A RAPID AND ACCURATE METHOD OF DETERMINING THE MOISTURE AND OIL IN LINSEED CAKES AND OTHER FEEDING STUFFS.[1]

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IT frequently happens that when the same sample of linseed cake is analyzed by different chemists very considerable differences occur in the proportions of oil and moisture found by them.

The explanation of these discrepancies is to be found, not only in the different methods employed, but also in the inconstancy of the results obtained by the same method.

Determination of Moisture.—As regards the determination of moisture, the common practice in this country is to expose one or two grams of a finely ground sample in a water-bath for two hours and to regard the loss of weight as the measure of the moisture. A recent examination of this method has shown me that it may be very inaccurate and that uniform results cannot be obtained by it.

The amount of heating which a sample gets in an ordinary water-bath during two hours may not be sufficient to deprive it of all its moisture. The temperature within the bath is not constant and it is always below 100° C. The temperature of the external air, the amount of ventilation, the frequency with which the door is opened, the quantity of the sample used. the nature of the vessel containing it whereby a greater or less amount of surface is exposed to the current of hot air, are all fluctuating conditions. Moreover, in the case of linseed cake, the sample continues to absorb oxygen during the whole time of its exposure in the bath and it does so the more rapidly the higher the temperature and the greater the surface exposed.

It thus happens that when a sample of finely ground linseed cake is exposed in a water-bath it goes on losing weight from loss of moisture for a time and thereafter gains weight from ab-

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[1] Read before the World's Congress of Chemists, August 22, 1893.

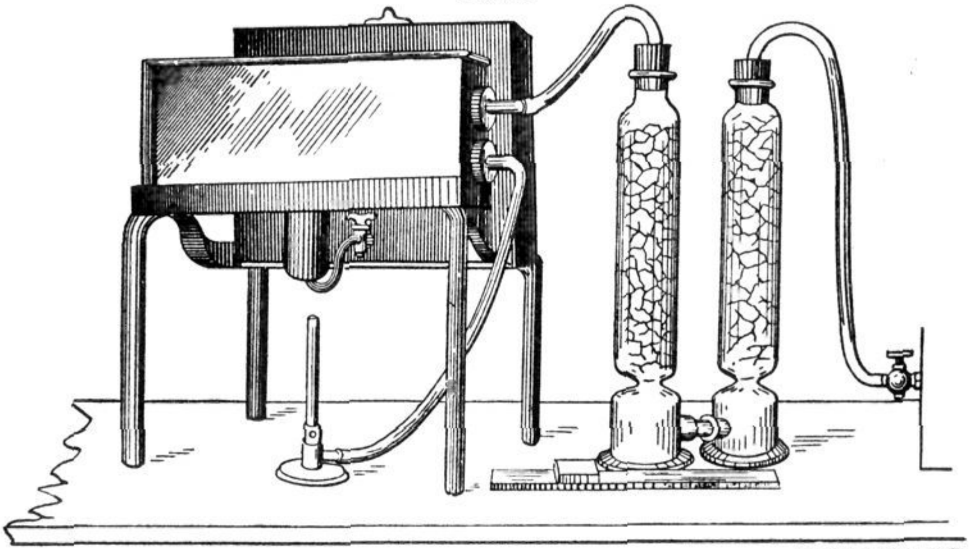
sorption of oxygen. Therefore, the time at which the sample ceases to lose weight is not that at which the sample is dry but only the time at which the loss of moisture and the gain of oxygen counterbalance each other.

In order that the sample may be thoroughly dried and that it may at the same time suffer no oxidation, it must be dried in an atmosphere from which air is excluded. An atmosphere of hydrogen is excellent for the purpose, but one of coal gas does quite as well and it is most readily obtainable. I have used coal gas for the purpose for some years and it is used also in some of the continental laboratories.

