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THE ANALYST

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NEW MEMBERS OF THE SOCIETY

(Elected July 5th, 1949)

George Anderson, A.R.I.C., M.Inst.F.; Alasdair William Armstrong, B.Sc. (Aber.), A.R.I.C.; Laurence Robert Bishop, M.A., Ph.D. (Cantab.), D.Sc. (Birm.), F.R.I.C.; David Geoffrey Elias, B.Sc. (Manc.); Dattatraya Manjunath Gangolli, B.A., M.Sc. (Bombay), F.R.I.C.; Joseph Wylie Gray; Benjamin Crowther James, B.Sc. (Lond.), A.R.C.S., F.R.I.C.; Thomas Moodie, A.H-W.C., A.R.I.C.; Alan Campbell Watson; Ronald Alfred Wells, B.Sc. (Lond.), A.R.I.C.

PHYSICAL METHODS GROUP

THE Eighteenth Ordinary Meeting of the Physical Methods Group was held at 8 p.m. on Tuesday, January 25th, 1949, in the Chemical Lecture Theatre of Imperial College, London, S.W.7. Dr. J. G. A. Griffiths, the Chairman of the Group, occupied the chair and there were 70 members and visitors present.

The following papers on "Rheological Methods of Control" were read and discussed (see pp. 387-405): "Industrial Applications of Rheology," by G. W. Scott Blair, D.Sc., Ph.D., F.R.I.C.; "The Application of Rheological Methods in the Milling and Baking Industries," by A. J. Amos, B.Sc., Ph.D., F.R.I.C.; "The Use of Rheological Tests in the Pharmaceutical and Cosmetical Industries," by R. H. Marriott, D.Sc., F.R.I.C.; "Rheological Methods and their uses in the Paint Industry," by P. S. Williams, B.Sc., A.R.C.S.

The Nineteenth Ordinary Meeting of the Group was held at 6 p.m. on Tuesday, February 22nd, 1949, in the Lecture Theatre of the Institute of Physics, London, S.W.1. Mr. B. S. Cooper occupied the Chair and about 110 members and visitors were present.

The following papers on "The Spekker Photo-electric Absorptiometer and Fluorimeter" were read and discussed: "Recent Modifications in the Spekker Photo-electric Absorptiometer," by R. A. C. Isbell, A.Inst.P., who demonstrated the improved form of the instrument; "Some Experiments with the Spekker Photo-electric Absorptiometer and Fluorimeter," by F. Wokes, B.Sc., Ph.D., F.R.I.C., and G. Slaughter.

The Twentieth Ordinary Meeting of the Group was held at 5.30 p.m. on Friday, March 11th, 1949, in the Chemical Lecture Theatre of Imperial College, London, S.W.7. The meeting had been organised by the Polarographic Discussion Panel. Dr. J. G. A. Griffiths, Chairman of the Group, opened the meeting and introduced Dr. W. Cule Davies, Chairman of the Polarographic Discussion Panel, who occupied the chair for the rest of the meeting. About 50 members and visitors were present. The following papers on "Polarographic Analysis were read and discussed: "Buffer Solutions and the Concept of Polarographic Buffer Capacity," by P. Welford, B.A., A.Inst.P.; "Paper Strip Extraction and Polarography," by J. A. Lewis; "The Polarographic Behaviour of Aromatic Nitro Compounds," by J. G. Waller, B.Sc., A.R.I.C.

The Standardisation of Hortvet Thermometers

By R. ASCHAFFENBURG* and J. A. HALL†

(*Read at the meeting of the Society on Wednesday, October 6th,* 1948)

The Hortvet technique of determining the freezing-point depression of milk requires the use of special thermometers. Their standardisation with the help of determinations of the freezing-point of 7 and 10 per cent. (w/v) sucrose solutions, a procedure adopted by the Association of Official Agricultural Chemists[1] and endorsed by the Society of Public Analysts and Other Analytical Chemists[2] has rightly been criticised by Stubbs and Elsdon.[3] These authors have recommended the determination of additional reference points with sucrose solutions of intermediate concentrations, so as to narrow the temperature intervals over which correction by linear interpolation has to be applied. Even so, the value of this type of standardisation remains questionable on account of the difficulties encountered when the Hortvet technique is used with sucrose solutions. When water or milk freezes out, the mercury column of the Hortvet thermometer rises to a well defined steady maximum, which is easy to reproduce. With sucrose solutions, on the other hand, the highest point reached by the mercury column tends to vary from determination to determination and is often difficult to observe, as it remains steady for a few seconds only. These difficulties are brought out by the following series of experiments in which the temperature changes in sucrose solutions were recorded at short, regular time intervals.

Determinations were made of the freezing-point of sucrose solutions (Merck, A.R.) ranging from 7 to 10 per cent. (w/v) in concentration, using the standard Hortvet apparatus and technique, except that a platinum resistance thermometer was substituted for the usual mercury thermometer.

The resistance thermometer was comparable in size with the mercury thermometers normally used with the Hortvet apparatus. It had a bulb 6 mm. in diameter and 50 mm. in length, and the combined lag constant of the thermometer and its associated galvanometer was about 5 seconds, which is of the same order as that of a mercury thermometer of similar size.

Readings were made to an accuracy of about $\pm 0{\cdot}0005°$ C., and four independent observations on the freezing-point of water, determined in the Hortvet apparatus in the course of the investigation, were concordant to within these limits. Determinations of the ice-point made in the normal manner by immersion of the thermometer in melting ice gave values indistinguishable from those obtained in the Hortvet apparatus.

The temperature observations were made at intervals of a quarter of a minute throughout each determination, except that usually one or two were missed when the temperature was rising rapidly after the super-cooled solution had been seeded. Super-cooling was allowed to reach $1{\cdot}2°$ C. before seeding was done and stirring was then stopped. The solution was stirred slowly three times just as the expected freezing-point was approached. The temperature at which this was done is normally indicated by a cross on the graphs of Figs. 1 to 5. In certain instances the temperature was too low to be indicated in this way and then it has been recorded in figures on the graph.

The upper curves of Figs. 1 to 5 show the whole course of each determination and the lower curves record the crucial part of the observation on a much more open temperature scale. The theoretical values given by Stubbs and Elsdon are indicated by broken lines.

The differences between the observed values obtained in the present investigation and the calculated values are plotted against sucrose concentration in Fig. 6. These differences shows a progressively increasing spread of the observations with increasing concentration, and a study of the curves of Figs. 1 to 5 shows that shorter "flats" are obtained on the curves relating to the more concentrated solutions and that, in general, the highest observed values of the freezing-point at any concentration are associated with the longest flats.

Two curves have been drawn to embrace the observations on Fig. 6.‡ The upper curve

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† National Physical Laboratory.

‡One of the observations at 7 per cent. concentration has been excluded as an examination of the form of the curve in Fig. 1 shows that it was abnormal.

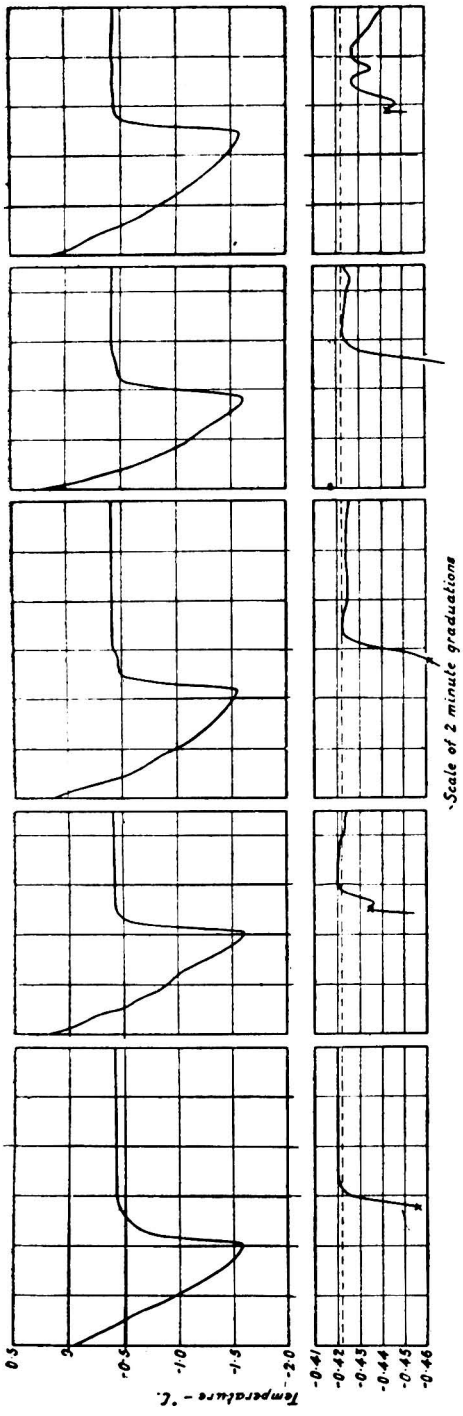

Fig. 1. Freezing points of 7% sucrose solution

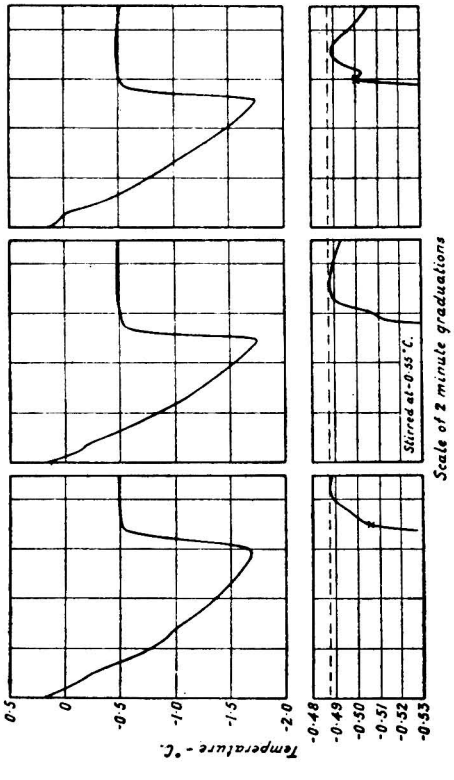

Fig. 2. Freezing points of 8% sucrose solution

shows that, if the highest observation for each concentration obtained in the present work is taken, it is in agreement with the calculated value to within ±0·003° C. At concentrations up to 8 per cent. inclusive, the result of an individual determination may be considered reliable to ±0·002° C. At higher concentrations, this limit must be widened, as the individual results tend to depart more and more from the calculated values until at 10 per cent. concentration there is a spread of 0·017° C., the observed minus calculated values ranging from −0·002° to −0·019° C. It appears that, beyond 8 per cent. concentration, whilst the highest observed value is not likely to be greatly in error, many observations would have to be made before one could feel reasonably sure that the highest possible value had, in fact, been reached. For example, had one of the observations at 10 per cent. concentration, given in Fig. 5, been omitted, we should have arrived at a value about 0·01° C. too low, and with four observations in quite good agreement at this value.

In view of these uncertainties we cannot endorse the recommended procedure for the standardisation of Hortvet thermometers with sucrose solutions. Instead, we suggest that thermometers should be standardised at a recognised testing institution to an accuracy of at least ±0·002° C. on the International Temperature Scale. In order to cover the essential parts of the thermometer scale adequately, the temperatures at which standardisation is carried out should include values close to +0·050°, 0·000°, −0·400°, −0·500°, −0·520°, −0·540° and −0·560° C. Acceptance of this procedure will facilitate the work of the analyst who will obtain correct results simply by adding to the temperature readings for water and milk the corrections for inequalities in the bore and graduation of the Hortvet thermometer obtained by direct comparison with standard thermometers. This should result in greater reliability of the freezing-point test, and lead to closer agreement between results found in different laboratories.

This paper is published with the approval of the Director of the National Institute for Research in Dairying and the Director of the National Physical Laboratory.

References

1. *A.O.A.C. Official and Tentative Methods of Analysis*, 1945, 6th Edition.
2. "The Freezing-Point of Milk," *Analyst*, 1933, **58**, 318.
3. Stubbs, J. R., and Elsdon, G. D., *Ibid.*, 1936, **61**, 455.

The National Institute for Research in Dairying
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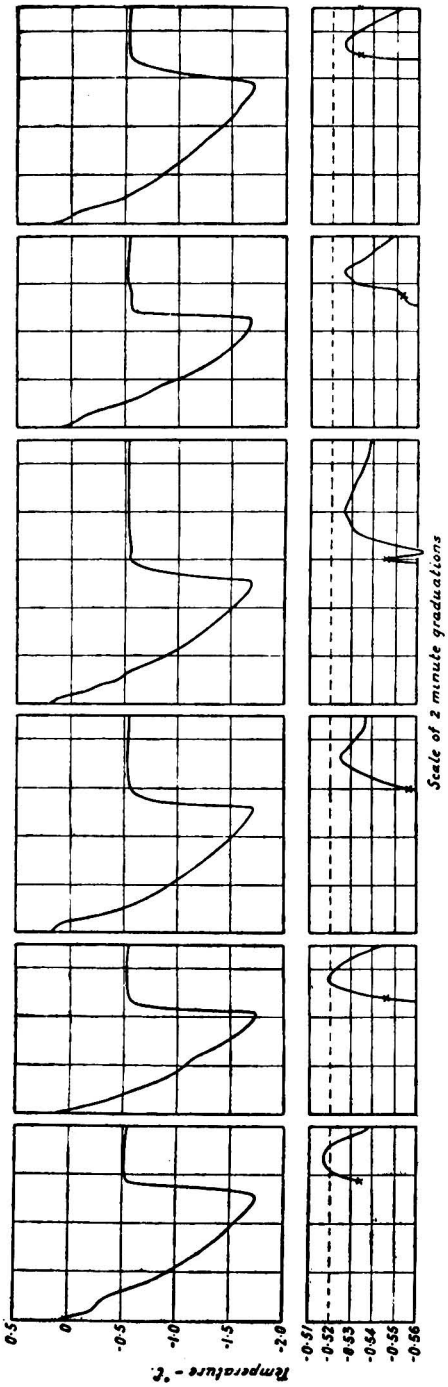
July, 1948

Discussion

Mr. R. W. Sutton, in opening the discussion, said the Society was indebted to the authors for their paper.

