ANALYTICAL AND TECHNICAL CONTRIBUTIONS

THE ANALYSIS OF CANNED RICE PUDDINGS

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The methods of calculation of the composition of milk puddings given by Dalley & Wood[1] are no doubt standard practice for foods containing a mixture of ingredients. The results of such calculations are subject to two sources of error. The first may be called analytical error due to lack of accuracy or lack of precision or both. The second may be called factor error because it depends on the accuracy of the factors used in converting the constituent determined by analysis to the ingredient contained in the mixed food. If these two sources of possible error are considered some of the problems posed by Dalley & Wood are solved.

The authors' methods for determining lactose are "well established and known to give accurate results." The same could be said of the other determinations but we can fairly ask - how accurate is an accurate result? For example, Dalley & Wood are comparing the milk content calculated from N x 200 with the milk content from lactose x 21.72. Thus an error of ± 0.005% in the nitrogen gives an error of ± 1.0% in milk, and an error of ± 0.05% in the lactose gives an error of ± 1.1% in the milk. To take a hypothetical example, if we are prepared to consider 0.500% and 0.505% reasonable agreement for duplicate nitrogen determinations and 3.50% and 3.55% reasonable for duplicate lactose determinations, then we must also accept that the difference between the two calculations of milk may be 2%. No doubt everyone will have their own ideas on standards of acceptance for duplicate analyses.

Factors are also subject to errors. There is no doubt a true average composition for the ingredients used. If we choose the average figure to calculate the factor there will be no systematic difference between the two assessments but there will be variation due to variation of the composition around the average. If we choose the wrong factor then systematic difference will occur. Dalley & Wood point out that a change of 0.1% in the nitrogen content of rice can lead to a difference of

2% in the assessment of milk from milk nitrogen but before they postulate that "the lactose content of the rice pudding is almost always too low. . . " they should surely consider that the factor chosen for nitrogen in rice might be too low. This would make the milk assessment from nitrogen too high. It may be that the rice samples analysed were used in the puddings which have analyses quoted but this will not always be true. It so happens that I have used a factor of 1.15% nitrogen in rice. This was taken from figures in the references quoted by Dalley & Wood and from a few analyses done some years ago. Either or both figures of 1.0 and 1.15 may be wrong but as both are individual assessments of substantially the same figures it seems that an error of $\pm$ 0.1% nitrogen in an individual sample of rice would be a reasonable assumption. This gives an error of $\pm$ 2% in the milk calculated from nitrogen.

It would be more important in this context if one of these estimates had a systematic error. For example, if 1.15 is the correct figure then the use of 1.0 would lead to an overestimate of the milk by 3.0%.

Dalley & Wood quote literature figures of 6.2% to 8.1% for protein and say this is equivalent to 0.99 - 1.30% of nitrogen. This is true if the protein has been calculated as N x 6.25. However if the more usual factor for cereal protein of 5.7 had been used, the nitrogen equivalent is 1.09% - 1.42%. McCance & Widdowson[2] certainly use 5.7, but Kent-Jones & Amos[3] do not specify the factor in the table giving composition of rice - however, in another part of the book, they do suggest that 5.7 should be used for cereals.

If 5.7 is accepted as the correct factor for rice protein and 6.38 for milk protein, then for a product such as rice pudding the conventional 6.25 factor is nearer the truth than 6.38. Accepting the assessment of rice nitrogen and milk nitrogen given by Dalley & Wood, the true factors would be 6.26, 6.27, 6.27, 6.24 and 6.26. However, this does not affect the calculation of milk to any extent.

In considering milk factors it is fair to assume that bulked milk is used and this will be of fairly constant composition. Probably the same assumption can be made for dried or condensed milk - I deal with the abnormal composition of dried milk later. Possibly a little seasonal variation will occur but this should not be serious in the context of testing agreement between two methods of assessment over a large number of samples. It is possible to use the average composition of milk to obtain factors but Dalley & Wood have relied on the Vieth ratio

and in so doing make two assumptions. One of these assumptions is of very doubtful validity and the other is wrong.

Various textbooks refer to the Vieth ratio as Lactose : Protein : Ash = 13 : 9 : 2. However, in the 1920 edition of his "Dairy Chemistry" Richmond[4] gave 12.7 : 9.1 : 2 and considered that he agreed with Vieth. If we take Richmond's figures as correct we find that the use of the 13 : 9 : 2 ratio leads to an overestimate of the milk assessed from nitrogen by 1.95% of the milk present and an underestimate of milk assessed from lactose by 1.5% of the milk present. Therefore, we would expect to find a systematic difference between the two estimates of 3.45% of the milk present. With 80 - 85% milk in rice puddings this gives us an expected systematic difference of 2.7 - 2.9%. If then Richmond's figures are correct, the findings of Dalley & Wood are to be expected. It seems that Dalley & Wood, in assuming the Vieth ratio to be 13.0 : 9.0 : 2.0 have introduced a systematic error.

The second assumption is an extension of the Vieth ratio to include SNF : Lactose and SNF:protein. In doing this, Dalley & Wood have assumed that in milk :

Lactose + Protein + Ash = SNF

This is not true; the sum of these constituents in milk is less than the Total solids - Fat by about 0.15%. Neglect of this factor causes an underestimate of the milk by about 1.5%. By a fortunate chance this error nearly balances the overestimate due to the use of $^{24}/_{9}$ ratio rather than $^{23.8}/_{9.1}$ for the protein assessment. Halliday, Burdon & Lamont[5] pointed to the possibility of this error but they also allowed for water of hydration in the lactose which is not relevant in this context.