The apparatus I am about to describe secures that the sample is dried exactly at the temperature of boiling water and is so constructed that the coal gas is heated to that temperature before it comes in contact with the sample. It may be made of any dimensions, but the size which I prefer is that described below and capable of drying eight samples in an hour and a half.

The apparatus consists of a small rectangular box, ten inches long, four inches deep, and two inches wide, placed on edge as shown in Fig. 1, and in sections longitudinally and transversely, Fig. 2, A.

FIG. 1.



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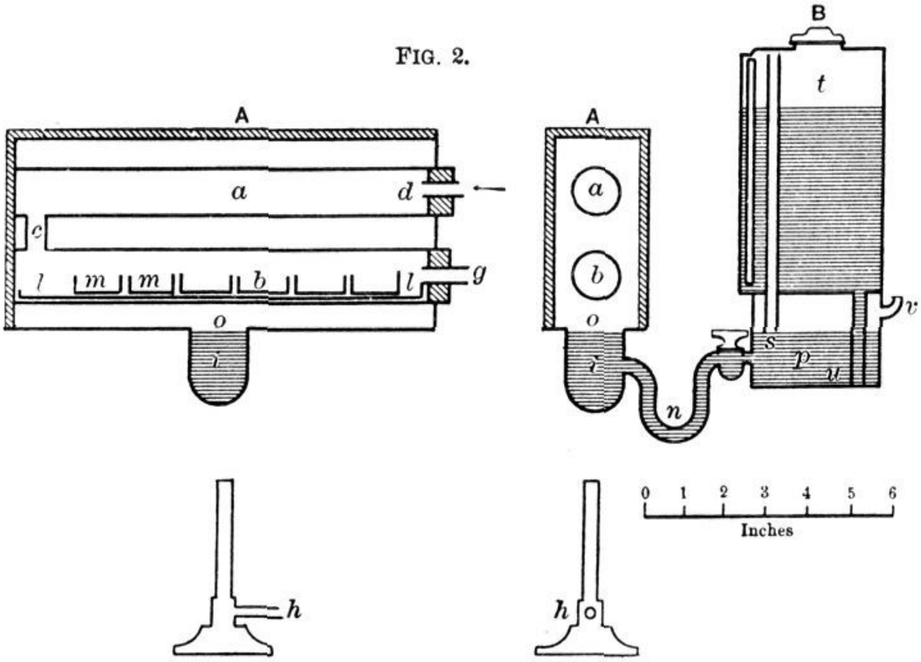
Through the box from end to end pass two hollow cylinders made of telescope tubing, and soldered into the box at each end.

The box is simply a steam-bath to heat the two tubular chambers, which are fitted at one end with the perforated corks and have the other end either closed with corks or entirely soldered up as in the diagram. The upper tubular chamber *a* is for heating the gas, and the lower one *b* for drying the samples, which are contained in little aluminum boats *m m* resting on a carrier of brass *l l* which slides into the chamber.

FIG. 2.



These boats, capable of holding one or two grams of cake, weigh only about one to two grams each, and are, therefore, very well adapted for weighing small quantities. The gas from the tap is led first through two drying bottles, filled, one with soda-lime and one with chloride of calcium, and enters the apparatus by the tube *d* in a perfectly dry state. It passes along the upper chamber *a*, where it is heated, and then through *c*, which is a tube connecting the upper and lower chambers. It arrives at the lower chamber *b* both hot and dry and passes along, drying on its way the samples (usually one gram each) contained in the little aluminum boats *m m*, eight of which can be accommodated on the carrier. The gas leaves the apparatus by *g*, and may be burnt there, but as the flow of gas is sufficient to keep a small Bunsen going, I connect the tube *g* with the Bunsen *h*.

