NOTE ON THE ESTIMATION OF FIXED OILS AND FATS WITH SPECIAL REFERENCE TO MILK.

By A. C. Abraham, F.C.S.

The plan generally followed for the estimation of fixed oils in such things as linseed meal has generally been maceration and percolation, or the latter alone, with ether, benzol, or some similar solvent. Anyone who has followed either course will, I think, readily admit the troublesomeness of it and the great care involved in preventing loss, especially when dealing with small quantities. To obviate these difficulties, I adopted a year or two ago for linseed meal the following plan, which I have since used for other substances and which I believe to be more accurate as it certainly is more easy, than those generally followed. The principle is simply that of macerating the substance to be estimated in the suitable solvent, taking half or a known proportion of the *total liquid resulting*, finding the amount of fat in it and calculating therefrom the amount in the whole.

To take linseed meal (or more correctly, crushed linseed, *i.e.*, the linseed crushed but not deprived of its oil) as an example. My procedure is as follows :—A tube is taken of about 1 inch in diameter and 14 inches in length, contracted at the neck and stoppered; in it is placed 100 grains of linseed meal and upon this is poured 2,000 fluid grains of spirit of wine less such an amount as will approximately represent the volume of the oil contained in a genuine and fair quality sample of the meal. The tube is now shaken to enable the spirit to expel all the air from the meal and when this has taken place the tube is graduated at the point at which the liquid stands. It is now ready for use. When it is desired to estimate a sample, 100 grains of the meal are inserted and ether added until it reaches the mark; it is then stoppered or corked and occasionally shaken during a sufficient time, when, if any loss has taken place by evaporation, or the volume has been apparently diminished by the loss of air from the meal, it is made up to the original point, again shaken and set aside. When it has completely subsided, 1,000 fluid grains of the clear supernatant liquid are removed with a pipette, evaporated and weighed as usual. By doubling the product so obtained, the amount of oil, together with such other matters contained in the meal as are soluble in ether, is arrived at.

It will be readily admitted, I think, that if the amount of matter soluble in ether were known before the estimation was commenced this process would be unexceptionable. I believe, however, that the error admitted by the want of this knowledge will upon consideration appear so trifling, even for an article containing so much oil as does linseed meal, as to be perfectly unimportant. Suppose, for instance, that the meal contains 20·2 per cent. of oil, &c., which we may assume to increase the bulk of the resulting solution to the extent of 20 fluid grs., now if no allowance at all were made for this the bulk of the solution would be 2,020 fluid grs. instead of 2,000, which is required. If only 1,000 of this were taken, that portion would be less than the remainder by 20 fluid grains, *i.e.* to say, supposing the 1,000 fluid grs. taken were found to contain 10

grs. of oil, the remaining portion would contain 10·2 grs., and by doubling the former amount we should get a result of 20 instead of 20·2, an error of one-hundredth of the product or 2 per cent., which if considered important can be neutralised by an allowance at the end of the operation. Or, if thought preferable, 2,000 fluid grs. of the solvent may be always used and an allowance made in proportion to the result found.

In this process it is assumed that all the solvent is capable of dissolving all of the matter to be dissolved, and that none of the latter will remain in a fixed condition, in or upon the tissues of the article containing it. Whether this assumption be absolutely true or not, I think it will be admitted, that if it is not, no process of percolation is likely to obviate it. In regard to milk, the case is somewhat different, because to follow the process, it is essential to evaporate the milk with either hydrated sulphate of calcium or powdered glass; the latter, perhaps, preferable on theoretical grounds, but the former what I have generally myself used.

The details of the process as applied to milk, are as follows :—

A 1,000 gr. specific gravity bottle is filled with the milk, the weight taken which gives the specific gravity. This is emptied upon 250 grs. of powdered glass or hydrated sulphate of calcium, and the flask either weighed or rinsed out with a few drops of distilled water, although practically, neither is necessary, as the amount of milk adhering to the flask, when once found, will be practically constant for all samples (unless sour). The milk taken is to be evaporated to dryness with the glass, and thoroughly powdered, when it is to be introduced into a tube; 2,000 fluid grs. of ether added from a pipette, so as to avoid loss by evaporation; the tube stoppered, shaken occasionally during some hours, after which 1,000 fluid grs. may be removed, dried, and weighed. This must not simply be doubled, as an allowance must be made for the fat dissolved by adding to the weight found $\frac{1}{9}$ (the specific gravity of butter fat being about ·900), deducting this from 1,000 and calculating the whole amount present therefrom, thus :—

Fat found, say	9
Add $\frac{1}{9}$	1
	10

∴ 990 fluid gr. of ether took up 9 grs. of fat, how much would 2,000 take up?

990 : 2,000 :: 9

11 | 200

18·18 Total fat present.

The difference between the amount which would be arrived at by simply doubling the weight found and that obtained as above will never amount to more than about ·005 per cent.

For this process of estimation it would be clearly much better, if possible, to extract the fat from the milk whilst still in a liquid condition, and if this could be done by simply boiling the milk down in a graduated tube, then adding the ether, making it up so that the ethereal solution should measure a convenient quantity, and drawing off half of this pipette, it would be much better; but I have not had time to try whether this can be done, although I believe it might.