There are better methods of assessing the errors involved in calculations such as these but if we accept the order of errors given above we get :

Source of Error	Error in Milk Calculated (a) from Lactose	(b) from Nitrogen
Analysis	$\pm$ 1.1	$\pm$ 1.0
Rice factor	0	$\pm$ 2.0
Milk factor (85% Milk)	- 1.3	+ 1.7
Neglect of other SNF components	- 1.5	- 1.5
	- 2.8 $\pm$ 1.1	+ 0.2 $\pm$ 3.0

Giving nitrogen assessment - lactose assessment as 3.0 $\pm$ 4.1.

If the rice nitrogen factor is taken as 1.15 instead of the 1.0 used by Dalley & Wood, we find the error in the milk calculated from nitrogen is + 3.0 ± 2.0, giving nitrogen assessment - lactose assessment as : + 6.0 ± 4.1. Thus, from the systematic errors considered, one would expect the milk assessment from nitrogen to be 6% higher than the milk assessed from lactose. Superimposed on this is a possible ± 4.1% due to random errors in the analysis and the rice factor. If these figures are accepted it means that one would expect Dalley & Wood's method to give a milk assessment from nitrogen between 1.9% and 10.1% higher than that assessed from lactose.

The corresponding differences recorded by Dalley & Wood are :-

Table (1)	(using 8.5% N.F.S. for milk)	± 7.3%
Table (2)	Can A	± 3.8%
	Can B	± 2.4%
	Can C	± 9.7%
	Can D	± 12.0%

McVey and McMillin[6] have used CaO as a means of estimating skim milk powder in sausages. They found dried skim milk to contain 1.84% CaO (1.72 - 1.97). Allowing 5% for fat and moisture this gives 1.92% on dry SNF. Richmond's Dairy Chemistry[7] also lists figures which, recalculated to dry fat free solids, give 2.01%, 2.05% and 1.95%. Since rice only contains about 0.03% of CaO the determination of CaO can give a valuable additional assessment of milk.

The presence of small quantities of water in rice pudding is clearly not easy to prove. The manufacturers can be sure only if :-

(a) no water is added either deliberately or by washing or soaking the rice.

(b) they are sure that the milk used is free from added water. It should be remembered that a freezing point of - 0.530° C probably means the presence of 2.5% of water in a bulked milk and this is equivalent to 2% water in a rice pudding.

and (c) when reconstituted milk, or its equivalent, is used, the amount of water added is not more than that required to give milk of normal composition. To take an example, if we mix one pint of dried full cream milk and seven parts of water, we shall

obtain eight parts of a fluid closely resembling the composition of the liquid milk from which the dry product was made. The manufacturer, however, may in error reconstitute the dried milk with a higher proportion of water.

In a similar way it has to be decided whether or not New Zealand dried milk of composition given by Halliday et al[5] is genuine. One would be highly suspicious if faced with a sample of dried milk of this composition. It is attractive to dismiss this as milk of abnormal composition. Such abnormality in Vieth ratio is certainly possible in milk from a single cow or even a single herd but dried milk will be a product of bulked milk and there appears to be no published evidence that cows' milk from different areas of the world is so different.

There is more important evidence in the one full analysis given where 84% of the protein is casein. The normal figure is 76%. When milk has such an abnormal Vieth ratio as is given by this dried milk, the proportion of casein falls in relation to the other proteins. In the example given the casein is high. It seems, therefore, that this product is most unlikely to have been produced from abnormal milk of cows.

If we consider the possibility that these were not genuine dried milks, the figures can be explained. Dried buttermilk made from soured cream could explain the lactose : protein ratio but the acidity or the ash would then be high. The simplest explanation is the addition of rennet casein. If this is considered quantitatively we find :-

(i) Assuming 76% of the protein in normal milk is casein, the proportion of casein in the sample can be explained by :-

Milk protein	29.0%
Added Casein protein	14.3%

(ii) Assuming a Vieth ratio of 12.7 : 9.1 : 2 for normal milk and calculation from lactose we get :-

Milk protein	29.2%
Added casein protein	14.1%

Similar but smaller effects come into the fat calculations. If we are to argue about the significance of milk containing 3.64% of fat and only 8.5% of SNF we must first allow for the facts that rice contains about 0.5% of fat and that the fat determination is subject to some error.

Summary

1. A critical examination of the paper by Dalley & Wood shows that a discrepancy between milk calculated from lactose and from nitrogen is to be expected because the factors used lead to a systematic error.

2. Some possible means of introducing water into canned rice puddings are suggested.

3. An explanation of the results of analyses of dried milk by Halliday et al. is suggested.

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2. The Composition of Foods, 1960, pp. 26, 27.
3. Modern Cereal Chemistry, 1957, pp. 125 - 127.
4. Quoted by Davies, H.L., Dairy Chemistry, p. 49.
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6. McVey & McMillin, J.A.O.A.C., 1940, 23, 811.
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8. Dairy Chemistry, Davies, H.L., p. 42.

