tempted by the writer of this communication; the results form a volume of over 1,200 pages just issued by the Smithsonian Institution as one of the series entitled Miscellaneous Collections. This "Select Bibliography of Chemistry, 1492—1892" embraces about 12,000 titles in twenty-four languages, yet makes no claim to completeness; it is moreover a bibliography, not an index.

In conclusion I have the honor to propose the appointment of an International Committee on Chemical Bibliography, to consist of one member from each country represented in this Congress. That this committee have unlimited power to add to its number, provided however no country have more than two representatives. That this committee, through the European and American Chemical Societies, report a scheme for an International Co-operative Index to Chemical Literature.

UNIVERSITY CLUB,
NEW YORK CITY,
August, 1893.

[EDITORIAL NOTE.—A committee consisting of Edward Hart, R. B. Warder, and Wm. L. Dudley was appointed by the Congress to consider the recommendations of Dr. Bolton set forth in the above paper. Their report with additional action by the Congress will be found on p. 309 of the June number of the *Journal* for this year.]

ACCURACY IN THE ANALYSIS OF DAIRY PRODUCTS.

BY H. DROOP RICHMOND, CHEMIST TO THE AYLESBURY DAIRY CO.

PART I. MILK ANALYSIS.

IN the July number of the *Analyst* for 1889 I published a paper on "Fat Extraction from Milk Solids;" the object of that paper was to show how the differences between the two rival processes of fat-estimation could be explained and rectified; I succeeded eventually in obtaining identical results by the processes due to Adams, Soxhlet, and Storch. Since that paper appeared it has been shown by Waller, Liebermann, and others that the processes of fat-estimation, especially the Adams method, should be modified by rendering the use of ether as a solvent inadmissible. The Werner-Schmid process has also come into extensive use.

In considering the accuracy of any process we have three

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

methods of obtaining evidence of exactitude; first a synthetical method, that of taking known quantities of the substance to be estimated, mixing it with the substances from which it is to be separated, and performing an estimation: if the substance is recovered in totality, and in a state of purity, it is a proof of the exactitude of the method; a second method consists in the comparison of the results obtained by the process with those obtained by a process distinct in principle, and in which the probable error lies in a different direction; this method does not give a proof of exactitude, but only brings the chance of exactitude to a high degree of probability. The third method is to examine the errors of the method in detail, and to prove that they can be neglected or that they do not exist: this method would be good could we be certain that all possible sources of error were known to us. The largely used method of obtaining concordant duplicate determinations must be absolutely rejected as a method of proving accuracy; it only proves accuracy in manipulation, and sheds no light on the real errors of the process.

To prove the accuracy of the estimation of fat, as we cannot employ the synthetical method, we must prove that first the whole of the fat is extracted, and second that nothing else is weighed as fat. It is hardly necessary to bring forward other proof that the fat is wholly extracted than the agreement between the Adams method, the Werner-Schmid method, and methods in which the milk is dried on some medium such as plaster of Paris, kieselguhr, or pumice, and this residue is ground fine, extracted, and reground and re-extracted until nothing more is extracted. Figures showing these agreements have been published so often that it is not necessary for me to take up space by giving such results here. It has been alleged that ether extracts other substances than fat (Waller, *J. Am. Chem. Soc.*, **13,** 52; Liebermann, *Ztschr. anal. Chem.*, **35,** 168). Their conclusions to my mind are not satisfactory, as my experience tends in a contrary direction. As an explanation of the results found by Waller and by Liebermann I may mention that the paper coils on which they experimented contain matter soluble in ether and totally removed with exceeding difficulty. These coils always give when extracted with ether a quantity of loose fibers; and commercial ether contains many impurities, such as water and alcohol, and these impurities may cause the appearance of substances other than fat in the extract. I am in the habit of purifying my ether by washing with water, shaking with a large quantity of anhydrous calcium chloride and distilling. For special use the distilled ether is rendered anhydrous by keeping over sodium, and distilling portions as wanted. I have already published experiments showing that ether, petroleum ether, and chloroform give the same results, if the time of extraction is sufficient (*J. Anal. Chem.*, **4**, 26, 241). I have further narrowed down the substances that can be extracted by ether from albuminoid by comparing the fat estimated by the Adams, the Werner-Schmid, or the Storch processes with that extracted from the casein or from the precipitate obtained in the Ritthausen process. As examples of the agreement the following figures may be quoted:

Fat from albuminoid	4.93	2.87	1.38	4.00	0.04
Fat, Adams, etc	4.97	2.89	1.43	3.99	0.17

In the last case (a separated milk) the casein was dissolved in ammonia and the solution placed on an extracted Adams coil, and a further amount of 0.12 per cent. of fat was obtained. As the hard horny mass of albuminoid is a most unsuitable medium for extraction I am of the opinion that the slight deficiency of fat extracted from albuminoid is due to incomplete extraction and not to the extraction of other substances from the total milk solids. It only remains to prove that no albuminoids are extracted by ether. The absence of nitrogen in the extract is I think sufficient proof of this. The next problems that confront us are, does the fat itself dissolve anything from the milk and if so should it be considered as a constituent of the fat, and does the weight of fat extracted represent the weight of fat in the milk or does it increase or decrease in weight during the extraction and drying, and if so can the amount of change be neglected as being too small to affect the results to any practical degree? My experiments (*loc. cit.*,) show that the acidity of the extract is practically the same whether ether, petroleum ether or chloroform be used as a solvent, and therefore that if lactic acid be extracted it must be dissolved in the fat. The agreement between the extraction from albuminoid and from milk solids shows the same thing, as the lactic acid if not in solution in the fat must have been washed away in the former case. I do not know of any other substance which exists in milk and is soluble in fat. I do not think on the whole that any correction need be made for anything soluble in the fat; but before an authoritative opinion can be given on this point an extended research must be made. Fat on drying at the temperature of boiling water undoubtedly increases in weight; but my experiments have shown that during the half hour or so during which the fat is dried the increase does not amount to more than 0.2 per cent. of the weight of the fat. Even if weighed quantities of fat are placed on some medium and extracted as in a milk analysis no appreciable deviation from the weight taken can be detected. I have concluded that the change in weight during extraction can be neglected, and that the weight of fat extracted can for practical purposes be taken to represent the weight of fat in the milk.

My general conclusions are:

1. That ether, petroleum ether, or chloroform are equally efficient solvents, if sufficient time be allowed for extraction, but that ether is the most convenient, as it extracts the fat more rapidly.

2. That an accurate estimation can be obtained only if the milk solids are subdivided either by the use of a paper coil free from matter soluble in the solvent, by evaporation of the milk on some medium which can be very finely divided, or by extraction from a solution in which every thing except the fat is dissolved (as in the Werner-Schmid process).

3. That if ether is used as a solvent it must be pure and anhydrous.

4. That the weight of fat obtained in the analysis may be taken to represent without appreciable error the amount originally existing in the milk.

5. That in order to minimize the chance of error due to impurities in the media used for extraction, change of weight of the vessels used to weigh the fat in, etc., it is advisable to do a blank experiment following the conditions of the actual experi-

ment as far as possible. I am in the habit of taring my flask against the flask in which the blank experiment is performed.

6. That it is necessary to secure a true average sample of the milk. The milk must be well mixed by slight agitation, and if a pipette is used it should have as wide an opening as possible to minimize the danger of separation of the cream during the passage through the narrow opening.

On the whole I am inclined to consider the fat-estimation one of the most reliable figures obtained in a milk analysis.