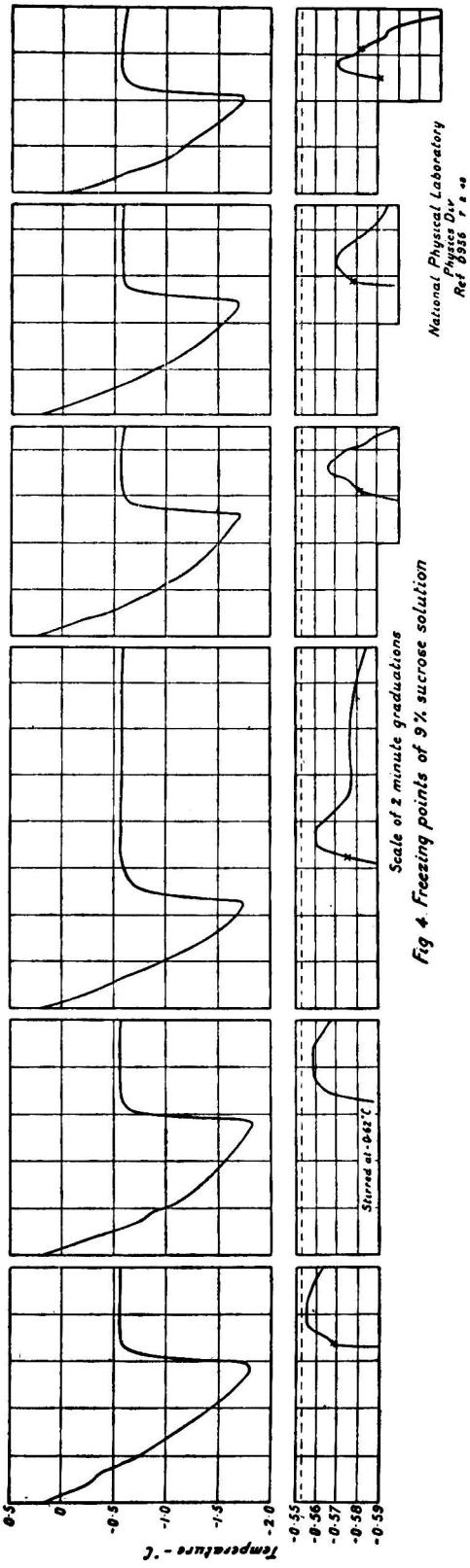
It was important in the first place to make a clear distinction between measurement of the freezing-point of a sample of milk, as accurately as possible, in the Hortvet apparatus and the measurement of a freezing-point by the Hortvet method. He thought that most workers had been concerned with the latter, which involved not only the use of the Hortvet apparatus but also the assumption that a 7 per cent. solution of sucrose in the Hortvet apparatus had a freezing-point of −0·422° C. and a 10 per cent. solution a freezing-point of −0·621° C. These figures might or might not be correct, but they had been accepted as a basis for the standardisation of Hortvet thermometers and any errors in Hortvet's determinations did not fall for consideration.

The difficulty in obtaining reproducible results with sucrose solutions was not new. It had been referred to by Hortvet himself, and later by Elsdon. Other workers were aware of the difficulty, and in his laboratory it had been the practice for many years to make a considerable number of readings with 7 per cent., 10 per cent. and intermediate concentrations of sugar in a full standardisation every two or three years and to check more frequently with 8·5 or 8·75 per cent. sugar solution. After a comprehensive standardisation it was possible to use the A.O.A.C. method of calculation for a smaller interval or to construct a table giving the appropriate "stem" correction to be applied to any reading. He felt that the authors had to some extent exaggerated the difficulty with sugar solutions, and he could not agree that the difficulty was encountered only with the stronger solutions. In his experience there seemed to be a direct correlation between the variability in the results and the concentration of the sugar solution. It must also be remembered that in the A.O.A.C. method any errors in the work with sugar solutions are not included in full and with cumulative effect in the final result. In fact, if the error with the 7 per cent. sugar solution is negligible, only about one-half of any error in the figure for the 10 per cent. solution would be included. Further, by using intermediate strength sugar solutions, the freezing-points for which had been calculated



Scale of 2 minute graduations

Fig. 3. Freezing points of 8·5% sucrose solution



Scale of 2 minute graduations

Fig 4. Freezing points of 9% sucrose solution

by interpolation from Hortvet's figures for the 7 and 10 per cent. sugar solutions, it was possible to reduce the error to quite low proportions at a point where the greatest accuracy was required, *i.e.*, −0·530° C.

In his opinion these proposals for a different procedure in the Hortvet test ought to be adopted only if they led to better agreement in results obtained on the same sample by different workers, and only if they did not involve any change in our standards. He was at present doubtful if either of these conditions would be satisfied, but this could only be determined by further experimental work.

On the first point it appeared that the N.P.L. would guarantee their corrections to ±0·002° C. On this basis a freezing-point depression (zero minus the milk reading) might be incorrect by ±0·004° C. To this possible error (entirely a feature of the thermometer and its certificate) must be added the normal experimental error, which he thought might reasonably be put at ±0·001° C. or possibly ±0·002° C. We then arrive at the fact that the results for a sample of milk examined by different workers might conceivably range over 0·010° to 0·012° C. This range would apply at any level and would be just as likely in measuring a depression of 0·530° C., where the greatest accuracy was required, as in measuring one of 0·470° C., where great accuracy was unimportant. It was his opinion that better results than this could be achieved by careful work with sugar solutions, and that by using the intermediate strength sugar solutions the error could be kept low at the point where the greatest accuracy was required.

On the second point he emphasised that many valuable records had been compiled over a period of years, and it was a fair statement that 0·530° C. could be accepted as the minimum depression obtained in the Hortvet method for genuine milk. Evidence to this effect had been given in the Courts on many occasions and it would be an unfortunate complication to have to alter this figure because of a new procedure for the standardisation of the thermometer. Hortvet's figures for 7 and 10 per cent. sucrose solution may not have been correct, and indeed it seemed to him quite likely that using the most accurate thermometers different results might be obtained in different Hortvet cryoscopes, owing to certain features in the apparatus itself, which in his opinion were defects when close measurements of temperature with a mercury-in-glass thermometer were to be made. The stirring was inefficient and variable according to the manipulation of the stirrer; the heat that was liberated was therefore expended in rather a variable way in raising the temperature of some parts of the apparatus and the solution under test, and all the time the outer cooling-bath, maintained at a lower temperature, was exerting a cooling effect. He had always thought that the move to standardise on sugar solutions represented an advance in that it tended to eliminate some of the variables that were peculiar to the particular apparatus being used.

There was no inherent defect in the use of sugar solutions. In his opinion the defect was in the Hortvet apparatus. He had recently made further experiments with Monier-Williams's apparatus and the contrast was marked. In using this apparatus, when the appropriate degree of super-cooling had been reached, the freezing-point tube was isolated from the cooling-bath (by the removal of the dilute alcohol between the two tubes) and the results with the 10 per cent. sugar solution were quite steady and quite consistent.

Lastly, the manner in which the results were expressed was for practical purposes quite unimportant There was no disadvantage in using the arbitrary scale of the Hortvet method and there was no particular merit in using the International Temperature Scale. The temperatures recorded were not true freezing-points, as there was no correction for heat exchange or the amount of super-cooling. The figures, however they were recorded, were quite arbitrary ones obtained in a particular apparatus and following a particular procedure.

He thought these proposals deserved very careful attention, but that before they were adopted there ought to be ample experimental evidence that they would enable us to obtain more consistent results and above all that there would not need to be any alteration in the figures that had been accepted for so long as typical of genuine milk.

Mr. J. MARKLAND said that Dr. Aschaffenburg had mentioned that there was no means of knowing when the freezing-point determination of a sugar solution should be accepted as correct, but the A.O.A.C. specified that a determination should be rejected unless the top of the mercury-column remained stationary for at least 1 minute.

He enquired if Mr. Hall could say how the heat capacity of the platinum resistance thermometer compared with that of a mercury-in-glass Hortvet thermometer. If the heat capacities were different, the amount of ice formed on freezing might also be different. The consequent effect on the freezing-point might, or might not, be negligible, but a different heat capacity was a theoretical defect in the method of checking Hortvet's figures for the 7 and 10 per cent. sugar solutions by use of a platinum resistance thermometer. This point could possibly be checked by determinations of the freezing-point of the same sample of milk, using on the one hand a platinum resistance thermometer and on the other hand a Hortvet thermometer standardised by the N.P.L. method.

Mr. H. F. BAMFORD pointed out that milk was a colloid and one might, therefore, expect that the molecular concentration and the freezing-point would be less altered by the separation of a small amount of ice than would that of a sucrose solution of the same freezing-point. The choice lay between two sets of errors, one occurring when each operator determines his own standard and the other when an accurately calibrated thermometer is used. Which of these procedures would be likely to lead to better agreement between different laboratories could only be decided by a statistical examination of the two sets of errors.

Mr. N. HERON thought that undue emphasis was being given to 10 per cent. sucrose solution, the freezing-point of which, −0·621° C., was well below the range for normal milks. The lowest point reached

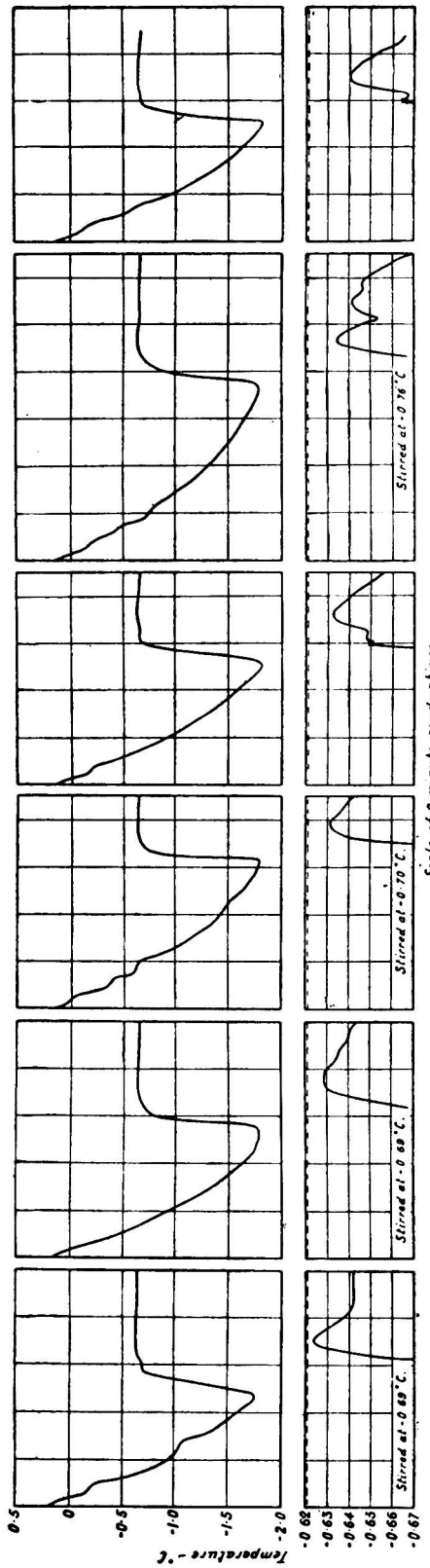


Fig. 5. Freezing points of 10% sucrose solution
Scale of 2 minute graduations

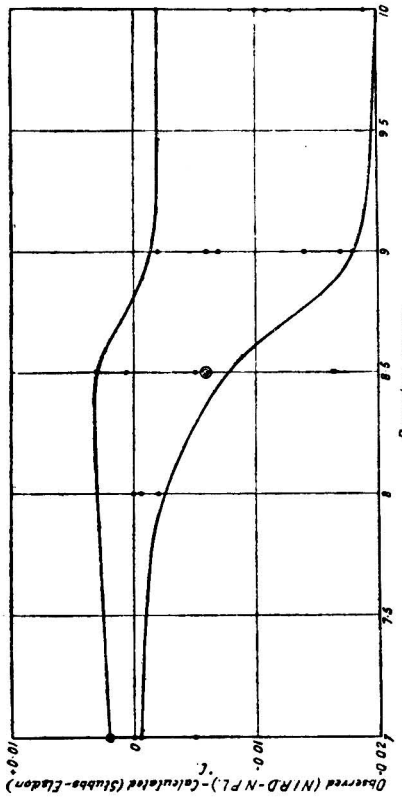


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Fig. 6. Freezing-points of sucrose: departure of observed from calculated values

by these was of the order of 0·550° and this was covered by 9 per cent. sucrose solution. The suggestion that satisfactory freezing-point determinations could not be obtained with sucrose solutions up to 10 per cent., however, was not borne out by the work of Elsdon and Stubbs nor by later work of many other analysts. In his opinion it was more satisfactory to standardise the thermometers in the laboratory in which they were to be used than to rely on external references, however reliable.