THE DETERMINATION OF TOTAL ALKALOIDS IN CHOCOLATE CAKE AND COCOA

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With the recent publication of the code of practice for the use of the word "chocolate" in flour confectionery, it is perhaps opportune to give details of a comparatively rapid method for the estimation of total alkaloids from which an assessment of the proportion of dry fat free cocoa in flour confectionery may be made.

The well known Moir and Hinks[1] method is the most common means of estimating theobromine but although giving accurate results, it is somewhat time consuming. Miles[2] suggested the use of U.V. absorption measurements for this estimation, separation of the theobromine being obtained by adsorption on to a fuller's earth column followed by elution with

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sodium hydroxide. In applying this method to flour confectionery, it was soon apparent that the rate of flow through the column was extremely slow even when kieselguhr was added as diluent. It was found, however, that the column technique was unnecessary, reasonably complete adsorption of the alkaloid being effected by shaking the solution with a small amount of the fuller's earth. Separation by centrifuging and washing, and elution by shaking with a known volume of sodium hydroxide gave satisfactory recoveries. Whilst the investigations leading to the final method were by no means exhaustive, discussion of some of the considerations leading to the proposed technique is given below.

Extraction of alkaloids from the sample

Numerous methods have been proposed for extracting the alkaloids because it has been claimed that (a) theobromine is very sparingly soluble and (b) glucosidic compounds retain the theobromine tenaciously in an insoluble form.

The solubility of theobromine in water is given[3] as 0.03% in the cold and 0.67% at boiling point. As the proportion of alkaloid is quite low in flour confectionery, solubility does not seem to be a limiting factor.

The presence of glucosidic compounds has not been convincingly established and although the recommended treatment with magnesium oxide designed to hydrolyse these compounds was tried originally, its use was abandoned when it was found that reduced recoveries were obtained with its use - see Table I. A direct extraction with hot water is therefore recommended, followed by simple clarification with zinc and ferrocyanide.

Table I	Theobromine found
Moir and Hinks method	0.201%
Extraction with MgO	0.150%
Extraction with water only	0.188%

Adsorption on to fuller's earth

Shaking of clarified extract with fuller's earth in a centrifuge tube was found to be sufficient to remove over 99% of the theobromine from solution. Increase in the amount of fuller's earth decreased the recovery in the whole process, possibly due to increased difficulty of elution with sodium hydroxide, e.g. :-

Table II

Weight of fuller's earth	Theobromine found
0.5 g	0.234%
1.0 g	0.227%
1.5 g	0.219%
2.0 g	0.215%

Elution with sodium hydroxide

The original method used was to mix with repeated 10 ml quantities of N/10 NaOH, centrifuging and decanting between each addition and making up to 50 ml. Subsequently the simple technique of transferring washed fuller's earth to a 50 ml volumetric flask with N/10 NaOH and diluting to the mark with the same reagent was used. Our results indicated that vigorous shaking for 2 minutes was effective in eluting 99 per cent of theobromine added.

Measurement by U.V. absorption

Theobromine has an U.V. absorption maximum within the range 270 - 275 mμ in both acid and alkaline media and direct measurement of the N/10 NaOH eluate was possible. However, the use of an alkaline solution in silica cells was preferably avoided and in addition, absorption of carbon dioxide from the air to give sodium carbonate might affect the U.V. absorption, particularly below 250 mμ. It was therefore decided to measure the U.V. absorption in N/10 HCl, some additional NaCl being derived from the neutralisation of the NaOH used for elution.

The following final method was therefore proposed :-

Reagents

1. Zinc acetate solution; 21.9 g Zinc acetate + 3.0 ml acetic acid in 100 ml.
2. Potassium ferrocyanide solution; 10.6 % w/v in water.
3. Fuller's Earth, Special for Adsorption (B.D.H. Ltd.)
4. N/10 NaOH.
5. N/1 HCl.

Method

Weigh accurately (to 1 mg) about 1 g of cake-mix or air-dried powdered cake, or about 0.1 g of cocoa, into a 100 ml beaker.

Add 25 ml of distilled water (measured in a cylinder) in small portions, mixing to a smooth paste. Raise to the boil with stirring, taking precautions against frothing, and allow to stand on a waterbath for 15 minutes. Transfer to a 50 ml volumetric flask with water and cool. Pipette 1 ml of zinc acetate solution into the flask, followed by 1 ml of potassium ferrocyanide solution with gentle mixing each time, avoiding inclusion of air bubbles. Dilute to 50 ml and mix well.

Transfer to a centrifuge tube, centrifuge at 2500 r.p.m. for 5 minutes and decant through a No. 4 filter into a clean dry beaker. Pipette 30 ml of filtrate into a dry centrifuge tube containing 0.5 g (± 0.1 g) of fuller's earth and mix thoroughly with a glass rod, finally rinsing the rod with a few ml of water. Centrifuge at 2500 r.p.m. for 5 minutes or until a clear supernatant liquid is obtained and then pour the liquid to waste without disturbing the residue. Add approximately 15 ml of water to the residue and mix with a glass rod; rinse and centrifuge as before. Discard the clear liquid, again avoiding loss of solid.

Transfer the residue of fuller's earth to a dry 50 ml volumetric flask with N/10 NaOH and dilute to the mark with N/10 NaOH. Shake vigorously for 2 minutes. Transfer to a centrifuge tube and centrifuge at 2500 r.p.m. for 10 minutes or until clear. Decant the clear liquid into a dry 100 ml beaker, avoiding any inclusion of fuller's earth. Pipette a 40 ml (or 30 ml if 40 ml are not available) aliquot into a 100 ml volumetric flask, pipette 14 ml (or 13 ml if a 30 ml aliquot was taken) of N/1 HCl, mix, dilute to 100 ml with water and mix well.