Estimation of Total Solids and of Water.—We may rule out all methods as inaccurate which fail to give a constant weight on continued drying, or which show signs of decomposition of the residue weighed, such as marked browning of the residue. For this reason Wanklyn's three hours method is inadmissible, though it has been claimed by him that it is the more accurate in that the water of hydration of milk sugar is not driven off during this period. Even were this the case, though no experimental proof has been attempted, it would be no argument for the greater exactitude. It would be equally reasonable to object to the determination of (say) sodium sulphate in a solution by evaporation, because the residue weighed does not represent the hydrates which occur in the solution. The method adopted by the Society of Public Analysts must also be rejected, as constancy of weight is not attained, and the residue shows marked browning. Of methods which I have found to comply with the conditions stated above I may mention that of taking about one gram of milk and evaporating in a large platinum basin with constant agitation of the basin while evaporating, to spread the milk over a large surface, and that of evaporation on some substance which largely subdivided the milk. Of these substances I give the preference to asbestos, on account of the fineness of the fibers, and the ease with which it can be reduced to constant weight which does not vary during the experiment. It must be borne in mind, however, that a very finely divided substance condenses more air on its surface than one which is of larger grain; and if accuracy is desired to the second decimal place or beyond all weighings must be made in vacuo. I mention this as milk analyses are frequently stated to the third decimal place, and the analyst may be therefore presumed to have desired an accuracy to the second decimal place. I am not in favor of enclosing the substance on which the milk is placed in a vessel of glass, as this is more liable to change in weight than platinum, and the same remark applies with more force to any connections of cork or India-rubber that may be included in the weighed portions of the apparatus. I do not see a way of proving the accuracy of the estimation of total solids other than the combined evidence of the attainment of constant weight, absence of apparent decomposition, the comparatively near agreement of total solids estimated with that deduced from the fat and specific gravity by an appropriate formula, and the near agreement to 100 per cent. of complete analyses. The evidence afforded by the two latter methods of those I have selected as the most reliable methods, I propose to give here. The probable error of specific gravity determinations is in my experiments ±0.00006, which would produce a probable error in the fat calculated of ±0.015 per cent. Three series of fat determinations gave:

		Per cent.	Experiments.
1.	Adams method	± 0.031	67
2.	Werner-Schmid method	± 0.040	19
3.	Both methods compared	± 0.036	15

The total probable error of these three series is 0.035 per cent. The probable error of total solid estimation is from the results of eighty-one experiments ± 0.021 per cent.

Assuming that the combined probable error of the three series is the square root of the sum of the squares of the three probable errors, this stands at ± 0.043 per cent. The probable error between estimated and calculated fat is ± 0.067 in 132 experiments (using the formula which is best suited to the results), and this gives a probable error of ± 0.043 per cent. of fat or of ± 0.0002 in the density for the variations due to differences of composition of the solids not fat, and for Recknagel's phenomenon; this certainly does not exceed my estimate of the error.

This method of calculating the accuracy of total solid estimation is only of service in showing that the method gives constant results, as we do not know the true formula for calculating the fat, it being deduced from the results themselves.

As evidence of accuracy shown by a near agreement to 100 per cent. in complete analyses, it may be stated that analyses add up to 99.8 per cent. when acidity, basic constituents, and salts other than the ash are not estimated; and the deficiency of 0.2 per cent. is, I conclude, a near approximation to the amount contained in milk. The estimations I have made give on an average about 0.05 per cent. of bases in milk and about 0.05 per cent. for the salts not included in the weight of the ash; and as the milks were fresh when analyzed 0.1 per cent. is a fair approximation to the amount of the lactic acid. In one or two more complete analyses the totals have been between 99.9 and 100. I append five specimen analyses:

Water	89.46	86.89	90.55	87.22	87.14
Fat	1.44	3.99	0.27	4.36	4.49
Sugar	4.76	5.48	4.74	4.18	4.17
Casein	3.21	2.07	3.45	2.76	2.82
Albumen		0.19		0.41	0.42
Albumoses		0.30			
Bases	0.05	0.16			
Lactic acid	0.17	0.20			
Ash	0.76	0.59	0.78	0.78	0.78
Total	99.85	99.87	99.79	99.71	99.82

This last method is not a very satisfactory one for proving the correctness of the total solid estimation, as it is dependent on the assumed correctness of all the other determinations, and especially on the exactitude of the deficiency. Reviewing the whole of the evidence, I am on the whole inclined to conclude that the method I have adopted (Babcock's) is not affected by any serious source of error. It may possibly give too high results for total solids and too low results for water, as I find that by evaporation in vacuo, I obtain slightly higher results than at 100° C. but I see no way of proving that this is not due to incomplete evaporation.