Dr. J. H. HAMENCE wished to thank the authors for bringing this matter before the Society and also for the work that they had done on what was undoubtedly a difficult matter.

He regretted very much the suggestion made by the authors that Hortvet thermometers should in future be standardised by the N.P.L. and that all the analyst should be required to do would be to confirm the zero point of the instrument with water. This procedure was a complete breakaway from the original Hortvet technique; he agreed that the N.P.L. would be doing a great service to analysts by checking the bore of the thermometer, but he was firmly of the opinion that the standardisation of the thermometer should still be done against a sugar solution. The authors had shown that a satisfactory standardisation could be made with a 7 per cent. sugar solution. Why, therefore, could not this be used to check the thermometer in the Hortvet apparatus?

The result of a freezing-point determination frequently led to legal proceedings and he felt that it was wrong to give evidence in court on an instrument that he himself had not standardised. This difficulty would be obviated if the thermometer were checked against a sugar solution.

It must be borne in mind that the Hortvet method was a purely empirical one and, therefore, in his view, it was important, particularly having regard to the wide variation that exists between different pieces of apparatus, that a sugar solution should be used for standardisation.

Mr. HALL, in reply to Mr. Sutton, said that it was of course possible, when either end of a range of temperature was specified to an accuracy of ±0·002°, that there might occur an error of ±0·004° in the interval. On an N.P.L. certificate, however, these limits were intended to include any accidental errors in the reproduction of the International Temperature Scale by the N.P.L. standards, and such errors were very unlikely to change from positive to negative over a short temperature range. Hence, in practice, it was extremely improbable that the intervals obtained from a certificate would be anything like so much in error. In fact, it was to enable differences to be measured to a higher degree of accuracy than absolute temperatures that the corrections on the certificate were always recorded to a higher degree of accuracy than the plus or minus limits. For example, when the limit of accuracy of test was stated to be ±0·002°, the corrections were recorded to the nearest 0·001°.

He would like to emphasize that, if the best observations only were taken, there was no difference between the scale defined by sucrose solutions and the International Temperature Scale. The difficulty was to know when one had got a really reliable observation with the more concentrated solutions. In fact, the use of sucrose solutions was simply a more roundabout way of attempting to reproduce the International Scale. Hortvet determined the freezing-points of the sucrose solutions on the International Scale by using thermometers standardised on that scale by the Bureau of Standards. Hence, if other thermometers were standardised in sucrose solutions, accepting Hortvet's values and assuming that the experimental work was ideally accurate, they should indicate temperatures on the International Scale. It was obvious, however, that there was less chance of experimental error if the thermometers were compared directly with the standards of a laboratory such as the Bureau of Standards or the N.P.L., than if the intermediary of sucrose solutions was employed. But, if the standardisation work by the two methods was satisfactory, the change from one to the other would not lead to a change in the numerical value of 0·530° for the minimum depression of genuine milk, so that the old values for milk freezing-point depressions would still hold good.

In reply to Mr. Markland he would say that the heat capacity of the bulb of their resistance thermometer would certainly be less than that of the normal Hortvet mercury thermometer, but he would not like to guess what effect any difference would have on the results. Did any marked difference in the weight of the freezing-point tube or of the stirrer have any effect? If the result was reasonably independent of variations in these other neutral masses, he would not expect it to vary with the heat capacity of the thermometer.

Dr. ASCHAFFENBURG, in reply to Mr. Sutton, said their observations had shown that, with the more concentrated sucrose solutions, one might obtain a series of temperature readings in close agreement, but definitely on the low side. Unless an analyst had a certificate of standardisation, he had no criterion that would enable him to conclude that the readings, though in good agreement, were in fact erroneous.

In reply to Mr. Markland, he said it was true that the A.O.A.C. defined a satisfactory determination as one in which the top of the mercury column remained stationary for at least 1 minute. The trouble was that, with 10 per cent. sucrose solutions, for instance, one could hardly ever get a result at all on this basis. As the data now presented showed, only a very short stationary temperature maximum was obtained with the more concentrated sucrose solutions.

In reply to Dr. Hamence, he said that the point obtained by checking with 7 per cent. sucrose solution was too far removed from the essential milk range to allow of extrapolation to that range. It was necessary to have at least one other point, obtained with a more concentrated sucrose solution, to find out what the error was in the region of 0·530°. He would like to emphasize again that their best observations were in agreement with the values given by Hortvet and by Stubbs and Elsdon. He did not think they were departing from what had been done in the past, except that they suggested a transfer of the onus of the basic standardisation from the analyst to the experienced thermometry experts at the N.P.L.

Rheological Methods of Control

The following four papers were read at a meeting of the Physical Methods Group on Tuesday, January 25th, 1949

Industrial Applications of Rheology

By G. W. SCOTT BLAIR

The accepted definition of the term "rheology" is "the science of the deformation and flow of matter." This includes a very large part of physics but, by convention, certain sections, such as hydro- and aero-dynamics and parts of the theory of elasticity, when not concerned with the flow *properties* of materials as such, are excluded.

There are many reasons why it may be of practical importance to measure the flow and deformation of raw materials, intermediates or finished products in industry: some of these reasons are well illustrated by the authors of the other papers in this symposium.

As an illustration from a raw material, it is not possible to mill wheat satisfactorily if the berries are too hard or too soft for the "break," and one purpose of wheat conditioning is to attain the correct moisture content and distribution so as to ensure the proper balance of brittleness and plasticity. For some materials, such as this, a rapid moisture determination* may be more practicable than a mechanical or physical test; but in others, as in assessing when the proper amount of whey has drained out syneretically from cheese curd in the scalding process in making hard-pressed cheese, a superficial density is more readily measured than a moisture content.[1] Occasionally, an indirect rheological test may be convenient when purely chemical information is required, as when the viscosities of certain fats and fatty acids are found to be highly correlated with their iodine numbers.[2]

There is, then, no particular necessity to use chemical analysis when chemical constitution is of direct importance and physical methods when mechanical behaviour is in question so long as the level of correlation between chemical constitution and mechanical behaviour is known and is sufficiently high. In general, it may be said that rheological analysis is seldom as accurate as chemical analysis, but is often considerably quicker and easier to carry out in the factory.

With finished products, rheological properties may be important for a variety of reasons. These may be classified as follows—(1) *Direct mechanical requirements* of the product, *e.g.*, adequate strength of a plastic, correct consistency and thixotropy of a drilling mud, brushing qualities of a paint; (2) *Indirect mechanical requirements, e.g.*, the "body" of a cheese determining the preponderance of different types of micro-organism and so, indirectly, of flavour, taste and keeping quality; (3) *Requirements of public taste, e.g.*, in cosmetics (see Marriott's paper in this symposium); (4) *Uniformity requirements*, the consumer often preferring a uniform consistency to a variable consistency even if the latter includes occasional improvements; (5) *Mixed requirements, e.g.*, spreading capacity of butter, which is, within limits, a matter of public taste but in extreme cases a "direct mechanical requirement" in relation to the crumbliness of the bread.

Although there are a number of rather ill-defined rheological properties that are not directly concerned with stress - strain - time ($S : \sigma : t$) relations, most rheological requirements may be said to depend on the functional relationships between these three variables.

The very definition of rheology suggests two principal types of behaviour: flow, in which the changes of form of bodies are functions of both stresses and time; and deformations which, while dependent on the system of stresses, are often immediately produced and can be recovered when the stresses are removed. The system of stresses can be defined in terms of a symmetrical second rank tensor with six independent components and the deformations, or rates of deformation, also by other tensors with six independent components. In the classical case of an elastic solid, the coefficients relating the components of stress and strain themselves form a fourth rank tensor which, being symmetrical, cannot have more than 21 independent components. For materials like wood, which are said to be "orthotropic," this number reduces to nine and, for perfectly isotropic materials, to two.

* Though even this is often done indirectly by measuring some physical property such as dielectric constant.

For a simple viscous fluid only one independent coefficient is normally required to specify the relationships between stress and rate of flow, though it must not be forgotten that the complete story is not nearly as simple as this statement might seem to suggest.[3]

Happy indeed is the industrial rheologist who can work with materials for which such comparatively small numbers of $S : \sigma : t$ properties are invariant. Frequently, a choice must be made between measuring simple physical properties, such as viscosity or elastic moduli, under conditions quite unlike those obtaining in practice, and designing empirical tests which imitate the processes that the material undergoes in manufacture or use or the way in which it is handled when judged subjectively by the expert.

Indirect tests, though occasionally very valuable (*e.g.*, the good correlation between the viscosity of certain solutions of cotton[4] and silk[5] and the resistance of the materials themselves to chemical attack), are more often dangerous and misleading. Early attempts to correlate "strength" of flour doughs with the viscosities of dilute aqueous suspensions of flour, and later with the size and strength of bubbles blown in dough,[6] illustrate the dangers of such indirect methods unless used under strict statistical supervision.

In studying the behaviour of complex materials like doughs, pastes and magmoids, it is usual to keep either S, $\dot{S}$, σ or $\dot{\sigma}$ constant,* measuring the changes of whatever is free to change, with the course of time. Ingenious devices for working at constant S[7,8,9,10], $\dot{S}$,[11] σ[12] and $\dot{\sigma}$[13] have been described, though too often there have been minor but important errors in design or calculation.[14]

The interpretation of data from such tests is always difficult. Some years ago it was usual to suppose that complex behaviour must be due to the interaction of a number of essentially simple factors, *i.e.*, that rheologically complex systems are actually built up of groups of molecules, some of which behave as simple elastic units ("springs"), some as truly viscous units ("dash-pots"), some as sliding frictional units, and perhaps some as ratchet mechanisms which inhibit the recovery of potentially stored energy. These ideas led to the construction of many ingenious and complex models which, in a few instances no doubt, helped to give an understanding of the molecular structures involved, the units being associated with different components of the system (*e.g.*, Schofield and Scott Blair's work on the protein and starch components of flour doughs.[15])

But in most instances it came to be realised that the use of such models meant no more than the empirical fitting of exponential equations to the data: the models could equally well be replaced by combinations of electrical resistances, capacities, etc. The use of such exponential treatments is often fully justified but the models become unnecessary in any case, and often better and simpler agreement with the experimental data is got by using other types of equation.[16]

It is, of course, almost always *possible* to describe the experimental data in exponential terms, provided enough terms are used, but there has been a tendency of late among those who still use rheological models to introduce imperfect or at least non-linear elastic springs, and "dash-pots" containing non-Newtonian liquids as an alternative to very large or even infinite numbers of units.[17] It is generally claimed for models that they enable complex behaviour to be described in simple terms. The best that can be said for such models is that they describe complex behaviour in perhaps rather less complex terms.†

In experiments in which stress relaxation is measured at constant strain, not only is it often necessary to introduce a number of truly Maxwellian units (*i.e.*, exponentially relaxing units) but very frequently a distribution spectrum of an infinite number of such units is postulated. (This type of treatment goes back to Wiechert's work in 1893. For a good modern account, see Simha.[18])

Maxwell[19] himself, however, when he first proposed the concept of "relaxation time," warned his readers that these relaxation times might well prove to be a complex function of stress, and it is indeed true that in the majority of materials, at least at room temperature, the relaxing stress is much more simply related to time by equations of quite a different type.[20]

It must be realised that, more often than not, rheological tests on complex materials are made under conditions which are not those of equilibrium nor do the "properties" of the

* A dot above a symbol indicates differentiation with respect to time.

† This type of treatment is closely parallel to the use of non-orthogonal factors in Factor Analysis by Thurstone and others—see below.

material remain unchanged as a result of the process used to measure them. There is a type of "uncertainty" here as significant, in its way, as the famous "uncertainty" involved in measuring the position and momentum of an electron. To measure a flow or a deformation, one must first produce a flow or deformation; and these, or the stresses associated with them, may well change the material even as it is being tested; so that we are in fact measuring a process rather than a property.

The advantage of the classical "property" lies in the fact that it is invariant to the process used for its measurement, for example, the viscosity of simple Newtonian liquids is the same whether determined in a rotation, a capillary or a falling ball viscometer. Unfortunately, many materials do not behave in this simple manner. Some show regular Newtonian behaviour in a falling ball viscometer but are non-Newtonian in a capillary.[21] Others show complex behaviour in all types of viscometer, and it is often best to describe their behaviour in terms of "quasi-properties." Such quasi-properties form a hierarchy: in some cases the processes which they measure can be produced by a variety of experimental methods; in others, though replicable* with fair accuracy provided that the same testing method is used, they are not invariant to the method of test. It is the writer's personal opinion that, where no invariant "properties" exist and especially under non-equilibrium conditions, quasi-properties, at least those of a high order, form the best concepts with which to describe the rheological behaviour of many complex systems. This opinion is based on the results of about a thousand experiments on a very wide variety of materials.