There is another process which I have to mention, one which has been less tried than the one I have named, for, although it has suggested itself to my mind some time, I have not tried it until within the last ten days. It is applicable to all emulsions such as milk, and, as far as I have gone yet, may be described as follows:—

A piece of Parker's paper fibre lint, 4 inches by 2, is made into a roll, a piece of thin wire is passed through the centre, wound once or twice round the roll, and fixed into the stopper of a suitable weighing bottle, in such a manner that the roll may be sufficiently far from the sides, to enable it to be lifted in or out without any fear of touching the sides.* The roll is then taken out of the bottle, and dried in a water-oven with the bottle, until its weight is constant, 5 c.c. of milk are then dropped upon it from a pipette, when the stopper with the roll attached is re-inserted in the bottle, and the whole weighed. The stopper is then removed, and with its attachment, placed in a drying oven with the bottle, and kept there until it ceases to lose weight.

The excess of weight over the original weight gives the total solids. The stopper and roll are now removed and placed in another similar bottle—preferably ground to fit the same stopper as the first—sufficient ether added, so that the roll may be covered (about 50 c.c. is a convenient quantity) and allowed to macerate some hours; it is then transferred to another similar bottle, and again to a third, after which, the fat will be found to have been entirely extracted.† It is now removed and again weighed as before; the loss is fat.

If desired, the fat may be weighed directly by evaporation of the ethereal liquids, or the tubes in which they are contained may be graduated, the volume made up to the graduation, the liquid stirred with a pipette, and half, or a known proportion, drawn off from each. The latter method, I think in some respects preferable, as it does not involve the removal of the liquid from one vessel to another, which, if done, introduces an element of uncertainty, owing to the adhesion of a certain amount of the fluid to the vessel from which it is poured, and also involves the washing of the vessels to obviate the last-mentioned difficulty. It will be noticed that I have made no reference hitherto to the estimation of the ash, and this is because I have thought it impossible to expect anything like a small or possibly even a constant ash from an article not specially made for analytical purposes. I am not without hopes, however, that by means of washing with acids, even Parker's paper fibre lint may be so freed from ash, as to enable the whole four determinations of total solids, solids not fat, fat and ash to be made with very great accuracy from the one small sample of milk. The sugar may also be estimated by immersion in water, but great care is required to prevent portions of the lint from falling off.‡

If the ash cannot be estimated from the same sample as the solids and fat, I do not think that it renders valueless the whole process, because at the worst the ash can be easily estimated as hitherto; and, moreover, I do not see why a special preparation

* Messrs. Becker & Co. have had some very suitable bottles made for me.

† It is important that the lint should not be too near the bottom, because the fatty solution which can be seen falling from it, should have room to collect below.

‡ To obviate this difficulty and to prevent fermentation, some alcohol, say about 25 per cent, may be added.

such as mononitrocellulose, dinitrocellulose, or some other body which would be sufficiently absorbent, and yet leave no ash on incineration, might not be found or specially made for the purpose. I have only made one estimation of milk by this process, and this with rather unsuitable and improvised apparatus, but I subjoin the results, which seem clearly to show that it is capable with experience of producing very accurate results, and in some respects, more accurate than the processes generally followed.

The estimation No. 1 was made, as far as total solids are concerned, in the ordinary manner, but the solids not fat were estimated by difference, which is by no means an accepted method. The conclusions that I would draw from the figures are that the total solids can be estimated with much greater accuracy than by the ordinary method and in shorter time; and that it is impossible to dry the fat completely at a temparature of 212°. Dr. James Bell, the principal of the Somerset House Laboratory, says in his recent work upon "The Analysis and Adulteration of Foods," according to the ANALYST, in the first place, that the determination of total solids is a comparatively easy operation, but later on that it is difficult to get a constant weight for the total solids, and that, therefore, the items, solids not fat and fat *are generally more satisfactory*, which as I understand it, means that the total solids are *very difficult indeed* to obtain by direct estimation.

The total solids in column No. 1 were dried until the weight appeared to be constant (using the quantity and apparatus recommended by Dr. Bell) at 212°, and yet they stand very much higher than those in column 2, which were estimated until of constant weight on the paper fibre lint.

Dr. Bell recommends the drying of the fat in a water-oven, and, therefore, presumably at 212°; and it will be seen that the results arrived at (see columns 1 and 3, which were both obtained by direct weighing), after drying at this temperature, very closely agree, but that the weight lost by immersion of the lint in ether is more than ·10 less. In other words the fat lost was ·11 less than the same fat when dried at 212°. This I think at least shows that 212° is *not* sufficient to dry the fat. I think that if I were a milkman I should be disposed very much to question a method of analysis which does not enable the analyst to rely upon his estimation of total solids, but compels him to fall back upon his weighing of solids not fat and fat, both of which weights are arrived at after manipulation, which may entail a loss.

With regard to the drying of the fat I have not tried whether a temperature of 220° would enable an accurate weighing to be made, and with regard to the total solids I do not think it would be right to apply so high a temperature, because we do not know exactly what effect it may have have upon the constituents of milk.

	No. 1.	By difference. No. 2.	By direct weighing. No. 3.
Total solids	11·97	11·38	—
Solids not fat (by difference only) ...	8·95	8·48	—
Fat	3·02*	2·90	3·01

* By the first mentioned process.

In conclusion, I should say that in the one experiment which I have made, the time occupied was certainly rather long; but I believe that this was due to the fact the roll was rather tight and an ordinary drying oven was used, whereas an oven which would allow a constant and rapid circulation of air around and through the roll would probably have produced results comparable in point of time with those attained by other means.