As the two determinations, total solids and fat, and by difference, solids not fat, are those which are chiefly relied upon for judging the purity of milk, a few remarks on the accuracy with which conclusions can be drawn, will not be out of place here. The most widely known limits for pure milk are those of the British Society of Public Analysts, *viz.*, 3 per cent. of fat and 8.5 per cent. of solids not fat. These were originally intended to apply to British dairy cows which are almost exclusively shorthorns, and for this cow the limits are reasonable. For breeds such as the Channel Island cattle they would be too low, while, for instance, for Holstein cows they would be in many instances too high. Even taking shorthorns the limits are in rare cases overstepped. In the milk of single cows I have records of fat as low as 2.0 per cent. and solids not fat down to 7.7 per cent. in genuine samples. It would be manifestly unfair for a chemist to swear that every sample giving 2.0 per cent. of fat or 7.7 per cent. of solids not fat was genuine, merely because one genuine sample out of many thousands examined gave such figures, and equally so to condemn every sample that was just below the limits adopted. With regard to low percentages of fat I see no way at present of discriminating between genuine milk low in fat, and milk from which part of the fat has been abstracted. I am not without hope that this may be accomplished. The size of globules, and the proportion of those of large to those of small size may afford a means to this end, and as cream undoubtedly contains a higher proportionate content of albuminoid, it is possible that an estimation of a deficiency of this in the milk may afford evidence of fat-abstraction. I have no evidence to offer on this point, but put forward the suggestions for the consideration of the Congress.

With regard to low solids not fat, much evidence can be obtained from a fuller examination. The whole of my experience goes to show that genuine milks low in solids not fat never furnish an ash of less than 0.7 per cent., while the majority of watered milks give an ash below that figure. Further the excess of ash in genuine milks is not due to chlorides or any water-soluble substance, but to insoluble phosphates. The ash of milk is neutral, is entirely soluble in dilute acids, and contains no boric nor carbonic acids. I have not found the nitrogen in genuine milks to fall below 0.5 per cent. A curious coincidence is that the percentages of nitrogen and insoluble ash are nearly the same in milk. I find an average of 0.531 per cent. of nitrogen and 0.530 of insoluble ash, with extreme differences of 0.02 per cent.

As many waters contain nitric acid, which I have never found in genuine milk, the diphenylamine test for nitrates is of service in deciding whether a given sample is adulterated. I curdle the milk by heating to near 100° C. and adding a small quantity of acetic acid, and filter the serum. I place a little diphenylamine in a porcelain basin and add one cc. of pure sulphuric acid, and allow a few drops of the serum to trickle down the sides of the basin over the surface of the acid. If nitric acid be present a blue coloration is developed in ten minutes round the edges. I have detected five per cent. of water in milk by this test.

If I find a milk of (say) eight per cent. of solids not fat, and I find in it nitric acid, and the ash falls below 0.7 per cent. and the nitrogen below 0.5 per cent., I condemn it; while if there is no evidence of nitric acid, and the ash is above 0.7 per cent., and the nitrogen above 0.5 per cent., and I find no extraneous body to account for the excess of ash and nitrogen, I decline to certify that it is watered, and should state that there was the strongest probability of its being genuine. I may cite examples:

Specific gravity	1.0280	1.0295	1.0290	1.0290	1.0285	1.0285	1.0290
Total solids	10.63	11.62	11.31	11.37	11.36	11.99	11.34
Fat	2.72	3.47	3.22	3.25	3.30	3.87	3.20
Ash	0.62	0.64	0.76	0.72	0.72	0.71	0.72
Solids not fat	7.91	8.15	8.09	8.12	8.06	8.12	8.14
Nitric acid	trace	trace	none	none	none	none	none
Conclusion	watered	watered	gen.	gen.	gen.	gen.	gen.

I did not determine the nitric acid in these samples, as other evidence was forthcoming to assist my conclusions.