Ordinary properties such as viscosity are described in terms of a single quantity. Quasi-properties require also one or more (usually two) quality factors which indicate the degree to which the material approximates towards the simple prototypes. These groups of magnitudes, comprising normally a quantity and two quality factors, must be treated as wholes in the description of materials. The "quantity" alone, for example, gives no means of comparing materials. Failure to realise this has given rise to unjustifiable criticisms of the whole treatment on dimensional grounds.† These criticisms would have been partly justified had the quasi-properties been split up,[23] but this obvious mistake does not seem to have been made.

The theory of quasi-properties has also the advantage that it links the physical rheological tests with the judgments of experts who assess quality by handling materials.

So long as physical theory remains as incomplete as it still is, it is certain that many industries will continue to rely for their rheological testing mainly on the subjective judgments of skilled craftsmen.

It is useless merely to deplore this—just as it is useless to deplore the lack of simple physical properties. Both facts must be faced and detailed studies have been and are being made of the psycho-physical processes involved in assessing the rheological behaviour of materials by handling them and of the nature of the craftsmanship involved.[14]

In classical rheology we have seen that we are concerned with stresses and rates of change of stress, and with strains and rates of change of strain, *i.e.*, with whole-number differentiations. Psycho-physical experiments strongly suggest that the entities by which "body," "spring" and so forth are judged when materials are handled, are fractional differentials of strain with respect to time and perhaps stress, and the theory of quasi-properties is based mathematically on similar fractional differential equations.

It is certain that the judgment of the rheological behaviour of materials in handling them depends not on isolated "physical properties" but on "*Gestalten*" which are closely related to the quasi-properties just described.

It has been objected that such concepts are unlikely to further our knowledge of the underlying molecular mechanisms of rheological processes. This is freely admitted, but it is equally strongly maintained that the elucidation of molecular mechanisms is far from being the sole purpose of rheology.

There is another type of entity by which the complex rheological behaviour of materials may be described when simple rheological properties are not measurable, nor is it yet known whether this new treatment links up effectively with the theory of quasi-properties.

In many industries a comparatively large number of empirical tests are performed as

* By "replicable," as distinct from "reproducible," is meant that the measurements can be repeated satisfactorily on replicate samples, but not reproduced on samples which have already been tested.

† For a defence of the treatment, see Dingle.[22]

a matter of routine on products or intermediates. Some of these tests are rheological, some chemical, some electrical: some measure simple "properties," others do not. Very often it is not known precisely what the test measures nor how far the results of one test overlap with those of another. The latter point is, of course, determined by calculating the correlation coefficients between the tests and, if all these are calculated, a square matrix can be written comprising all the tests. But each sample is still virtually described by as many magnitudes as there are tests (say n), even though it is known that all or most of the relationships between the measured behaviour could be accounted for by considerably less than n magnitudes.

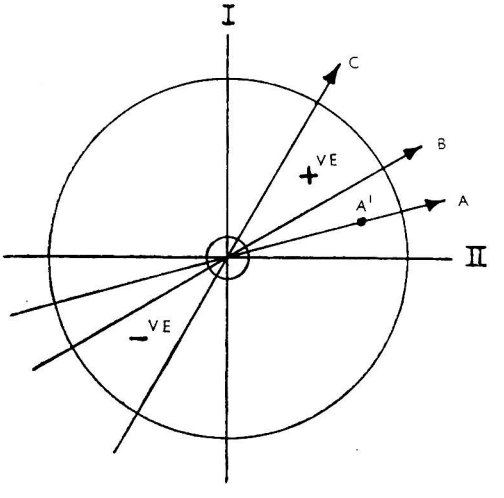
In simple cases the behaviour is, of course, described by $m(< n)$ "physical properties," but in most of the materials of interest to rheologists this cannot be done, since no invariant "physical properties" can be found.

The problem is, then, to reduce a space of n dimensions to one of $m(< n)$ and preferably to choose m in such a way that its co-ordinates are independent of one another, *i.e.*, "orthogonal."

A very similar problem has arisen in psychology in an even more acute form, since large batches of psychological tests are often used on a big population, and there is no independent way of expressing in objective terms what it is that each test measures.

The treatment of this problem is revolutionising psychometry and has probably done more towards its establishment on a scientific basis than any other single development. It appears likely that factorial analysis or some similar statistical method may simplify very greatly the handling of complex industrial rheological data. Preliminary experiments on cheese[24] and plastics[25] give much cause for encouragement.

There are a number of ways in which factorial analyses can be carried out.[26] Only a brief account of the method can be given here. Suppose, for the sake of simplicity, that we wish to reduce the data from a number of tests in terms of two independent factors. The tests may be represented as straight lines passing through a common origin (see Figure).



Three such tests, A, B and C, are shown in the figure, the correlation coefficients between them (r_{AB}, r_{BC}, r_{AC}) being given by the cosines of the angles between the lines. It is clear that each test requires two magnitudes for its complete description on this diagram* and, since we have chosen to use two-dimensional space, the tests may be represented as vectors and are therefore marked with arrow-heads.

The use of only two dimensions, that is, a reduction to only two factors, is, of course, an over-simplification. No doubt other factors will be required for the complete description of the data, nor are the tests without experimental error. The circle is really part of a sphere, if not of a hypersphere, and the fact that the tests are displaced into at least a third dimension means that the projections of the displacements will bring the test-points into positions

* A vector requires for its specification as many magnitudes as there are dimensions. If we reduce our tests in terms of m factors, we shall require m magnitudes for their specification.

intermediate between the origin and the periphery of the circle in our figure. Such a point is shown at A'. Also, the angles between the vector lines will no longer have for their cosines the simple correlation coefficients.

If we scale each test so that the radius of the circle is equal to the standard deviation, then the area $[O A']^2$ is a measure of the extent to which our two-factor solution accounts for the variance and is called the "communality." The value of $1-[OA']^2$ is called the "uniqueness."

In the correlation matrix, instead of the more obvious procedure of filling the diagonal cells with 1·0's (since the correlation of any test with itself is presumably unity) we insert here the communalities, thus making allowance for errors and for any factor unique to the test itself. It is this procedure, which has to be done by trial and error, that makes the analysis rather lengthy, but there is, as yet, no way of avoiding it. If "ones" are used in the diagonal cells we shall not reduce our number of dimensions.

Any pair of axes at right angles, such as those marked I and II in the figure, can serve as independent factors (since cos $90° = 0$) and the choice of the position of the principal axis is in our power. By the use of matrix algebra we can, of course, handle any number of factors which would require hyperspheres for their geometrical representation. But for those who are helped by models, three-dimensional "cross-sectional" models are easily made.

It will be appreciated that we may take wide liberties not only with the sign but even with the scaling of our tests. An instrument measuring some rheological property, say hardness, on a "linear" scale might equally well and more meaningfully have been designed with a reciprocal ("softness"), a square or a logarithmic scale. But if we change the scaling of a test, care must be taken to ensure that correlations are improved throughout the whole matrix.

The factor matrix itself (F) is derived from the equation $R = F.F'$. The correlation matrix, R, is of course square: F and its transpose F' are rectangular, the divergence from squareness representing the amount of saving which the factor analysis has been able to effect.

Where very large correlation matrices are available, or if there are artificial limits to the parts of the distribution curve in which samples may be found, it is sometimes advantageous to make at least a preliminary analysis in terms of non-orthogonal axes, a procedure which, as stated above, is similar to the use of non-Newtonian dash-pots and non-Hookean springs. In the writer's opinion, such methods should serve only as a first stage and, if models are to be used, the treatment should be followed up by making simple models of the units of the complex models.

So far as the writer is aware, he and his colleagues are the first to take up Thurstone's suggestion[26] that factorial analysis should be applied to purely physical processes. A comparatively large proportion of the present paper has been devoted to this method because it is our belief that its use will prove of great practical importance in the interpretation of empirical rheological tests and perhaps in developing theories of the behaviour of complex rheological systems.

I am indebted to my colleague, Mr. R. Harper, for reading through my short account of factorial analysis—a technique with which he is much more familiar than I am.

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Rheological Methods in the Milling and Baking Industries

BY A. J. AMOS

WHEATEN flours contain two main proteins, gliadin and glutenin, which in the presence of water form a complex, known as gluten, possessing both elastic and plastic properties. In a properly made dough the gluten takes the form of an interwoven network of fibrils which constitutes the skeletal structure of the dough mass. The nature of this network, and hence the number and nature of the individual gluten fibrils, must be such that the dough can be inflated with gas to a suitable degree without serious distortion of its moulded shape and can continue to exhibit a fine and even vesiculation internally. It is no wonder, therefore, that from the very early days of cereal science attempts have been made to evaluate the physical properties of gluten. Since 1886, when the first attempt was recorded, well over thirty different rheological methods have been devised for assessing the breadmaking quality of flour. Many of these are of only historical interest, and of the others only about half a dozen have gained popularity.

None of the few well known dough testing instruments in use in cereal laboratories to-day is the outcome of a fundamental approach to the problem. By that I mean that the designers of these instruments did not first ascertain the significance of certain strictly definable physical attributes of dough behaviour and then devise suitable methods of measuring these attributes. Rather did they evolve a technique for obtaining mechanically in graphical form reproducible representations of stress/strain relationships imposed upon a dough and then interpret the curves thus obtained in the light of the observed breadmaking quality of a replicate dough. If often happens, therefore, that a particular measurement derived from the curve furnished by an accepted dough testing instrument is not an index of a strictly definable and individual physical property, and indeed it may even not be possible to express in absolute terms exactly to what the measurement does refer. On the other hand, the measurement will have a very real meaning in terms of dough behaviour, and this is why these instruments have proved such valuable tools to the cereal chemist. Within the last decade, however, excellent work by investigators in this country has established the correlation between certain aspects of baking quality and definable physical properties of doughs. These workers have devised methods of measuring these physical properties, but commercial models of their instruments are not yet available.

The dough testing instruments which are empirical in principle but are widely used are of two main types. There are those in which the resistance of the dough to a given mechanical mixing operation is recorded graphically throughout a continuous mixing of 5 to 20 minutes, and the other type in which the dough is stretched until it breaks and throughout this operation, which takes only a matter of seconds, the stretching force and the corresponding amount of stretch are recorded in graphical form. In this country the best known instrument of the former type is the Brabender Farinograph (Fig. 1). The essential features of this machine are a twin-bladed, water-jacketted mixer of special design and a directly coupled electric motor, which is supported so that it is free to rotate in a vertical plane and to the housing of which is connected a pen that can write upon a clock-work driven band of ruled paper. When a dough is being mixed in the mixer of this instrument, the resistance that it offers to the movement of the mixer blades causes a rotational movement

of the suspended motor and a corresponding movement of the pen. The type of curve furnished by this instrument is shown in Fig. 2. The mean height of the band that the pen produces is directly related in the early stages of the mixing operation to the proportion of water that has been added to the flour. Hence, if the height of the band which corresponds to the dough consistency desired by the baker is known, this instrument can be used to determine the water absorption of a flour. As the mixing operation continues the height of the band produced by the pen decreases owing to the effect of the continued mechanical abuse of the dough.

The curves produced by this instrument do not provide numerical assessments of individual physical properties of the dough, but they are capable of furnishing data that are correlated with certain aspects of dough behaviour of importance in the breadmaking process. Thus, the distance AB is a measure of the time needed under the conditions of the test to attain proper dough development. Flours that exhibit a prolonged dough development time are generally what the baker calls "strong" flours and will usually give good results in high-speed mixers. Sometimes, however, a prolonged dough development time may arise from an unusually slow rate of imbibition of water by a protein of only fair quality. The distance BC, which represents the time during which the curve continues at the initial level, is regarded as a measure of dough stability. The distance DE, which is the units of consistency lost during a given period of mixing, is termed the "dough weakening time" and is an index of the ability of the flour to withstand fermentation and mechanical abuse.

In Fig. 3 appear the Farinograph curves of flours of very different breadmaking qualities. It will be seen that the flours from the Manitoba wheats, which contain a high quantity of good quality protein, give curves indicative of very great stability. The curves of the flours from the Plate wheats show much less stability and the smaller widths of these bands agree with the less springy or elastic natures of their doughs. The short development time and poor stability exhibited by the bottom right-hand curve are characteristic of the curves of weak flours more suitable for confectionery work than for breadmaking.

The principle upon which the Farinograph operates permits tests to be made with fermenting doughs. In such tests it is customary to run the mixer until the dough is properly developed (normally 3 to 5 minutes), and then to give the dough a further mixing for 2 minutes at hourly intervals during a fermentation period of, say, 5 hours. This procedure furnishes curves such as those depicted in Figs. 4 and 4*a*. It will be seen from these figures that such curves do provide information upon the ability of a flour to withstand fermentation and can give some indication of the period at which the dough should attain correct ripeness.

Other forms of recording mixers which furnish curves similar to those produced by the Farinograph are in use in America, although they have not been adopted in this country. A good example of these is the Mixograph, which is shown in Fig. 5. The mixing head carries four vertical pins which move among four fixed vertical pins in the mixing bowl with a planetary motion when the head is lowered into position. The tendency for the bowl to rotate as a consequence of the pressure exerted on its fixed pins is impeded by a standardised spring in a manner that permits the torque to be recorded. Curves produced by the Mixograph are shown in Fig. 6.