Measure the U.V. absorption between 270 mμ and 275 mu at 1 mμ intervals against distilled water, and also that of a 'blank' of 40 ml N/10 NaOH + 14 ml N/1 HCl up to 100 ml. Theobromine has a maximum absorption E(1%, 1 cm) of 548 at 272 mμ and the sample should have a maximum at 272 ± 1 mμ for the assay to be valid.

$$\text{Total Alkaloids } {}^{w}/_{w} = \frac{E(272\ m\mu,\ 1\ cm)\ (\text{sample} - \text{blank}) \times 50 \times 50 \times 100}{548 \times 30 \times \text{aliquot taken} \times \text{wt. taken}}$$

$$= \frac{E(272\ m\mu,\ 1\ cm)\ (\text{sample} - \text{blank})}{\text{Weight taken}} \times 0.38 \text{ for 40 ml aliquot.}$$

$$\text{or } \frac{E(272\ m\mu,\ 1\ cm)\ (\text{sample} - \text{blank})}{\text{Weight taken}} \times 0.51 \text{ for 30 ml aliquot.}$$

Collaborative Trial

The results of an A.P.A. collaborative trial of this method, organised by Mr. A.L. Williams, Public Analyst, Portsmouth, may be summarised as follows:-

	Total alkaloids w/w		
	Mean	No. of determinations	Standard deviation
Cocoa (71.7% dry fat-free matter)			
Moir and Hinks method	1.98	11	0.17
U.V. Absorption method	1.95	15	0.13
Cake			
Moir and Hinks method	0.115	11	0.016
U.V. Absorption method	0.115	16	0.011

Using the mean results the proportion of dry fat-free cocoa found in the cake was :-

Moir and Hinks method	4.17%
U.V. Absorption method	4.23%
Formula of cake required (subject to probably 10% variation in bakery)	4.33%

Conversion Factors

To obtain a measure of the factor for conversion of total alkaloids to dry fat-free cocoa, three commercial samples of cocoa from local bakeries and three retail samples of ordinary cocoa were examined with the following results :-

	% Total alkaloids in dry fat free material		
Commercial cocoa	2.73	2.99	3.11
Retail cocoa	3.25	2.88	3.05

These results, together with the results from the collaborative test, suggest the following factors to convert to dry fat-free cocoa :-

Average dry fat-free cocoa	=	Total alkaloids	x 33.3
Minimum " " " "	=	" "	x 30.8
Maximum " " " "	=	" "	x 38.7

Discussion

Criticisms made by collaborators suggest that -

(a) The type of fuller's earth is important.

(b) Recovery experiments do not always indicate satisfactory recoveries.

(c) The good results obtained may be, to some extent, due to cancellation of errors.

(d) No allowance has been taken of the effect of any caffeine present, although the U.V. spectrum of caffeine is similar to that of theobromine and the effect would be small.

Whilst, therefore, further investigation of the method is desirable in respect of both the actual analytical technique and the factors for conversion to dry fat-free cocoa, the method as used does appear to give a rapid assessment of the cocoa content of flour confectionery with reasonable accuracy.

We are indebted to Mr. A.L. Williams for helpful suggestions and for organisation of the collaborative trial and to Mr. H.H. Bagnall (Birmingham), Mr. F.C. Bullock (Leicester), Mr. A. Houlbrooke (Staffordshire), Mr. J. Markland (Durham), Mr. D.D. Moir (Surrey), Mr. H.E. Monk (Kent), Dr. G.H. Walker (Lancashire) and Mr. E.G. Whittle (Bristol) for their co-operation in the collaborative assays.

References

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2. Miles - Anal. Abs., 1954, 1, 1972.
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THE DETERMINATION OF FREE SALICYLIC ACID IN SOLUBLE ASPIRIN TABLETS

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In a recent survey of soluble aspirin tablets, excessive amounts of free salicylic acid were indicated by the B.P. limit test and repeat determinations gave widely differing results. This method separates the salicylic acid (and aspirin) from the neutralising constituents of the tablets by extraction with chloroform and the free salicylic acid is then estimated after evaporation of the solvent by the colour given with ferric salts. The standard used in the limit test is equivalent to 0.16% free salicylic acid expressed on the aspirin present.

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Results on three typical samples are given below -

	% free salicylic acid expressed on aspirin present						
	1	2	3	4	5	6	7
Sample A	0.14	0.15	0.14	0.93	0.32	0.37	0.31
Sample B	0.31	0.29	0.30	0.95	0.54	0.57	0.53
Sample C	0.22	0.16	0.21	0.09	0.14	0.11	0.11

(The colours developed were measured in a Spectrophotometer (Uvispek) using 4 cm cells at 525 mμ.)

In all these assays, the B.P.method was used except that the method of evaporation was varied to include -

(a) Official B.P. method:- Spontaneous evaporation at room temperature.

(b) Rapid evaporation by blowing warm air (hair dryer).

(c) Rapid evaporation by drawing dried air through liquid at approximately 30° C.

