

ANALYTICAL ELUTRIATION METHODS OF SEPARATING CACAO HUSK FROM COCOA POWDER.

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In the cocoa and chocolate industries the principles of wind-separation are almost universally employed. In separating the crude husk from the nibs after roasting, the nibbing and husking machine, in which the stream of crushed cacao beans meet strong currents of air, is a most efficient separator. This problem, as well as that of grading cocoa powder by wind-separation, is comparatively easy of solution in practice, and, in well-run factories, at least 95 per cent. of the total husk can be removed. It is generally reckoned that of the 15 parts of husk present in the roasted beans (an average figure), 10 parts are coarse, 2 to 3 parts are finer débris, and 1 to 2 parts are very fine dust which last, are hardly possible to remove. The nibs themselves, that is the kernels of the beans freed from the outer husk, will show, on analysis, about 2 per cent. of husk, and cocoa powder, containing a lower percentage of fat than the nibs, will show a higher proportion according to the degree of expression to which the nibs have been submitted. This husk can be attributed both to the fine dust, already mentioned, and to the inner fine membrane or "bran" which adheres tenaciously to the lobes of the nibs.

In spite of the efficient husk separating machines on the market there are many factories which do not attempt to remove completely all the husk from the nibs in the preparation of cocoa and chocolate. The reason is not far to seek since cacao husk has little or no commercial value when completely separated. In considering later the separation of powdered husk from powdered cocoa for analytical purposes, it should be borne in mind that all husks are not the same, that some have a very high proportion of clay or sand present, due to the fact that certain beans, such as Trinidad and Venezuelan, are deliberately treated with clay to secure brightness and cleanliness and to render them less liable to attack by moulds. This is one reason why the analyst without a thorough knowledge of the technical side of the industry is so often confused by the apparently unexpected and diverse results obtained with different brands of cocoa powder. We have had as much as 20 per cent. of crude husk from clayed Venezuelan cacao and 17 per cent. from Trinidad, the husk of the former containing nearly 20 per cent. of mineral matter as against an average of 10 per cent. for unclayed beans.

Considering for the moment the presence of mineral matter which, of course, will increase the specific gravity of the husk containing it, we will see how this fact can be turned to account in estimating the percentage of husk present in a finely-divided cocoa powder. If the percentage of mineral matter present in all husks were constant, the most obvious method would be to ash the sample and to deduce by direct calculation the amount of husk present from the ash figures found. But, as we have said, the

mineral matter varies very considerably with the cacao bean used, and, again, there enters into the problem another complication in the fact that cocoa powders are often treated with alkali, a process which again increases the normal ash-content of the nib. Thus—cacao husk (average) contains 10 per cent. mineral matter, cacao nibs (average) 3 per cent., and alkalisied cocoa powder (average) 6.5 per cent. Nor are the chemical methods of estimating husk any more satisfactory when based on the separation and estimation of cellulose, pentosans, etc. In fact, it is generally recognised by those who have to do analyses of cocoa powders frequently that no simple method of estimation affords absolutely correct information on the subject.

On the other hand, in any one factory where the types of cacao used are kept as uniform and consistent as possible, the works chemist can make use of both the ash method and the levigation method, described next, for checking the efficiency of the husking machine and for controlling the amount of husk that may be included along with the cocoa powder.

So far as the methods of elutriation and levigation are concerned, the results obtained from the hands of one analyst can be made to be fairly accurate and constant—though, according to the method employed and the differences in manipulation, so will results obtained by one analyst vary from those obtained by another. A general history of the levigation processes will not be without interest.

Goske¹ was one of the first to base a method of analysis on the separation of husk from cocoa powder in a calcium chloride solution. One gm. of dry fat-free cocoa is mixed with a calcium chloride solution (sp. gr. 1.535 at 30° C., prepared by dissolving 107.1 grms. of calcium chloride in 100 c.cs. of water) in a stoppered tube. After thorough shaking, the stopper is removed, and the whole boiled for 2 minutes. While still hot, the tube and contents are submitted to centrifugal action for 6 minutes. The top liquid portion is poured off, and the sediments collected on a weighed filter-paper, washed well with hot water, until the filtrate is free from chloride, dried and weighed.