In this country and on the Continent, wide use is made of two instruments of the other type, in which the dough is stretched until it breaks and both the stretching force and the degree of extension are mechanically recorded during the stretching operation. The older of these two is the Chopin instrument; initially it was known as the Extensimeter, but the improved model, which has been developed during the last ten years, is known as the Alveographe. In this instrument, shown in Fig. 7, a disc of non-yeasted dough of fixed dimensions is clamped across an air inlet and then blown into a bubble until it bursts; the varying pressure within the bubble is depicted throughout the operation by a recording manometer. The dough is mixed, moulded and cut into discs under rigorously standardised and controlled conditions and throughout the inflation procedure its temperature is kept constant.

There is a radical difference between the technique of evaluating dough properties by means of the Chopin Alveographe and by the Farinograph. In the Farinograph method all doughs are made to the same consistency and a preliminary test is always performed in order to determine the proportion of water that has to be added to the flour to arrive at the standard of consistency that has been adopted. The doughs used in the Alveographe, on the other hand, vary greatly in consistency, but they are constituted so that in each of them

the ratio of total water, *i.e.*, added water plus water natural to the flour, to dry solids is a constant.

Three curves furnished by the Alveographe are shown in Fig. 8. The measurements usually made from these curves are three. The height of the peak is measured as an index of the stability of the dough, the length of the base of the curve is, of course, a measure of its extensibility, and the area enclosed by the curve is a measure of its "strength." Although the mathematics of this technique and the curves it furnishes are very complicated and it is doubtful whether the curves provide a numerical assessment of any single property, this instrument does provide extremely useful information upon the nature of the protein of a flour. It is particularly valuable as a means of evaluating the blending potentialities of wheats, where what is required is a knowledge of the inherent protein characteristics of the wheats rather than information upon how they will behave in a commercial flour when subjected to the influence of enzymic action and of chemical improvers. The use of the Alveographe for evaluating wheats is well illustrated by the curves in Fig. 8. The top left-hand curve is that of a flour with good breadmaking qualities. It has a high strength and is well balanced; it would give a dough with properties pleasing to the baker which would stand up well to mechanical treatment in the bakery. The flours represented by the other two curves are identical in strength with the first flour, since the areas of the three curves are identical, but they are quite unsuitable for breadmaking. The top right-hand curve reveals excessive stability and very poor distensibility, corresponding to a clay-like dough. The bottom curve indicates poor stability but excessive distensibility, in other words, a soft "flowy" dough. The importance of the balance between the individual physical attributes, and hence the value of the curves furnished by this instrument, can be appreciated from the fact that, whereas neither the flour giving the top right-hand curve nor that giving the bottom curve is at all suitable for breadmaking, a fifty - fifty mixture of the two would give a well balanced and completely satisfactory dough, corresponding to a curve very similar in general shape to that of the satisfactory top left-hand curve.

The strength and stability figures furnished by various wheat samples when tested on the Alveographe, expressed in empirical units, are shown in Table I.

TABLE I

ALVEOGRAPHE FIGURES FURNISHED BY VARIOUS WHEATS

Type	Stability	General strength
Manitoba	80–110	65–105
Garnet..	100–125	60–75
Canadian Durum	65–90	25–40
Hard Winter	60–90	40–70
Russian	50–85	30–65
Rosafe Plate	60–80	30–50
Barusso Plate	65–95	55–70
Australian	25–55	15–35
Indian	70–95	25–35
Danube Basin Wheats	30–65	25–40
Soft White Pacific	25–45	15–25
English	25–55	10–25

The other dough testing instrument in use in this country in which an applied stretching force and the degree of extension are measured is the Extensograph. In this instrument, shown in Fig. 9, a cylinder of dough supported at each end has a force applied mechanically to the middle so that it is stretched downwards into the form of an elongated U until it breaks. The applied force and the degree of extension are recorded on a moving band of ruled paper. As in the Farinograph, the doughs are tested at constant consistency and hence carry different amounts of water. The curves produced by the Extensograph are illustrated in Fig. 10. It is usual to attach importance to the maximum height of the curve, which is termed resistance, the width of the curve, which represents the extensibility, and the area enclosed by the curve, which is referred to as the energy and is a measure of the strength. The ratio of maximum height to width is used as an index of balance of properties; a low ratio indicates a soft "flowy" dough and a high ratio a stiff and tough dough.

Each of the three instruments that have been discussed, namely, the Farinograph, the Alveographe and the Extensograph, is being used for routine testing in cereal laboratories in this country and certainly permits various aspects of the baking qualities of flour and/or

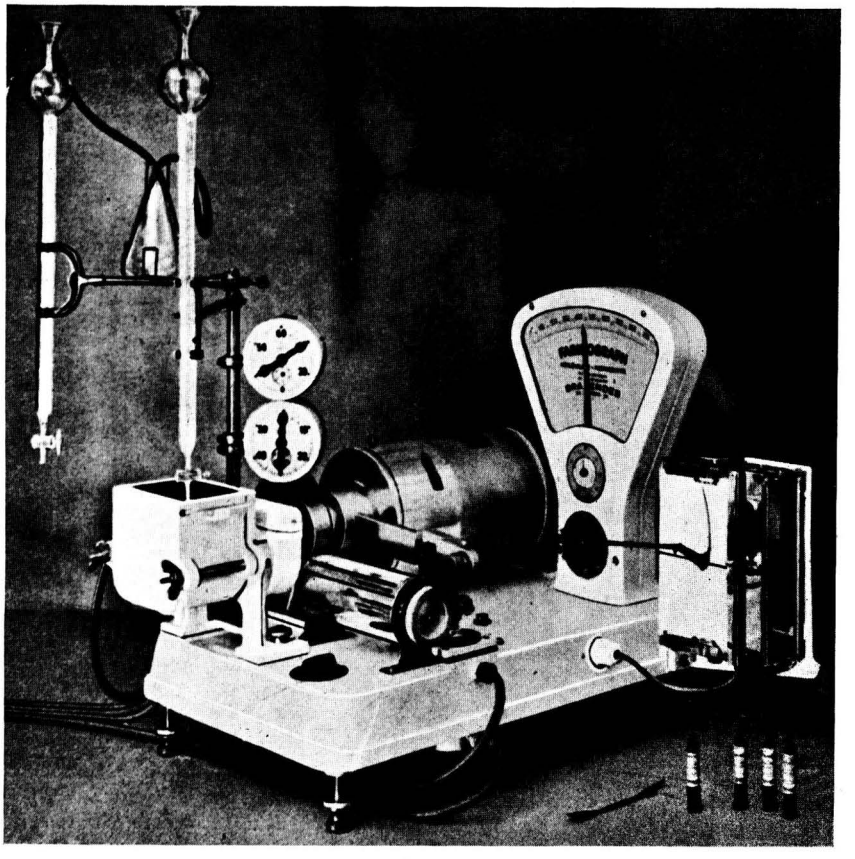


Fig. 1. The Brabender Farinograph

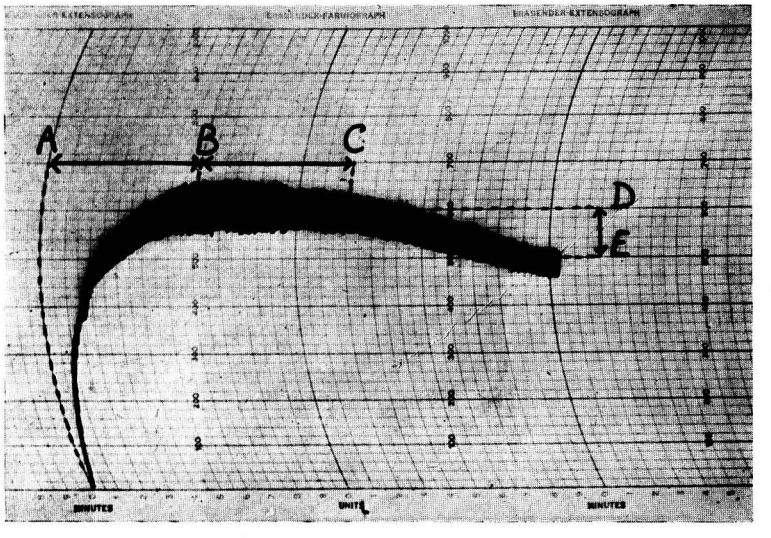


Fig. 2. A Farinograph curve

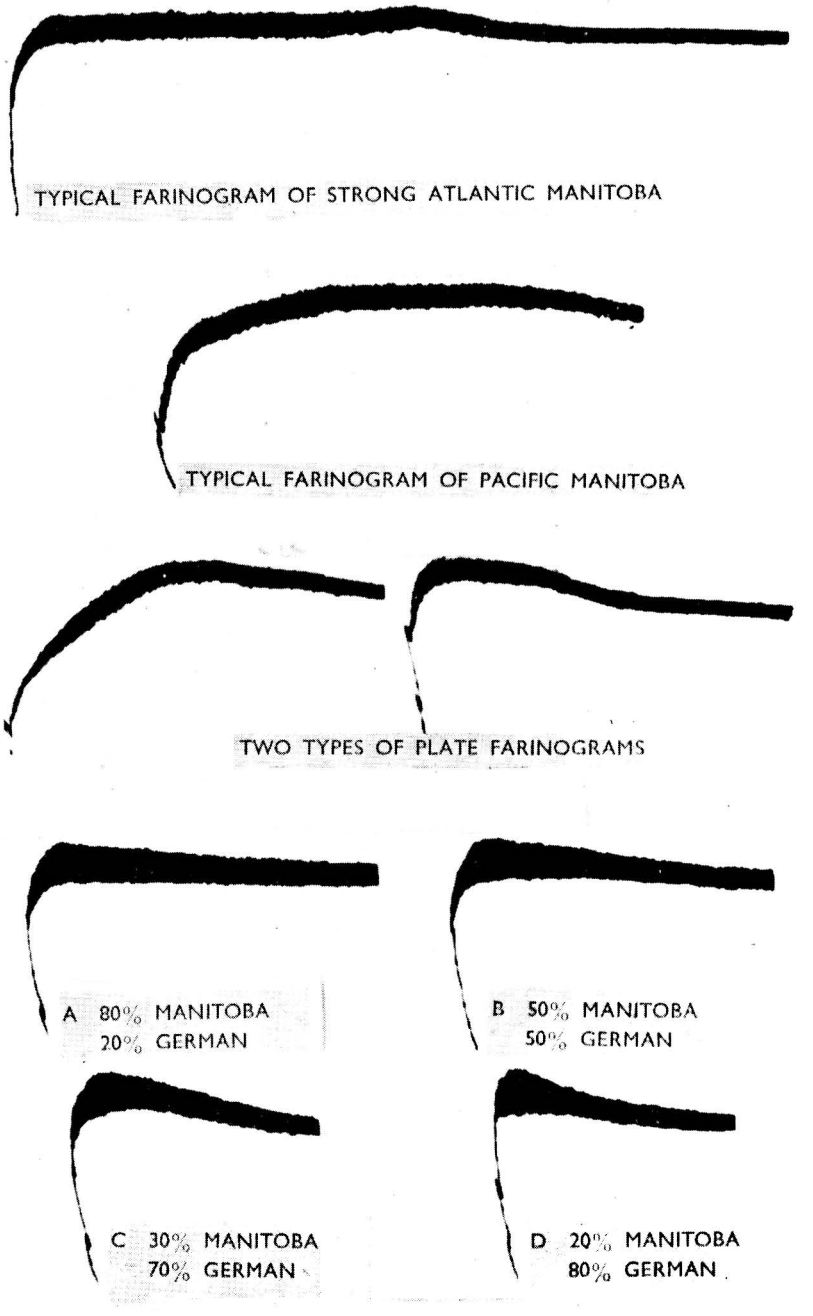


Fig. 3. Farinographs from strong and weak flours (Kent-Jones and Amos[4])

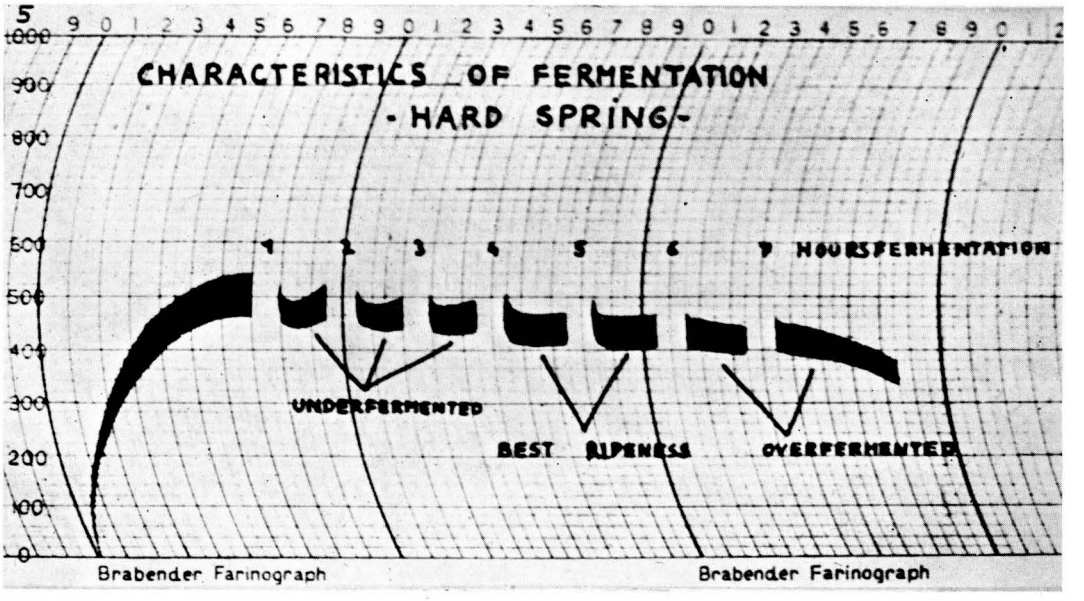


Fig. 4. Farinograph of Fermenting dough (Brabender[1])