The flame of this little Bunsen keeps the water in the thimbleshaped cup *i* briskly boiling. The water in the thimble (about 1–2 ounces) is kept constantly at the level *o* by its connection with the automatic cistern B connected with the bath by the tube *n*, which is bent downwards and up again so as to prevent hot water from passing back into the lower section of the cistern *p*. As soon as the level of the water in this lower section falls below the mouth of the tube *s*, a bubble of air passes up the tube into the upper cistern *t*, and a corresponding quantity of water flows into the lower section through *u*, and restores the level of the water. A small hole *v*, into which an upwards bent tube is fitted, allows air to enter the lower section. The object of the upturned tube is to prevent water from spilling out of the airhole, when the apparatus is carried about. This cistern contains more than a day's supply of water, and gives no trouble, and is supported along with the bath, on a light iron frame, as shown in Fig. 1. The inside of the bath is thus constantly full of steam, which escapes by a hole at the top about $\frac{3}{16}$ of an inch in diameter. The bath is made of copper, but its entire surface is protected against contact with the surrounding air by means of asbestos sheeting $\frac{1}{8}$ inch thick.

The temperature in the upper chamber is thus kept constantly at the boiling-point of water, and not several degrees below it, as is usually the case in even the best water-baths. By means of this small apparatus, eight one-gram samples of cake can be dried within two hours. They are removed by drawing out the carrier, transferred to an exsiccator, and weighed in the aluminum trays, whose weights are known and deducted, thus giving the moisture. The results are perfectly accurate, and the cost in gas is very small—only about one cubic foot per hour.

The samples are now ready to have their oil extracted and estimated.

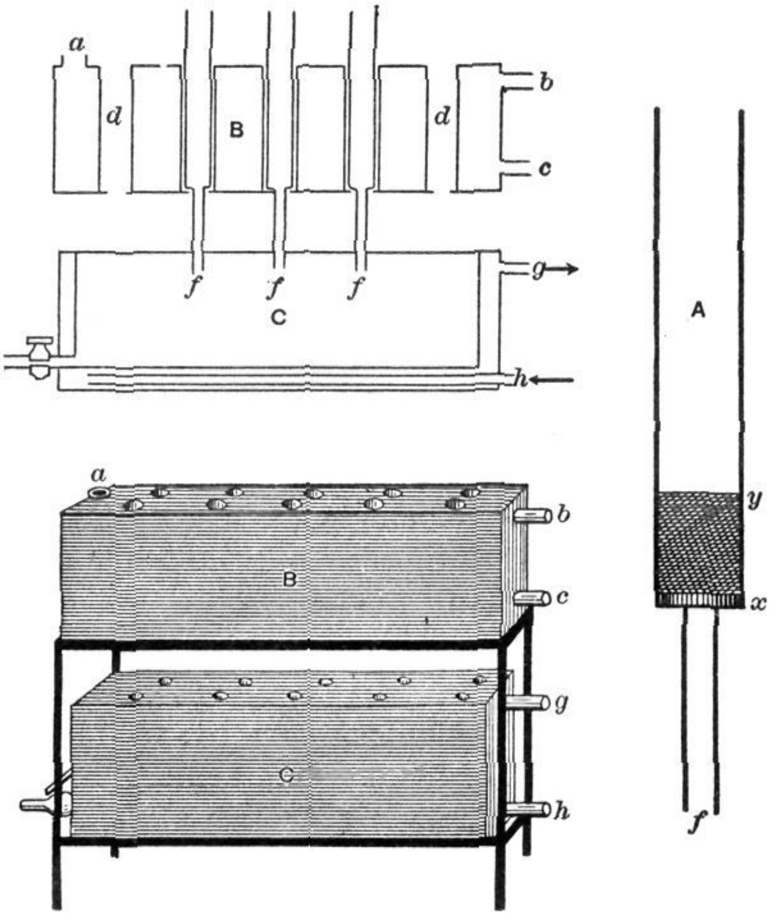
It is not essential that the last traces of moisture should be removed before the oil is extracted. If the sample is dried for half the time required to completely dry it, it is in a suitable condition for oil extraction. Nine-tenths of the moisture will have gone by that time, and the presence of about one per cent. of moisture does not appreciably affect the amount of oil extracted.