None of these methods gave consistent results. Edwards et al [1] noted that aspirin in aqueous solution hydrolysed to salicylic acid, giving high results in the tests for free salicylic acid in aspirin preparations. They corrected for this effect by making several observations over timed intervals and extrapolating the results to zero time. Although predominantly non-aqueous, observations on chloroform solutions of specially purified aspirin indicated that slow hydrolysis occurred, and a completely water-free process appeared desirable.

The U.V. absorption curves of salicylic acid and purified aspirin in chloroform suggested that determination of the absorption at 320 mμ should give a sufficiently sensitive measure of salicylic acid even in the presence of 1 per cent aspirin. However, measurements on chloroform solutions of aspirin at 320 mμ showed a steady increase in U.V. absorption, presumably due to slow hydrolysis by moisture in the chloroform.

Attempts to dry the chloroform by a variety of desiccants were not completely successful. Although the rate of hydrolysis could be reduced by drying with magnesium perchlorate, sufficient of the chemical dissolved in the chloroform to give turbidities during measurement, which were difficult to avoid.

The alternative approach of suppressing the rate of hydrolysis by the presence of excess of acetic acid was tried and tests

with various mixtures of acetic acid and chloroform indicated that a reduction in the speed of hydrolysis is obtained by increasing the acetic acid concentration. Even glacial acetic acid, however, allowed very slow hydrolysis to occur, but the rate is sufficiently reduced to allow measurements to be made up to ten minutes after addition of solvent. It is interesting to note that the addition of acetic acid to chloroform containing magnesium perchlorate produced a decrease in U.V. absorption with time, presumably due to acetylation of free salicylic acid promoted by the presence of the dehydrating agent.

Proposed Technique

Weigh into a clean dry glass-stoppered test tube, approximately 0.2 g of finely powdered tablet. Add a measured amount of glacial acetic acid to give an approximately 1 per cent solution of aspirin, and shake vigorously for 1 minute. Filter rapidly through a clean dry sintered glass crucible (porosity 4) into a clean dry test tube with the aid of vacuum, and measure the U.V. absorption as rapidly as possible, in a 1 cm cell at 320 mμ, using glacial acetic acid in a "blank" cell. Calculate the amount of salicylic acid present from a calibration graph previously prepared from salicylic acid dissolved in acetic acid. A correction should be applied to the final result to allow for the slight U.V. absorption of aspirin at 320 mμ. This was found to be 0.02% as salicylic acid on a specimen of aspirin recrystallised from alcohol, which gave no colour with ferric salts.

In this process, it is important that the wavelength should be set as accurately as possible, since the measurement is being made on a very steep part of the curve. In addition, fine grinding of the tablets is essential to enable rapid extraction of salicylic acid to be made.

The graph gives a typical calibration curve. Calculation of the best straight line gives the formula :-

$$\% \text{ Free salicylic acid (assuming 1\% aspirin)} = E(320\ m\mu,\ 1\ cm) \times 0.502$$

expressed on the aspirin present.

From this result, deduct 0.02% to give corrected figure (see above). Using this method, the three samples mentioned previously gave the following results :-

	% Salicylic acid on aspirin present			
	1	2	3	4
Sample A	0.17	0.15	0.16	0.17
Sample B	0.23	0.20	0.21	
Sample C	0.05	0.05		

Comparison with the previous results shows that (a) they are more consistent; (b) generally the U.V. method gives lower results. The proposed technique is not ideal because corrosion of the cell compartment by acetic acid vapour is a possible danger. We have shown it to give more reproducible results than the B.P method, but until a more suitable solvent is found, it can only be considered as an interim technique.

Reference

1. Edwards L.J., Gore D.N., Rapson H.D.C. and Taylor M.P. J. Pharm. Pharmacol., 1955, 7, 892.

COPPER IN ANIMAL FEEDING STUFFS

by Joan Peden.
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During the latter half of 1961, concern was felt in Somerset regarding the increasing number of additives of various kinds, such as vitamins, minerals, antibiotics, etc., which some manufacturers were known to be mixing into their feeding stuffs. This was apparently being done without, in many cases, any information being supplied to the purchaser concerning the nature or amount of the addition. Some feeding stuffs bore mysterious letters of the alphabet after their title, such as A.B, H/C, or A.V, respectively denoting the presence of antibiotics, high copper, or added vitamins, but it was suspected that very many more did not make even this elementary form of declaration.

For various reasons, it was decided to concentrate on copper determinations; for one thing, there was reason to believe that addition of this metal was being made to many of the pig foods and it was also found, not surprisingly, in a sample of Anti-teart Cubes. Estimations were therefore made as a routine on all feeding stuffs submitted under the Act from the beginning of 1962.

For some time results were low, the first seventeen samples, with one exception, giving proportions of copper below 20 p.p.m. Then a sample of Creep Feed was discovered to contain 150 p.p.m. of copper. Even at this early stage, such a result was obviously not of natural origin and was thought unlikely to be due to accidental contamination. Since a regular veterinary dose of copper to young pigs could be of the order of 250 p.p.m. it could not be stated that such a dose in a feed constituted a danger to health, but there was, of course, the possibility that regular ingestion of this feed, containing

undeclared copper which was unsuspected by the farmer, could well add up to an undesirable intake if the pigs were receiving copper medicinally from some other source.