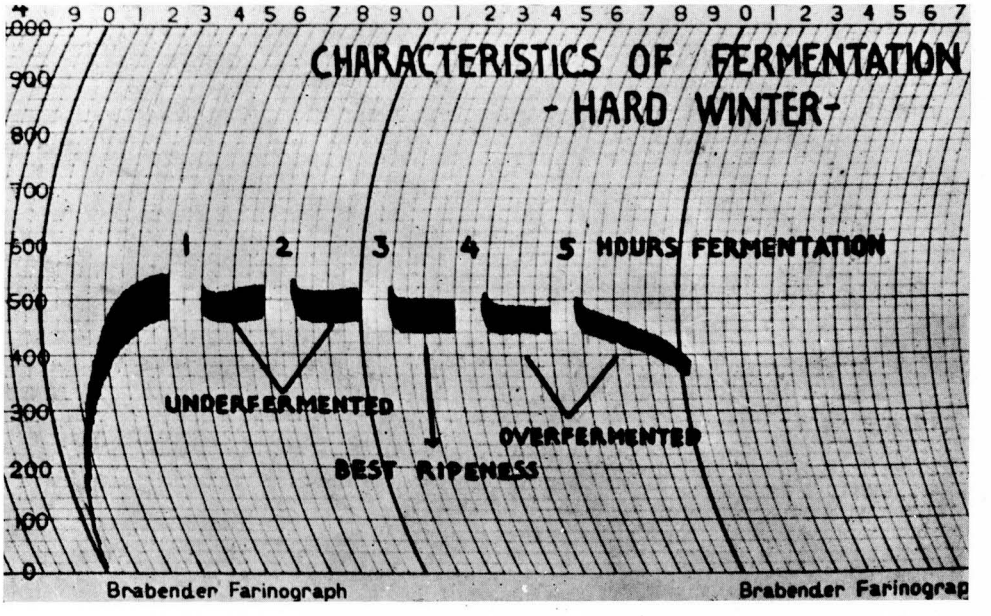
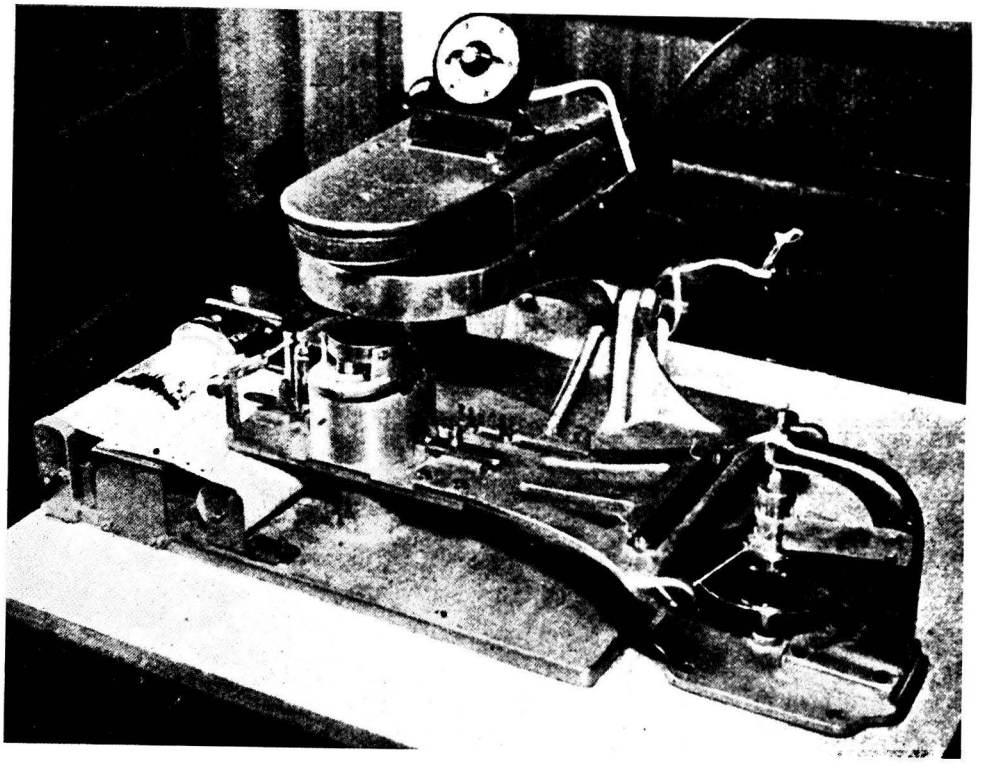


Fig. 4a. Farinograph of fermenting dough (Brabender[1])



Fia. 5. The Mixograph (Kent-Jones and Amos[4])

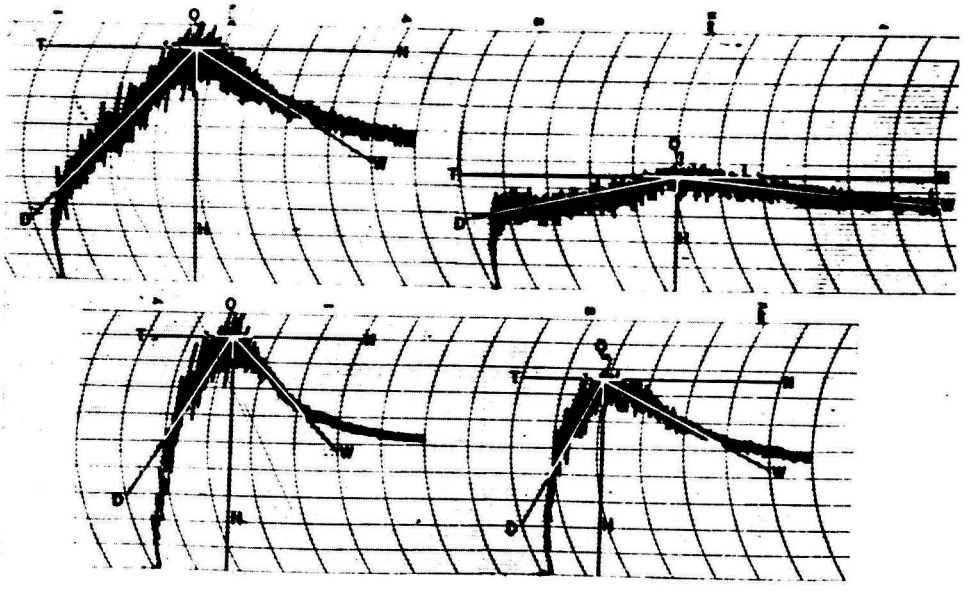


Fig. 6. Mixograph curves (Swanson and Johnson[9])

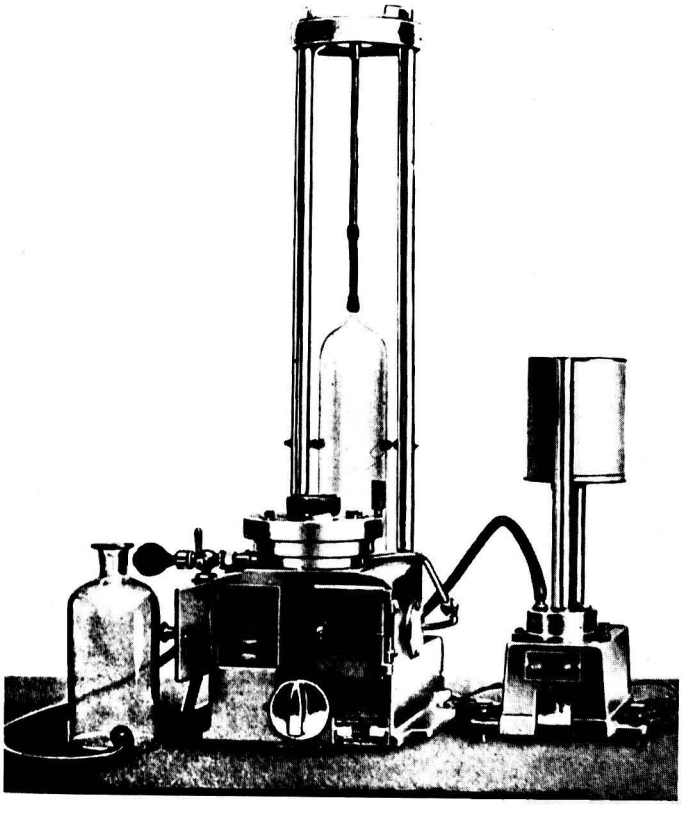


Fig. 7. Chopin Alveographe

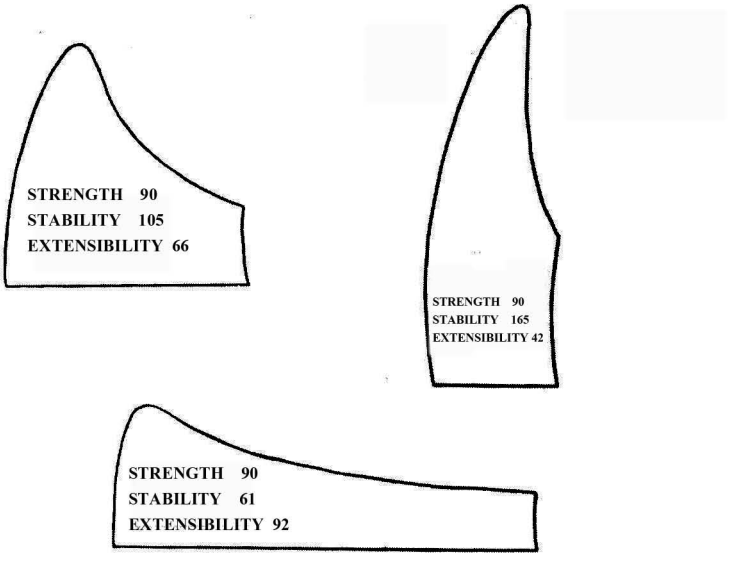


Fig. 8. Alveographe curves of equal area.

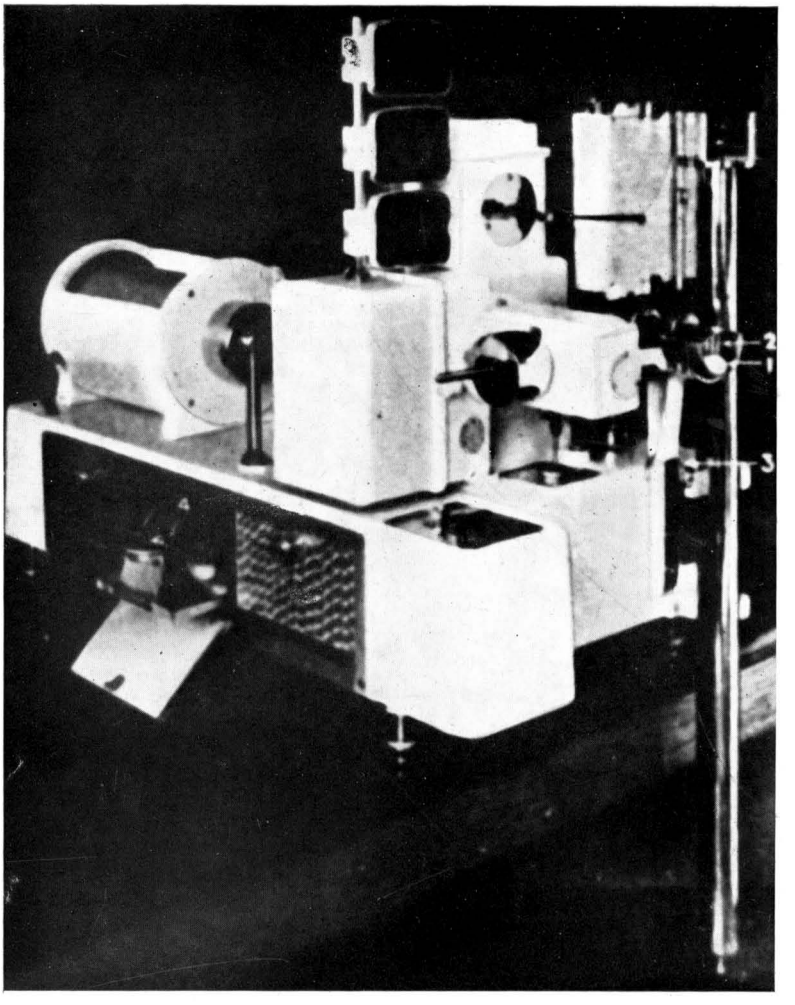


Fig. 9. The Brabender Extensograph

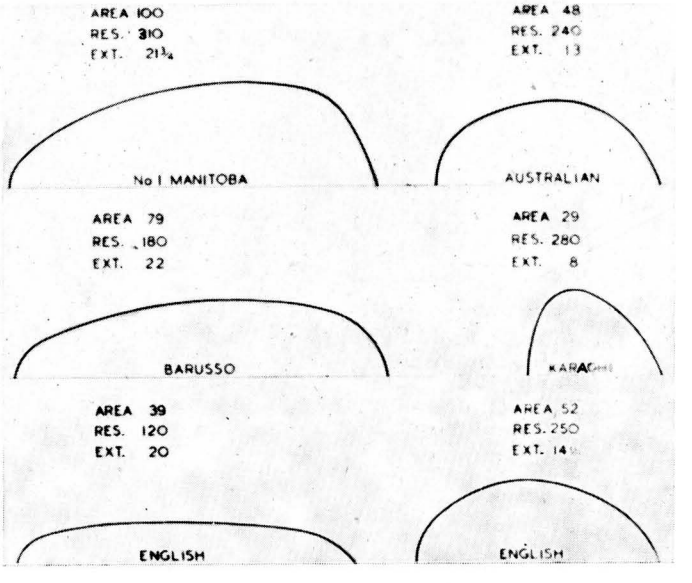


Fig. 10. Extensograph curves (Lockwood[5])