On the assumption that cacao husk yields 38.7 per cent. of dried sediment, this being a maximum figure found for the husk, and that commercial cocoa powders yield 6 per cent., the percentage of added husk in a cocoa powder is calculated, allowance being made for the fat removed.

Since the publication of Goske's method, many observers have condemned it. Filsinger and Böttcher² showed that separation of husk from cocoa was by no means complete by this method, *e.g.* that an equal mixture of shell and nib yielded only 19.6 per cent. of shell by the Goske calculation but 53 per cent. by Filsinger's original method. The correction of subtracting 6 per cent. as the mean unavoidable shell-content was, in the opinion of these experimenters, an impossible method of reaching even approximately correct results, especially when dealing with very pure cocoa powders.

Filsinger and Drawe³ had certainly devised an elutriation method before Goske, but for various reasons it had fallen into disrepute, and Ulrich⁴ later in 1911 mentions it as capable of giving only fairly accurate results. Dubois and Lott⁵ had also condemned Goske's method as unsatisfactory, but did not put forward any improvement. Schenk, Schmidt, and Görbing⁶ similarly examined Goske's method and found that the

¹ *A. Zeitsch. Nahr. Genussm.*, 1910, **19**, 154.

³ *Ibid.*, 1903, **9**, 161.

⁵ *Jour. Ind. Eng. Chem.*, 1911, **3**, 251.

² *Zeit. öffent. Chem.*, 1910, **16**, 311.

⁴ *Arch. Pharm.*, 1911, **249**, 254.

⁶ *Zeit. öffent. Chem.*, 1912, **11**, 201.

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degree of fineness of the sample was more responsible for the variation in the results than anything else, 5 per cent. and 7.4 per cent. of husk only being found from samples containing 25 per cent. and 50 per cent. respectively of added husk when the samples had been minutely powdered.

Grosse¹ improved upon Goske's method and suggested the following treatment: 1 to 1.5 grms. of the cocoa are ground with 20 c.cs. of hot water, boiled and centrifuged (about 500 r.p.m.). The liquid portion is decanted, the sediment mixed with 25 c.cs. of hot water and again centrifuged. The sediment, now obtained, is found to be divided into two portions by a white layer, the upper portion being cacao mass, the lower and dark brown portion the cacao husk. The upper layers are removed, the lower layer twice centrifuged in a small tube, transferred to a basin, dried and weighed. The sediment should be ground and centrifuged again if large pieces of cacao mass are found in the shell-layer. The amount of shell so obtained is multiplied by 3 to obtain the actual quantity present, as, by this treatment, cacao shell loses two-thirds of its weight. By this method a cocoa powder yielding a sediment corresponding to 6 per cent. of cacao shell, mixed with 33.3 per cent. of its weight of cacao shell, showed on analysis 31.6 per cent. of added shell. This method is very similar to that adopted by Baker and Hulton, described later.

Kalusky² found that the cell-tissue of the nibs, obtained by treating the fat-free substances with diastase and subsequently with hydrochloric acid, varied in specific gravity from 1.1131 to 1.3503 (usually 1.25), whilst that of the husk lay between 1.4324 and 1.9337 (usually 1.50). Separation was possible in a mixture of chloral hydrate, glycerol and water (sp. gr. 1.415 at 17° C.), and a mixture was eventually selected having sp. gr. = 1.5. Kalusky's method is as follows: 1 gram. of the dry fat-free powder is boiled for five minutes with 500 c.cs. of water, then cooled to 65° C. and maintained at this temperature for one hour after the addition of a small quantity of diastase. Twenty-five c.cs. of 25 per cent. hydrochloric acid are added, and the mixture boiled for thirty minutes. The insoluble matter or tissue is filtered off on a weighed filter-paper, washed with hot water, dried for two hours at 100° C. and weighed. The dry tissue of fibre is detached from the filter, ground finely in a mortar, and again dried. A weighed portion is then mixed in a suitable tube with 20 c.cs. of the medium (prepared as described below) and centrifuged for five minutes.