It was therefore decided to report the copper content on the usual certificate, with the following comment:-

> "I am further of the opinion that the amount of copper found is in excess of that normally associated with the ingredients, that its presence should be declared and that it is a potentially deleterious ingredient."

It was hoped that, presented with this opinion, the manufacturer might be induced to make the required declaration of additive as a result and, happily, it has succeeded in all cases to date.

The average value for copper content, without obvious addition, appeared to lie around 20 p.p.m., and it was accordingly decided that a generous maximum allowance would be 50 p.p.m. before any critical comment was made. At the end of the year, in fact, the average content for the 130 samples not criticised in this way was just under 23 p.p.m. copper, so that those in the late 40s were decidedly suspect, but nevertheless passed. Of the remaining 26 samples found to contain copper in excess of 50 p.p.m. copper was declared on the statement of four, the proportions lying between 125 and 175 p.p.m., and these were passed as satisfactory for this reason. As a matter of interest, three were in fair agreement with the statement, but one contained only 85 p.p.m. on a declared 170 p.p.m. However, it was thought a little unfair to rush to the other extreme and take any action for a deficiency of added copper.

The Anti-teart Cubes before-mentioned were also passed, as were two Dairy Nuts with copper of 59 and 70 p.p.m. Towards the end of the year, slight excesses over the limit for poultry and cattle feeds were tolerated, as the danger is less than it is for pigs and sheep.

The remaining 19 samples were nearly all pig foods. Three contained 50-60 p.p.m., three 60-70 p.p.m., one 85 p.p.m., two 110 p.p.m., five 120-150 p.p.m., two 150-200 p.p.m., and three over 200 p.p.m. copper.

The distribution of the results for the 130 samples with less than 50 p.p.m copper is given overleaf.

No. of samples	Copper (p.p.m.)
Nil.	Less than 5
11	5-10
31	10-15
28	15-20
21	20-25
12	25-30
9	30-35
6	35-40
6	40-45
6	45-50

DRUGS AND THE FOOD AND DRUGS ACT

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Warrington, Lancs.)

(The following article is reprinted by permission from the County Councils Gazette.)

Under Section 2 of the Food and Drugs Act, 1955, it is an offence to sell to the prejudice of the purchaser any food or drug which is not of the nature or of the substance or of the quality of the food or drug demanded. Ever since the first effective Sale of Food and Drugs Act was passed in 1875, it has been the duty of the administering authorities to safeguard the interests of the purchaser of drugs no less than the purchaser of food. Within the last few years much publicity has been given to the suggestion that the sampling and testing of drugs should be removed from the Food and Drugs Act and vested in some central authority or Government department.

With few exceptions the advocates of this policy are directly or indirectly connected with the pharmaceutical industry. Thus, at the British Pharmaceutical Conference in 1961, the Chairman proposed that the sampling and analysis of drugs and prescriptions should be administered on a nation-wide scale by regional laboratories established for this purpose, and set up under the direct control of the Ministry of Health. At that time it was already known that the Ministry had appointed an inter-departmental Working Party to consider the law in relation to the sale of drugs and had, in fact, invited interested organisations, including the local authorities Associations, to submit

comments. To the advocates of centralisation, therefore, the time was opportune to press for a complete reorganisation of drug testing. Accordingly, during the past two years, quite a large volume of correspondence on this subject has appeared in technical journals. Unfortunately, it has revealed a good deal of confusion of thought and some lack of knowledge of the working of the Food and Drugs Act.

It is not surprising to find this shared by the ordinary man in the street. The unfortunate thalidomide incident has led to a demand from all sections of the community for the more adequate clinical testing of new drugs - a different thing altogether from the testing of drugs under the Food and Drugs Act, the object of which is to see that accepted drugs conform to well-known standards of purity and potency.

It is clear that the transfer of this kind of drug testing from local authorities to Government control would involve the disuse of much of the sampling and testing machinery that already exists on a nation-wide scale under the Food and Drugs Act. Every transfer of power from local authority to national government strikes at the principle that local authorities have the best knowledge of local conditions : central control is impersonal and remote, and although justice may be done, it is not always seen to be done. Any proposal to reduce still further the powers and duties of local authorities is, therefore, regarded by many citizens with disfavour, unless there is some compelling reason for a fundamental change. The proposal to transfer all drug sampling and testing to a central authority should be considered against this background.

Two main reasons have been put forward by the advocates of central control : they are (a) that drug sampling under the Food and Drugs Act has not kept pace with modern developments in medicine ; too few samples of drugs are taken, and those that are sampled are not of the right type ; (b) that the quality of the vast number of drugs that are supplied to hospitals throughout the country remains virtually uncontrolled.

It must be admitted that there is some foundation in fact for both these criticisms of the operation of the present system. The proportion of drugs included in the sampling programmes of many local authorities is often very low, and the samples taken tend, all too frequently and save in a few instances, to be confined to the simpler household remedies ; there is little evidence that any change in the pattern of sampling has occurred during the past twenty or thirty years. Sampling officers have authority to take samples of any drug, including drugs and medicaments that are available to the public only on medical prescription, but

there are practical difficulties in using these powers because taking samples of the more potent drugs necessarily involves the disclosure to the vendor of the purpose for which the sample is demanded. Sampling officers have difficulty in keeping abreast of the names and uses of modern drugs, the number and variety of which increases year by year.