The season of the year should also be considered. Thus in England the recent drought in June and July has caused the milk to be of poorer quality than has hitherto been recorded. It would be advisable in every country to establish a Government Laboratory to study the mensal fluctuations of the composition of milk, and to communicate the results to chemists charged with the working of the adulteration acts. In England no such laboratory exists but the function is very partially filled by a private dairy company of whose laboratory I have the honor to be in charge, and on numerous occasions I and my predecessor have been consulted by public analysts. The apparent disadvantages of a trading company under the supervision of the adulteration act performing a function properly belonging to the state, only shows the necessity of the establishment of Government Dairy Laboratories. Other countries are more fortunate than England in this respect, and I have no doubt that representatives of those countries will testify to the usefulness of these laboratories.

Estimation of Milk Sugar.—Vieth's modification of Wiley's method of polarization (*Analyst, 1888*, 63) gives results which agree well with the gravimetric method of estimation by Fehling's solution. I am in the habit of making an estimation of the copper oxide reduced by a known weight of pure milk sugar, as nearly as possible equal to that in the quantity of milk taken for analysis, performing the two estimations under the same conditions.

The probable error of each estimation, and of the two estimations together was found to be ± 0.06 per cent. The work of Wiley on the polarization of milk sugar is so conclusive that it is not necessary to search for further proof of accuracy, but this determination may be accepted as one which can be depended upon.

Estimation of Albuminoids.—Chemists are far from being agreed upon the albuminoids existing in milk, thus the following chemists give as follows:

Bechamp	Caseinates, albuminates and galactozymase.
Biel	Syntonin.
Blyth	Casein, albumen, galactin, lactochrome (nuclein?).
Danilewsky	Caseo-protalbin and caseo-albumen (nucleo-protalbin and nucleo-albumen) and six other albuminoids.
Duclaux	Only casein.
Hammersten ...	Casein and albumen only.
Palm	Hemialbumose.
Sebelien	Globulin.

I have no hesitation in rejecting Duclaux's view that there is only one albuminoid, casein, in milk, as two certainly, having distinct properties and inconvertible, have been proved to exist in milk.

Hammersten and later Chittenden have disposed of Danilewsky's view, and with this the existence of lactoprotein, which is accepted by many, galactin, nuclein, and hemialbumose, becomes an untenable theory; as Blyth alleges the presence of only 0.01 per cent. of lactochrome in milk this body may be neglected. We are then reduced to casein, albumen, globulin, syntonin, and galactozymase. The first two are almost universally accepted; and as Halliburton now admits the correctness of Sebelien's observation that globulin exists in traces in milk, this may also be accepted: From an analytical point of view its presence can almost be neglected, as the amount present in normal milk is very small. The existence of syntonin and galactozymase cannot be considered as fully established.

I am inclined to favor Bechamp's view that casein and albumen exist in milk as salts, chiefly on account of the behavior of neutral milk with copper salts. I find that if milk be neutralized the albuminoids are completely precipitated by a solution of copper sulphate; and this would not be the case were there no base for the sulphuric acid of the copper sulphate to combine with. Soldner's work on the salts of milk (*Landw. Vers. Stat.*, **35**, 351) offers some confirmation to this theory, as he finds in milk more base than will combine with all the acid that has been found. He attributes this excess of alkali to the fact that organic salts other than citrates occur in milk, but these have not yet been found (if we neglect Bechamp's acetic acid). Many of the reactions of the albuminoids in milk resemble those of casein or albumen dissolved in dilute alkali, for instance the behavior of heat on milk.

In the analysis of milk I regard the albuminoid precipitated by a saturated solution of magnesium sulphate as casein (including globulin), and the further precipitate by tannin or phosphotungstic acid in the filtrate from the casein as albumen (following Sebelien). If I have reason to suspect that from some change in the milk albumoses are present I separate the albumen by heating after slight acidification and precipitate by tannin. This precipitate I regard as albumoses; but the determination is not a very exact one. The precipitate produced by adding sulphate of copper to the neutral milk I regard as casein and albumen and, following Ritthausen, designate this total proteids. A second determination of albumoses may be made in the filtrate from this; but the accuracy of this determination is questionable. I have only estimated albumoses in whey and mixtures of this with milk; and the two albumose determinations have been fairly concordant. I also calculate albuminoids from the total nitrogen, a method which may be expected to give results which are slightly too high.