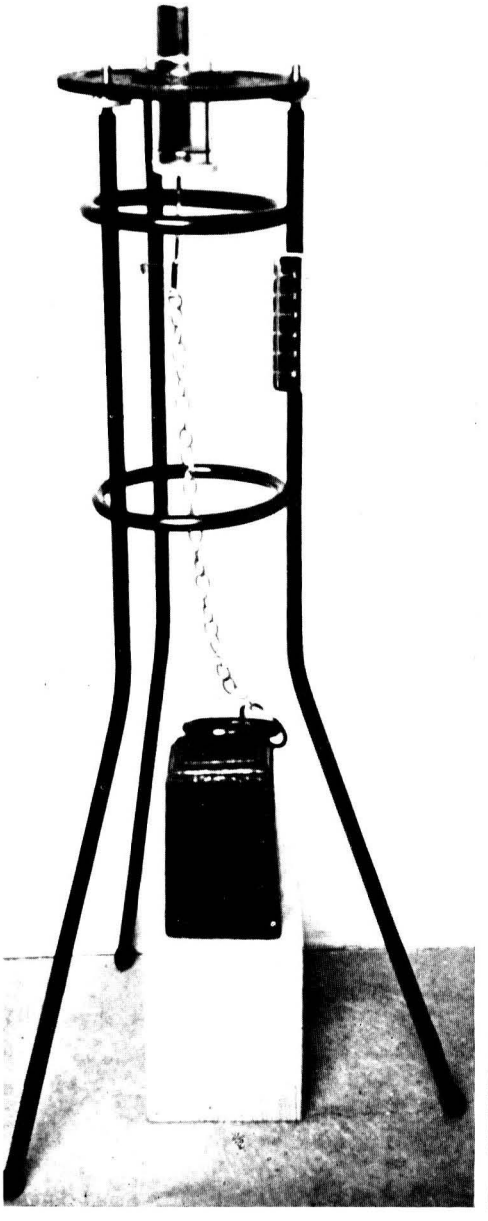


Fig. 11. Halton's Absorption meter

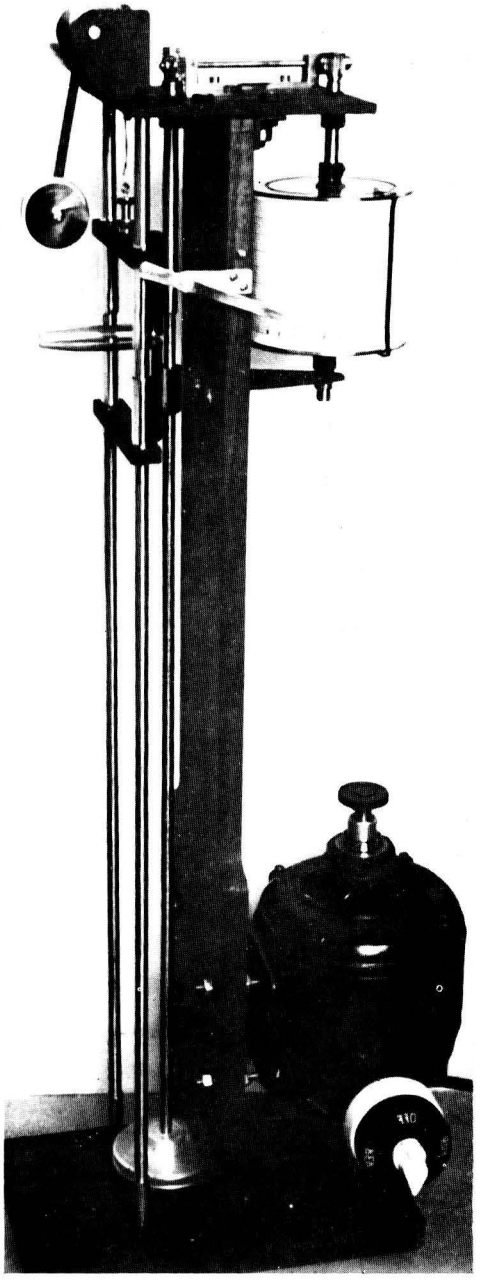


Fig. 12. Halton's Extensometer

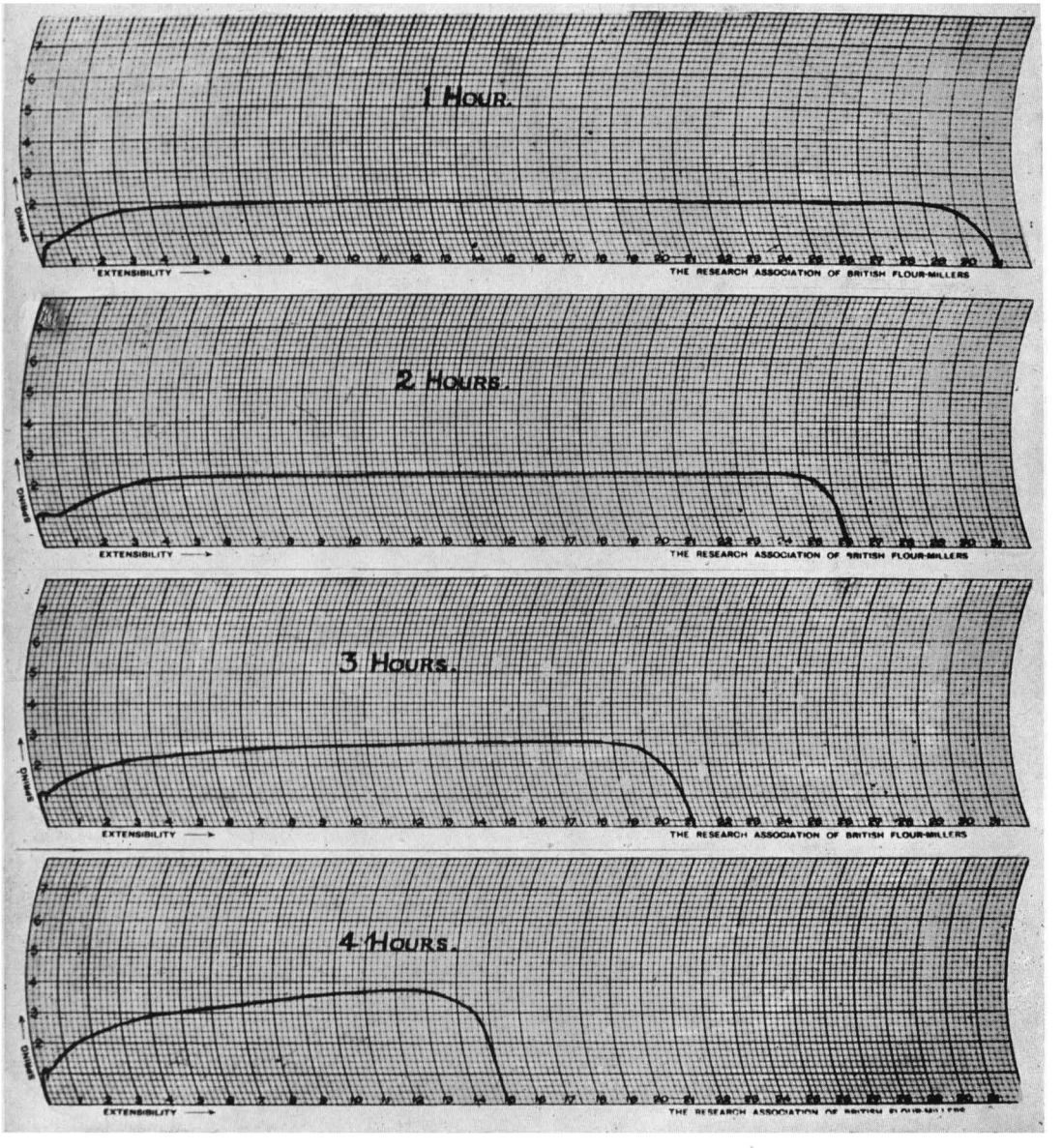


Fig. 13. Extensometer curves (Halton[2])

of the blending potentialities of wheats to be reliably assessed. Not one of these undoubtedly valuable instruments, however, is the outcome of study of dough properties from the angle of fundamental concepts; in each instance the sequence of events was the perfection of a method of recording the response of a dough to an imposed stress and the interpretation of the records in terms of baking behaviour determined in the test bakery. Schofield and Scott Blair,[6,7,8] however, made a fundamental approach to the problem by devising methods for determining certain strictly definable physical properties of flour dough, and this work was developed by Halton and Scott Blair,[3] who studied the relationship between these properties and baking quality. Extensive use was made by these workers of an apparatus in which a cylinder of dough floating on a bath of mercury is stretched by means of a given force for a given time and measurements are made of the extent to which the dough stretches and the extent to which it recovers after removal of the stretching force.

Halton and Scott Blair established that two of the most important factors in dough behaviour were viscosity and elastic modulus, two properties which they were able to measure in absolute units on their apparatus. They suggested that for the production of good bread a dough should possess high viscosity, since the viscosity is a measure of the stability of the dough, that is, its ability to resist flowing out under its own weight, but a low modulus, which would permit the dough to expand properly during fermentation and the early stages of baking. On this theory, good breadmaking value calls for a high viscosity/modulus ratio, a ratio which Maxwell termed "relaxation time." Halton and Scott Blair believe that what the baker terms the "spring" of a dough, *i.e.*, the degree to which a dough recovers after deformation, is closely associated with relaxation time. Since both the viscosity and the modulus of a dough are related to the proportion of water present, and the influence of water content is not the same for the two properties, the *ratio* of viscosity to modulus, or the relaxation time, for a dough will depend upon the proportion of water used in making the dough. Halton and Scott Blair decided, therefore, that they must bring each of their doughs to a water content which corresponded to optimum handling and baking quality for the particular flour used, or in other words, to the correct commercial water absorption.

Further investigation revealed that the amount of water a baker incorporated in his dough was determined not by the viscosity but by the modulus of the dough. In other words, doughs prepared by a baker for breadmaking from different flours would be likely to exhibit a wide range of viscosity, but their elastic moduli would be very similar. Halton and Scott Blair, therefore, decided to make their measurements of the relaxation time at a constant modulus which would correspond to the mean of the moduli of the doughs used in a range of commercial bakeries.

Following on from these fundamental studies, Halton has devised an instrument for determining the correct amount of water to be used in making the test dough and another instrument, a marked advance upon the original mercury-bath apparatus, by means of which the dough can be stretched mechanically and the stress/strain relationships automatically recorded. These instruments, however, are not yet on the market. His water absorption apparatus is shown in Fig. 11. A yeasted dough is prepared under standard and controlled conditions and after a 3-hour fermentation period is placed in the cylinder. It is then forced through an orifice in the bottom of the cylinder by a plunger operated by the attachment of a weight, and the time taken for a given volume of dough, as measured by the pointer, to be extruded is noted. It has been established that the extrusion time is a function of the modulus of the dough. The test is performed at three different levels of water content and a curve of extrusion time against water content is plotted. From this curve is read the proportion of water required to give the extrusion time which is known to correspond to the desired modulus.

Halton's dough testing instrument is shown in Fig. 12. A ball of yeasted dough prepared under standard and controlled conditions is pushed on to the two pegs until they have passed right through the middle of the ball. By means of the motor the lower of the two pegs is caused to descend at a constant rate, which stretches the dough and thereby exerts a force upon the upper peg. This peg is connected to a balance weight so that the force exerted on the peg causes it to move through only a small distance. The movement of this peg is recorded upon a moving band of ruled paper. The height of the curve drawn on the paper is a measure of the tension in the stretched dough, and the length of the curve is an index of the extent to which the dough is stretched.