The absence of organised testing of the drugs that are supplied to hospitals certainly requires earnest consideration. It is true that drugs are paid for by the Ministry of Health; but the patients that the hospitals serve are the rate-payers and citizens of the local authorities, and it is their welfare that is ultimately involved. Hence, a progressive local authority cannot be wholly disinterested in quality control, merely because it is not financially concerned. Some local authorities, by arrangement with regional committees, do arrange for samples of foods supplied to hospitals to be analysed: it is probable that the committees would welcome an extension of the system to the supply of drugs, and it would not be difficult to arrange.

Nearly everyone is agreed that the existing system of drug sampling and testing requires overhaul but it seems necessary for local authorities to be on the qui vive for attempts to deprive them of an important function. The Association of Public Analysts is considering the problems involved and will be putting forward proposals to provide, within the machinery of the Food and Drugs Act, remedies for the defects and omissions of the present system.

CONTROL OF PESTICIDE RESIDUES ON FOOD IN THE UNITED STATES

by Bertha Munks,
Chemist IV, Florida Department of Agriculture.

(A summary of an address given at the Annual General Meeting of the Association of Public Analysts, 11th May, 1963.)

Control of pesticide residues on foods starts with the manufacturer who wishes to market a pesticide. He is required to present evidence that the pesticide will do the job for which it is intended, suggest recommended application rates per acre, waiting interval before harvest, and petition for a residue tolerance if necessary, etc. These tolerances are enforced on interstate shipments by the Federal Food and Drug Administration in Washington and numerous Federal district offices. States such as Florida are officially adopting the Federal pesticide residue tolerances for application to intrastate shipments.

Upon request by the producer or broker, samples may be drawn by our inspector prior to shipment. Usually samples are drawn as the products enter commercial channels for sale but may also be drawn at any time prior to purchase by the housewife.

In Florida mobile laboratories operate in the vegetable-producing areas, examining nearly 1,000 samples per laboratory during a highly productive season. The vegetable samples, consisting of 5 sub-samples, have a combined weight of 20 pounds. After sub-dividing the sample it is chopped and blenderized with volatile solvent to remove the pesticide residue. On the mobile laboratories paper chromatography and specific colorimetric methods are used. A written record of the sprays used on the crop is obtained from the grower and submitted by the inspector with each sample. If possible, samples are analysed and reported the same day they are received. This is of prime importance when train-loads of vegetables are moving out of the state each night. During the summer when it is too warm to grow vegetables, the work on the mobile laboratories is focussed on dairy products, meat fats, stock feeds and other samples. Examination of pesticide residues on citrus crops is under the supervision of the Citrus Commission.

The chemists and technicians who man the mobile laboratories are trained, especially for the job, in the State Chemist's office. In addition to the training programme investigations of new methods and equipment are conducted in this laboratory.

During the past year chlorinated pesticide residues have been investigated by the micro-coulometric gas chromatograph, developed by Coulson. We have found as many as four different pesticides on one sample. Thus by one analysis an insight is obtained into the amount and kind of pesticide present. If 15 minutes is allowed to chromatograph one sample, some of the peaks overlap each other. Qualitative identification is confirmed by inspector's reports, paper chromatography and specific colorimetric methods.

LEGAL NOTES

Sausages deficient in Meat Content. E.R. Pike, Public Analyst for Leicester, informs us that a conviction was obtained in a recent case regarding pork sausages containing only 49.5% of meat and alleged to be deficient in meat content, a fine of £5 being imposed. The defendant pleaded guilty and did not dispute the meat content stated on the certificate. The defending solicitor pointed out to the Magistrates that the sample purchased had been split into three parts and that the other two parts could have had a very different meat content. In fact, he stated that he had calculated that the meat content of the remaining portions would not have had to be very much greater to bring that of the whole to the required 65% - but he gave no figures as he did not wish to bore the Magistrates with statistics! (The defence had not had their portion analysed.) He also criticised the certificate because it was not stated whether the analysis was performed on the whole or the skinned sausages, and no indication was given whether the percentages were weight in weight or weight in volume!

The prosecution, in order to establish the minimum requirement of 65% meat, made the following points:-

1. The official view of the A.P.A. was quoted.
2. The standard recommended for canned pork sausages in the Food Standards Committee's Report on Canned Meat was quoted. (Editor's note - this seems unnecessarily tortuous; why not quote the same Committee's Report on Sausages ?)
3. It was inferred that the trade generally adhered to this requirement because of 94 samples examined by Pike since 1.1.62, the average meat content was 67.4%. Only 6 were less than 62% and only 3 less than 60%.

Antioxidants in Lard; Necessity for Declaration. At Park Petty Sessions on the 31st May, 1963, John Morrell & Company, Ltd. of 57 Victoria Street, Liverpool 1, were fined £5 and ordered to pay £7.7s.0d. costs for selling by retail certain prepacked food, to wit, an 8-ounce packet of Morrell Pure American Lard to which Article 3 of the Labelling of Food Order, 1953 applied and without there appearing on a label marked on or securely attached to the wrapper or container the appropriate designation of the ingredients of which the food consisted.

The case arose out of the sale of the lard by a local shop to the Sampling Officer of the Royal Borough of Kensington which on analysis was found to contain two antioxidants, being 80 parts

per million by weight of butylated hydroxytoluene and 100 parts per million by weight of butylated hydroxyanisole, and no statement of their presence in the food appeared on the wrapper.

