed with ether, yields a substance which

has the aroma of coffee and also the bitter flavor, and this peculiar flavor differs according to the brands, or blends, of coffee. Yet, this process, usually followed with a chemical process designed to give quantitative results, can be regarded as of qualitative value only. It would be interesting to have the chemical nature of these bodies definitely stated but statements thus far made give only a suggestion of their possible composition.

Recently, valuable papers have been published, which bear upon this subject, of the volatile products of coffee. One of special interest was published in the *Bulletin General de Therapeutique*, Sept 15, 1913, by M. I. Burmann, who states, in substance, that the volatile "toxic" principle in coffee is not caffeine, but lies in the associated principles of that alkaloid; that "decaffeinated coffee is as noxious as the caffeinated," and that an "atoxic coffee" is one that has these toxic principles removed. These, he finds to be the volatile principles and separable by distillation.

An aqueous distillate is collected in refrigerated ether. The ether separated from the aqueous distillate and the ethereal layer dried by means of calcium chloride. The ethereal solution is then distilled under diminished pressure and the noxious principle, in very small percentage, is left behind in the residue. This principle, which the author terms, "caffeo-toxine" is a colorless, refractive liquid which soon decomposes into a yellow and finally to a black color. This principle, the author refers to as of phenolic, aldehydic or ketonic character.

In an abstract of an article by G. Bertrand and G. Weisweiler, published in the *Analyst*, Sept., 1913, p. 417, the volatile principle of coffee is referred to as a "pyridine-like body." This statement seems to agree with the results which we have obtained in our laboratory.

Burmann, in extracting the volatile principle, made use of 10 kilograms of the finely ground roasted coffee, which was distilled with steam until about 30 liters of distillate were obtained. This was extracted with 10 liters of pure ether, etc. It is unnecessary to point out that such a process would be impracticable for any routine analytical procedure. But the necessity for estimating chemically the essential qualities of coffee becomes urgent and apparent when we remember the present loose and inadequate commercial classifications based on purely geographical data.

Doctor C. F. Nelson and myself have endeavored to find reagents that will determine quantitatively the constituents above named, i. e., the tannin-like bodies, which belong to the polyphenols, and the pyridine-like bodies, and to make these determinations by "micro-chemical" methods.

We are encouraged to believe that we may be able soon to furnish data concerning these two constituents by means of both colorimetric and "nephelometric" methods. We are at present working with the color reaction, produced by phosphotungstic acid, which we have found, thus far, to be extremely delicate. By this method a quantitative accuracy of five parts per million seems to be attainable.

To say the least, this topic opens up an interesting question. The recent investigations point also to a correlative one which has a bearing on the dietetic problem in connection with the beverage.

If it can be proven that this volatile principle is toxic, it is detrimental to public

welfare to place a high value, commercially, on that which is injurious physiologically. If we estimate a coffee in proportion to the amount of the toxic ingredient, this is not in harmony with the principles regulating the value of dietetics.

Finally, if the pyridine-like body is developed by the roasting process, does not the same principle develop in the roasting of cereals and in chicory? Our experiments seem to indicate that this may be true.

DISCUSSION.

MR. WM. C. KIRCHGESSNER:—I would like to ask, if I may, if you cannot estimate the value of the coffee by the caffeine content?

PROF. SAYRE:—You cannot estimate the value of coffee by the caffeine content. You can sometimes obtain a very high caffeine content from cheap coffee, and from a very expensive coffee you may get a very low yield in caffeine content.

MR. KIRCHGESSNER:—Why is it that all the Decaffa Coffees are so dark? I have had men who make it a business of roasting coffee tell me that they could produce Decaffa Coffee at the same price that any other coffee could be sold. They would put the coffee in a roaster, tighten the cap and apply heat and after the coffee was roasted for a certain length of time let the roaster cool, cap up. After taking off cap a dark brown powder would adhere to the top of the roaster which they claimed was the caffeine. I got some of this coffee roasted in this way and the people who used it said that they could not see or taste any differences from coffee which they paid twice as much for.

PROF. SAYRE:—I suppose you know that roasters of coffee always expect a loss in caffeine in the process of roasting. This constituent is sublimed to a greater or less extent in the operation and it is well known that the crude caffeine collects on the walls of the coffee roasters and this sublimate is very valuable because of its caffeine content,—because of its richness in this alkaloid.

PROF. KREMERS:—I would like to ask whether the acid gives the aroma to the coffee, or aromatic residuent?

PROF. SAYRE:—It is given by the so-called oil which is associated with pyridine. The pyridine like constituent is associated with the aromatic principles or is a part of them. Dr. Nelson has been working with me on this problem. He is at Harvard during the summer and he hopes in the fall to work out the final result as to this toxic constituent which is present only in very minute quantities. We find it has a very close connection with the aromatic or so-called toxic principle.

PROF. KREMERS:—Do you know of any pyridine content, so-called that is suggestive of the aroma of coffee?

PROF. SAYRE:—No, I do not. It is well known that pyridine *itself* is not suggestive of coffee. But it is well known, however, that you can modify odors by certain combinations, especially when they are present in minute quantities.

THE ASSAY OF OPIUM.

A. R. L. DOHME.

There is no more important nor more frequently used assay process in the pharmacopœia than that of opium. There is no drug used in which the monetary value of variation in assay results is greater, for above all other drugs the price of opium is directly determined by and based upon its assayed strength of morphine. There is hence every reason why this assay process of all processes in the pharmacopœia should tell the truth or as nearly the truth as is possible. Hence the great question before the Revision Committee is the process of assay for opium and again this committee is confronted as it was in 1904 by two opposing factions favoring respectively the U. S. P. method which exhausts the opium by water and the lime method which exhausts the opium by the use of lime. Manufacturers of morphine probably know best the relation of assay of drug to yield of manufacture because