I prefer to take the samples whose moisture I have estimated, and which are completely dry, because I have a method of extracting oil by which even very small quantities of oil can be accurately estimated, and which possesses the further advantage of being more rapid than any other method that I know of.

Solvent for Oil in Cakes.—Ether, bisulphide of carbon, or benzene, are the solvents usually employed, but as ether is the one which is most common, most rapid, and most comfortable to work with, I prefer it to the others. It is a little more expensive, but the quantity used in oil determinations is small; the additional cost is more than compensated by the advantages mentioned. Ordinary pure ether, as supplied by wholesale chemists, having a specific gravity of 0.73, is sufficiently pure and dry for the purpose of oil extraction; but as most of the ether used is recovered by redistillation in the laboratory and may contain water, it must be dried before being again used. This is sufficiently accomplished by shaking it up with chloride of calcium repeatedly for some days, and redistilling.

Determination of Oil.—The oil may be determined either by directly weighing the oil extracted, or by weighing the dried substance before and after the oil is extracted, and determining the oil by the difference of the two weighings. There are two objections to the former method. In the first place, the flask in which the oil is caught is itself very heavy and presents too great a surface; and in the second place, the evaporation of the residual ether in the drying chamber takes a long time, and the surface of the oil becomes covered with a thin pellicle due to oxidation. The latter method is much to be preferred if a suitable apparatus can be had for doing the work simply and rapidly. The apparatus I have devised for that purpose is very simple, and is shown in Fig. 3. It consists of a set of brass tubes, polished smooth inside, see Fig. 3, A, which is half the actual size, and is represented as charged with the dried sample. In charging the tube, the first thing required is to drop into it a small disk of wire gauze x, and then to insert a single or double wad of filter-paper, which is cut to fit the tube tightly, and pushed home with a ramrod. (I use a cork borer of the proper size for cutting the wads, and a piece of glass rod flattened out at the end while hot as a ramrod.) The object of the wire gauze disk is to facilitate the flow of the ether through very fine powders, such as ground grain, and also to enable the sample to be removed from the tube more easily after the oil is extracted. In the case of oil cakes the wire gauze disk may be dispensed with.

FIG. 3.



The sample is then poured in through a little metal funnel whose neck just fits the extraction tube. Any powder adhering to the funnel is brushed in with a camel-hair brush, then another wad *y* is patted in on the top of the sample, carrying with it any powder that might have adhered to the side of the tube and leaving the upper part of the tube clean and bright. The tube is now put into one of the holes in box B, which is simply a warming box made of zinc, shown also in section.

The holes *d d*, etc., are tubes which pass through the box from top to bottom, and are made a shade wider than the extraction tubes, which should drop in easily. As soon as the extraction tubes are filled they are dropped into these tubular openings, which are provided with a ledge at the base to sustain the extraction tubes.

Hot water is poured into the box at *a*, or a constant current of hot water may be made to flow through the box, entering at *b* and flowing out at *c*, by attaching these by means of tubes to a copper coil under which a Bunsen is burning at a safe distance. At first I used the circulation method, but now I prefer to have no gas burning anywhere near the extractor. It is quite convenient to supply hot water at *a*, and withdraw the cooled water at *c* from time to time. As soon as the extractor tubes are dropped into their places, ether is poured into them to within an inch of the top, and by the time that the five tubes are thus filled the ether will be boiling in the first tube. A cork is now firmly fixed into each tube in succession, thus preventing the ether-vapor from escaping, and the presence of the confined vapor forces the boiling ether down through the samples and out through the lower openings *f* into little bottles placed beneath, so that the oil may be collected from each tube separately. If the oil of each tube is not to be kept separate, the mouths of the extractor tubes are made to dip into a zinc box C beneath, through small holes on the top, and there the oily ether collects and is run off from time to time, and redistilled for future use. There is considerable loss of ether by this method, but that is much reduced as one becomes expert in handling the apparatus; and if the other box below is provided with double walls between which a current of cold water is kept flowing through the openings *g*, *h*, the loss from evaporation is still further reduced.