I assume that both casein and albumen contain 15.7 per cent. of nitrogen. For albumen I believe that this is the correct figure, as both my own determinations and those of other observers are very close to that figure. For casein Hammersten gives 15.65 and Chittenden and Painter 15.91, so it is probable that no very great error is committed by taking it at 15.7 per cent.

In ten experiments the average difference between casein and albumen, nitrogen and total nitrogen is 0.02 per cent. with extremes of 0.00 and 0.05. The average difference between total proteids by copper sulphate method and total proteids by calculation from total nitrogen in five experiments is 0.17 per cent., with extremes of 0.10 and 0.27. In one experiment the casein and albumen together summed up to 0.21 per cent. less than the total proteids by copper; but in this case the total proteids by copper showed the minimum difference from the total from nitrogen and the casein and albumen nitrogen was 0.05 per cent. below the total nitrogen. The above figures show the error incidental to albuminoid estimations; but at the same time, though few in number, lead me to believe that the methods of albuminoid determination that I have adopted give fairly good results. A full description of the mode of working that I adopt is to be found in a paper by Mr. Boseley and myself in the *Analyst* for July of this year and need not be reproduced here. Bases I calculate in milk by multiplying the non-albuminoid nitrogen by 3.2; and this determination is of very questionable accuracy.

The estimation of ash calls for no remark. I may, however, remark that the ash does not represent the salts which exist in milk, as it contains phosphates obtained by the combustion of the casein, and does not include citrates which occur. These two errors tend to compensate each other, though probably not entirely.

I do not propose to touch on the estimation of the small amounts of other bodies that have been described in milk, as I feel that our knowledge is not far enough advanced to permit of this, and in presenting this paper to the Congress I can only say that it is very incomplete and is to be considered more as a nucleus for discussion, and, I hope, concerted investigation than an exhaustive resumé of the subject.

In conclusion, I think that the methods that I have touched upon for the estimation of total solids and water, fat, ash, milk sugar, casein, albumen, and total proteids are not liable to any great error, and further that we are enabled to detect watering of milk with fair exactitude. The detection of fat abstraction is not so satisfactory.

PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

Ore Separators, Etc.—504,665, September 5, Bradford, H., ore separating machine. 505,169,-505,412, September 19, McGlew, T., ore concentrator. 504,931, September 12, Monell, I. F., ore separator and concentrator. 504,923, September 12, Humphries, D. W., concentrator. 504,678, September 5, Fuller, W. M., amalgamator. 504,859, September 12, Boss, M. P., amalgamating pan. 504,508, September 5, Wiswell, J. C., amalgamating machine. 504,689, September 5, Albrecht, H. S., disintegrator for ores, etc. 504,548, September 5, Bauer, T., and Mendheim, G., coke-oven. 505,112, September 19, Ludwig, O., smelting furnace. 505,538, September 26, Sheedy, D., and Iles, M. W., blast furnace. 505,549, September 26, Iles, M. W., tuyere. 505,551, 505,552, September 26, Iles, M. W., process of and apparatus for treating slag. 504,666, September 5, Bradford H., process of concentrating ores by gravity, on a shallow basin over which water flows, the table being jarred to facilitate separation.

Gold and Silver.—504,706, September 12, Calhoun, H., extraction of metal from ores; roasting in presence of carbon and ammonium chloride.

Iron and Steel.—505,132, September 19, Sague, S. A., manufacture of sheet iron or steel, apparatus for. 505,131, September 19, Sague, S. A., galvanizing sheet metal. 504,322, September 5, Brustlein, H. A., mold for casting ingots. 505,728, September 26, Shaw, A. J., soaking pit for ingots.

Zinc.—505,408, September 19, Moore, G. E., willemite and franklinite, in limestone gangue, are calcined in non-reducing atmosphere, the lime