The medium is prepared by mixing 210 grms. of chloral hydrate, 50 grms. of glycerol, and 35 grms. of water. This should have sp. gr. = 1.50 at 17° C. More chloral hydrate or water, as the case may require, is added to secure the desired specific gravity.

The portion of tissue settling to the bottom of the tube is separated, mixed with 100 c.cs. of water, collected on a filter-paper, washed with hot water, dried and weighed. The weight of heavy tissue thus obtained is calculated as a percentage of the original cocoa, and the result is multiplied by 3 to give the percentage of husk present. This factor (3) was obtained after many estimations of heavy tissue in cacao husks. When husk is absent, the whole of the tissue is found floating on the surface of the medium, after the mixture has been centrifuged.

Baker and Hulton³ adopted an average of 27.6 per cent. of levigation sediment from cacao shells and 1.4 per cent. from clean cacao nib. These

¹ *Chem. Zeit.*, 1915, 39, 816.

² *Zeitschr. Nahr. Genussm.*, 1912, 23, 654.

³ *The Analyst*, 1918, 43, 189-197, 507.

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experimenters pinned their faith in the accuracy of the levigation method they used rather than in the chemical methods of analysis. We are inclined to agree with Baker and Hulton for estimating the percentage of husk in the majority of cocoa powders in which husk and cocoa are ground together, but when carefully and finely ground husk, subsequently wind-sifted, is added to a cocoa powder of the same degree of fineness, carried an equal distance by the current of air, we are convinced from a large number of experiments that the two cannot be separated by any system of levigation or elutriation yet devised. The levigation method adopted by Baker and Hulton is as follows: "10 grms. of the finely ground material to be analysed are extracted for twenty hours with ethyl ether in a Soxhlet apparatus. The extracted mass is exposed to the air to remove adhering ether, dried in a water-oven, well ground in a mortar, then stirred into a thin paste with water, and transferred with washing to a 500 c.c. cylinder. The volume in the cylinder is made up to 400 c.c.s., the whole inverted a few times to ensure admixture, and an arrangement inserted in the neck for blowing off the supernatant liquid. The leading tube should be turned up at the lower end to avoid any disturbance of the sediment. The contents of the cylinder are allowed to stand for fifteen minutes, and the liquid blown off. The volume is again made up to 400 c.c.s. with water, and the procedure, above described, repeated after ten minutes and again after two periods of five minutes' stand. Should the residue in the cylinder show the presence of much starch it should be finely ground in a mortar and again submitted to levigation. The residual sediment is transferred to a platinum basin, the water removed by evaporation, and the residue dried in the water-oven and weighed. The ash, obtained from the residue, is then deducted. We have adopted the figures for the sediment obtained from nib and shell as found by Bolton and Revis—namely, 3 per cent. for dry fat-free nib and 30 per cent. for dry fat-free shell. The percentage of shell in the original sample may be calculated from the formula—

$$S = \left(\frac{100M}{100 - (F + W)} \right) - 3 \times \frac{100 - (F + W)}{27}$$

where S = percentage of shell on sample.

M = percentage of ash-free levigation sediment on sample.

F = percentage of fat on sample.

W = percentage of water on sample."

It will be seen that the limitation of the levigation or elutriation methods for determining the amount of husk present in a cocoa powder are decided by the processes of manufacture of the cocoa. A well-washed husk, finely ground and wind-sifted is practically inseparable from true cocoa powder that has undergone the same processes owing to the similarity of their specific gravities. Fortunately for the public analyst this fact is not too well-known among the manufacturers, though, of course, most of the large firms would not stoop to such adulteration. The admixture of any large quantity of husk, however finely ground, is readily detected by the palate and, however carefully washed and prepared, husk will always feel slightly gritty on the teeth.