This process of filling the tubes with ether is repeated ten, fifteen, or even twenty times, according to the difficulty of extracting the oil. The operation is complete when a drop or two of ether, falling from the exit *f* towards the end of an extraction, is caught on a clean watch-glass and evaporated without leaving any residue. The extractor I use in my laboratory is fitted for ten tubes, and after a little practice the oil from the ten samples of cake can be extracted with it in one hour. The extraction of oil from a sample, by means of Soxhlet's apparatus, which is the one chiefly used at present, takes about five hours, so that this little apparatus has a great advantage over it as regards speed; but many comparative tests have proved that it also has the merit of making a more thorough extraction of oil. This is due to the fact that the extraction is made with boiling ether, and that no oily ether that has once been washed through is able to run back upon the sample again, as is the case with Soxhlet's apparatus. In extracting the oil from some substances, such as grain or other starchy powders, the resistance to the passage of ether is so great that even a tightly-fitting cork is apt to be blown out by the pressure of the vapor. In such cases I use caps with a cork washer inside, which fit on to the top of the tubes with a screw of half a turn which is very rapidly adjusted.

When the oil has been completely extracted, the removal of the sample is a neat and easy operation. It is done by inserting the cut end of the glass ramrod into the opening *f* and slowly pushing out the sample (wads and all) into a weighed aluminum capsule. The wads are now removed, after brushing off any particles of powder adhering to them with a camel-hair brush, and the dry powder, after exposure for a short time to a temperature of 100° C., is cooled in an exsiccator and weighed. The difference between that and the former weighing is the weight of the oil extracted.

It is evident that the accuracy of the oil determination by this method depends upon the accuracy of the determination of the moisture; but as by the method above described the moisture can be accurately determined, there is no danger, if that method is adopted, of making any error in the estimation of the oil. In estimating moisture in the ordinary way it is considerably underestimated, usually to the extent of one-twentieth or more, and in such circumstances that which is underestimated in the moisture is usually added to the oil; for the common practice is to determine the percentage of moisture in one part of the sample, the percentage of moisture and the oil together in another, and to subtract the former from the latter, so as to give the percentage of the oil.

It thus happens that in the analysis of an ordinary linseed cake differences of two or even three per cent. are not unusual in the percentage of oil found by different analysts.

I have submitted this method to a long series of tests in my laboratory during the past winter and I have been so satisfied with the accuracy and uniformity of the results obtained by it and with the simplicity and rapidity of the whole process that I cordially recommend it to agricultural chemists in America and especially to those who have small laboratories and a large number of samples to analyze.

The apparatus is not costly and I hope the description I have given of it is sufficiently clear to enable it to be easily understood and imitated.

ON THE DETERMINATION OF NITRATES IN POTABLE WATER.

BY AUGUSTUS H. GILL.

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PART I.

THE remark of Tiemann,[1] that the estimation of no other substance has so constantly occupied the attention of the analytical chemists of the last decade, to the extent to which the determination of nitric acid has engaged (literally "enchained") them, will, I think, be appreciated by all those who have worked upon the subject. Perhaps no determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question.

There are two general modes of procedure:

a. The direct estimation, and
b. The reduction to ammonia.

a. DIRECT ESTIMATION.

The direct processes which have been found to give the best results are those of Schulz-Tiemann,[2] Schloesing-Reichardt,[3] Crum-Lunge,[4] and Marx-Trommsdorf.[5] These are only appli-

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[1] Tiemann Gaertner "Wasseranalyse" 3rd. Ed'n., p. 168.

[2] *Ber. d. chem Ges.*, 6, 1041.

[3] *Ztschr. anal. Chem.*, 9, 24.

[4] *Phil. Mag.*, (3), 30, 426.

[5] *Ztschr. anal. Chem.*, 9, 171.