After the facts had been proved, Mr. Turner of Counsel for the Defendants submitted that no offence had been committed on the following grounds :-

(1) The addition of antioxidants to foods had been considered and was controlled by the Antioxidant in Food Regulations 1958, and by these Regulations the antioxidants found in the lard were permitted in the amounts stated. Regulation 6 of the Regulations states :- "No person shall sell, consign or deliver, if it contains added antioxidants, any specified food or any mixture thereof or any margarine except in a container bearing a label in accordance with the provisions of the Third Schedule to these Regulations :-

Provided that these Regulations shall not apply -

(a) . . . . .

(b) to any sale, either by retail or pre-packed, of any such specified food, mixture thereof or margarine."

That, as lard was a "specified food" and the action concerned a retail sale of pre-packed lard, the proviso to Regulation 6 of the Regulations, which had been formulated specifically to control the use of antioxidants in food, exempted the article the subject of the prosecution from these Regulations.

That it ought to be inferred that the Labelling of Food Order, 1953 had been superseded by the Antioxidant in Food Regulations 1958, with respect to the labelling of "specified foods", in dealings concerned with retail sales and sales of pre-packed foods and was, therefore, of no effect in this case.

(2) Lard is a preparation which is the subject of a monograph in the 1948 issue of the British Pharmacopoeia, and therefore, by reason of section 8 of Table 'A' of the First Schedule to, and Paragraph 5 of, the 1953 Order is a food which, if sold pre-packed by retail, is exempt from the Order to the extent that the ingredients need not be stated on the wrapper.

Mr. J. Heyes, Legal Assistant, prosecuting for the Council, agreed that the addition of the two antioxidants to the lard in the amounts found was permitted by the Antioxidant in Food Regulations, but that, as far as the labelling of the food was concerned,

these Regulations did not apply. Neither he nor Counsel could find anything in these Regulations which affected the operation of the 1953 Order, and he submitted therefore that the Order was still in force and that it regulated the labelling requirements on retail sales of all pre-packed food (unless specifically exempted), and required the ingredients to be specified on a label marked on or securely attached to the wrapper or container of the food.

As to the second ground, it was again agreed that lard formed the subject of a monograph in the B.P., but that monograph defined lard to be "the purified internal fat of the hog". The lard the subject of the action did not comply with that definition as it contained two added antioxidants, and therefore was not exempt from the requirements of the Order.

(Editor's Note.) We are indebted to Dr. H. Amphlett Williams, Public Analyst for the Royal Borough of Kensington, for the above report. Following the legal proceedings, the Secretary of the Lard Association wrote to the Hon. Sec. of the Association of Public Analysts informing him that immediate steps had been taken to advise all members of the Lard Association to take appropriate action as quickly as possible and asking that Local Authorities should allow a period of grace and withhold legal proceedings while old stock was being sold and new labels printed. He enclosed a copy of a circular that had gone out to all members of his Association drawing attention to the prosecution and stating that all lard packers must make an antioxidant declaration on wrappers where one is present, and adding "Although it is not necessary to state the actual percentage of antioxidant present, it is necessary to refer to the presence of propyl gallate, butylated hydroxyanisole and butylated hydroxytoluene as the case may be."

ITEMS OF INTEREST

Lead Content of Plastic Sheet. J.H.E. Marshall (Public Analyst, Canterbury) informs us that samples of P.V.C. sheet have been found to contain on dry ashing 1,300 p.p.m. of lead, and after wet oxidation 5,000 p.p.m. In use, these sheets of plastic would have been in contact with chocolate and with chocolate eclairs. It is believed that the difference in analytical results by the two processes is due to the use of a volatile lead compound, such as lead tetra-propyl, as plasticiser.

Chemical Compounds used in Agriculture and Food Storage. Recommendations have been received from the Ministry of

Agriculture, Fisheries and Food relating to the safe use of the following compounds -

Captan - home garden use; agricultural and horticultural use.
Carbon Tetrachloride and Ethylene Dichloride - food storage practice.
Disulfoton - an organo-phosphorus insecticide.
Endothal - a herbicide - revised recommendations.
Fenocrop - a herbicide, also known as 2, 4, 5, -TP and Silvex.
Linuron - a herbicide.
Tenoran, active principle of - a herbicide.
Ruelene and Hypolin, active principle of - an organo-phosphorus insecticide and anthelmintic for veterinary use.

Public Appointments, Changes in.

M. M. Love is appointed as P. A. to the Borough of Halesowen
and
W. E. Jones as D.P.A. to that Borough from the 1st October, 1963.

PUBLICATIONS AND REVIEWS

British Pharmaceutical Codex 1963. It was announced in the last issue of the Monthly Report that a new B.P. would be published on the 1st July. We are now informed that a new Codex has also been published; both publications will come into force on the 1st January, 1964. A new edition of the British National Formulary has also appeared.

No detailed review of either the B.P. or the B.P.C. appears necessary, since every Public Analyst will of course be purchasing both as a matter of routine; but it is worth noting that for the first time, doses, statements of strength, and the like, are given entirely in the metric system.

Drugs, Approved Names For. The General Medical Council have issued a list of approved names dated July 1963 which consolidates all previous lists. Many of the substances named are included in the new B.P., and a leaflet is enclosed with the latter providing a list of the Approved Names appearing in the Pharmacopoeia for the first time, with their proprietary equivalents.

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