Some curves produced on this instrument, which is called an Extensometer, are shown

in Fig. 13. The product of the maximum height of the curve and the length of the curve, that is, the product of load and extensibility, is accepted as a measure of the potential strength of the dough. Since all doughs are made to the same modulus, the height of the curve is an index of the relaxation time of the dough, *i.e.*, of the viscosity/modulus ratio, and is, therefore, a measure of the spring of the dough. The length of the curve is, of course, a measure of its extensibility. The Extensometer curves in Fig. 13 were made at hourly intervals on the same dough and reveal the changes in the physical properties of a dough which occur as fermentation proceeds. In the early stages of the fermentation the dough is very distensible but has only fair spring, as is revealed by the 1-hour curve. As fermentation proceeds the dough becomes less distensible or "flowy," tightens up and becomes more springy, as can be seen from the gradual change in the shapes of the curves.

In Table II are given the results of Extensometer tests on doughs containing various quantities of chemical improvers, that is, substances that alter the physical properties of the dough in the direction of improved breadmaking quality.

TABLE II

EFFECT OF ADDITION OF IMPROVERS TO FLOUR ON EXTENSOMETER CURVES
(Halton, 1949)

	Height	Length	Product
Flour A:			
Potassium bromate, 0 p.p.m.	2·0	19	38
" " 10 "	2·4	16	38
" " 20 "	2·8	14	39
" " 30 "	3·2	12	38
Flour B:			
Nitrogen trichloride, 0 g./280 lb. ..	1·5	21	31
" " 3 " ..	2·0	16	32
" " 6 " ..	2·2	14	31
" " 9 " ..	2·3	13·5	31

It will be seen that as the proportion of improver is increased the height of the curve becomes greater, which indicates more spring in the dough, whilst the length of the curve is decreased, indicating a reduction in the extensibility. An interesting feature is that the product of these two figures, which Halton calls the potential strength of the dough, is more or less constant. In other words, the action of an improver as judged by this instrument is not a matter of increasing the strength of the dough but rather the production of an optimum balance between the individual physical properties, so that the potential strength of the dough is fully realised.

This necessarily extremely brief survey of a very important and very complex subject can do little more than reveal the value of the information which the cereal chemist obtains as a routine measure by the application of rheological methods to doughs, and suggest problems that still await elucidation. It is true that the mechanical dough-testing instruments in regular use are empirical in principle and do not measure individual physical constants, but they nevertheless furnish information of very great value. There is little doubt, however, that the fundamental work which has been done in this field in recent years will be followed up and we may look forward to the appearance of new or improved dough testing instruments and to the disappearance of some of the empiricism of long-established dough testing methods in favour of an interpretation of results on a more fundamental basis.

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88 MADELEY ROAD
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The Use of Rheological Tests in the Pharmaceutical and Cosmetical Industries

By ROBERT H. MARRIOTT

Many pharmaceutical and most cosmetical products are required to possess a "consumer appeal." The chemist employed in this branch of industry has therefore to pay attention to uniformity of production and the maintenance of a good appearance of the products, and also to consider fully the form of a product most likely to ensure that the user can employ it to the best advantage.

In order that a formulator can investigate the effect of modifications of a recipe and of the method of manufacture, and the production department can ensure a uniform product, there is need of a means of evaluating the consistency or "body" of a product. This is a complex summation of a variety of physical attributes and even if it were possible to resolve consistency into all its component items, the task of finding an equation in which each component contributed its correct quantum would be almost insuperable. The usual method

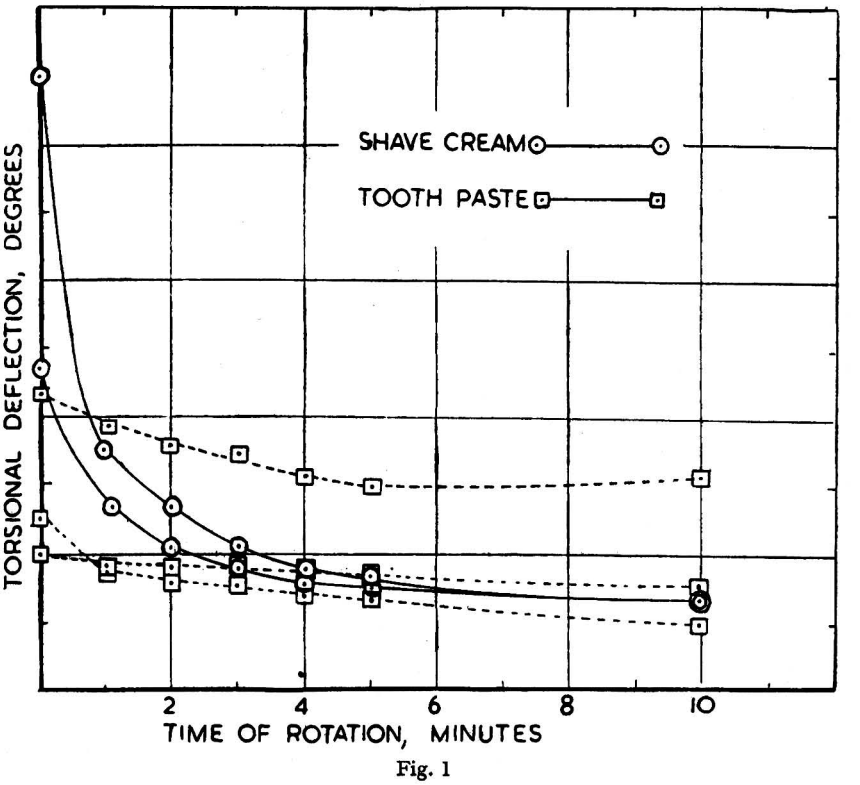

Fig. 1

adopted is the practical one of touching with the finger or squeezing a tube, methods only of use when the assessor is gifted in that way and has experience. Attempts by means of mechanical devices to imitate these tests never seen to be successful. It has been found, however, that the rotating cup viscometer does give values that have some sort of relationship with quality and are reproducible not only on samples from the same batch but also on the same sample, provided that the conditions of experiment are not varied.

It is the purpose of this note to indicate some of the ways in which such a viscometer can be applied in the works control laboratory. Mention is made of the value of this instrument in following the effect of variations in the manufacturing processes and of the changes that can occur in di- or multi-phase systems on storage.

Dentrifices and shaving and hair creams must possess "body." At the same time this body should not be so great that difficulty is experienced in the filling of the product into tubes or bottles. If the degree of "body" required of the preparation when in the hands of the user is such that filling would be difficult, then the cream or paste must be comparatively fluid when made and become firmer on storage, *i.e.*, it must possess thixotropy. When the cup of the viscometer is filled, the plunger dipped into the material under test and the motor started, the torque is taken up by the torsion wire until a point is reached when the plunger ceases to be carried round. The angular deflection at this point is a measure of the viscosity of the material. If the substance has structure, the torsional deflection will decrease as this structure is broken down and in the course of time the torsional deflection will reach a constant value. Fig. 1 shows curves for the torsional deflection plotted against time, for shaving cream and tooth paste. The upper of the two curves for shaving cream indicates the highest values found in practice for a particular well-known product and the lower curve gives the minimum permissible values if the product is to be deemed satisfactory. For the tooth paste, the highest curve is one relating to a popular brand and the two lower curves are characteristic of another make. These curves were obtained with the freshly made unstored product.

The effect of the conditions of manufacture of hair cream is indicated in Fig. 2. When

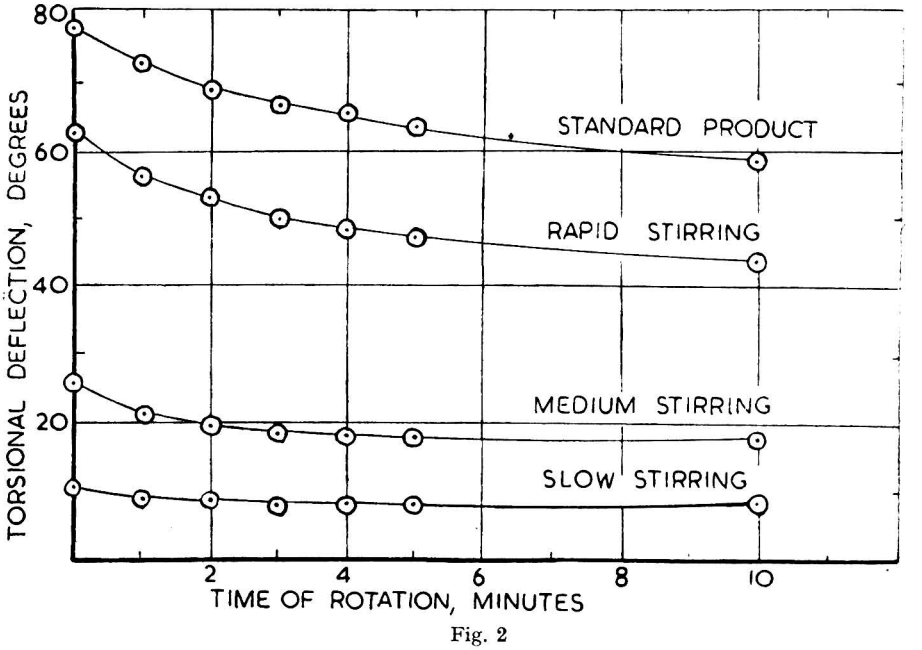

Fig. 2

the ingredients are mixed at a slow rate of stirring, the cream is almost Newtonian in character. As the rate of stirring is increased, the amount of thixotropy becomes more marked and at the same time the viscosity becomes significantly greater. The top curve indicates the values for the emulsion when made in large bulk, but prior to homogenisation.

In making ointments or lotions, cetyl alcohol is often employed as a stabiliser of the emulsion. While it is known qualitatively that increasing the percentage of the fatty alcohol increases the body or consistency, the rotating cup viscometer enables a numerical assessment of this effect to be rapidly made. Fig. 3 shows the torsional deflection plotted against the cetyl alcohol content of an oil-in-water emulsion. The upper line shows the variation in the yield value, the lower the variation in the equilibrium viscosity. The distance apart of the two curves is a measure of the thixotropy.

Fig. 4 shows the equilibrium viscosity values of shaving cream, tooth pastes and hair cream plotted against time of storage at ordinary laboratory temperature. The shaving cream appears to reach a constant value after about 8 weeks. One of the tooth pastes rapidly increases in viscosity, probably attaining an equilibrium in 2 weeks, whilst the other

appears to require about 12 weeks. The hair cream behaves rather differently in that there is only a slow increment for the first 4 weeks, after which the consistency rises rapidly to a

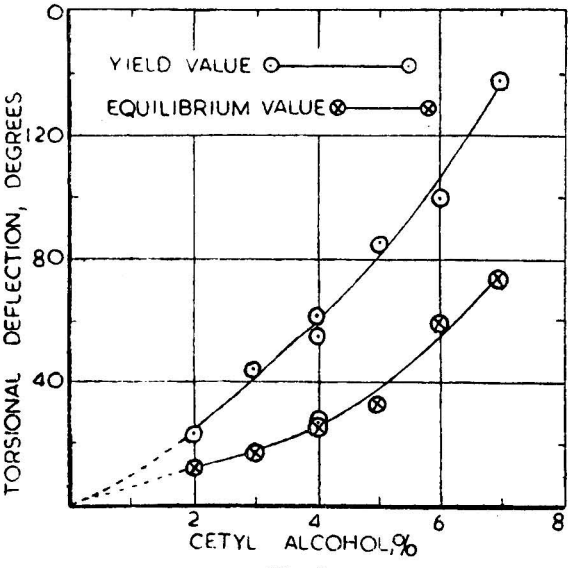

Fig. 3

constant value. During the increase in the equilibrium consistency there is also a gain in the yield value, the thixotropy, *i.e.*, the difference between the yield and the equilibrium values, often becoming greater. In this state the cream would be difficult to shake out of the bottle and it would be necessary to stir it or else subject it to vigorous shaking.

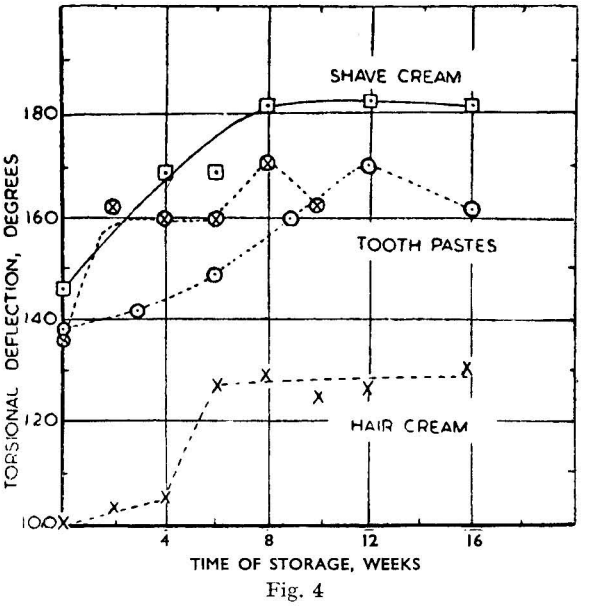

Fig. 4

It will be seen that this form of viscometer can be used to give a numerical assessment value to pastes and creams which will enable the manufacturer to maintain a constant quality. Its value in the factory is twofold. Firstly, the determination can be quickly carried out, so that the rate of production is not prejudiced, and secondly, it enables a mass of experience to be built up which will lead to a quick decision as to the steps to be taken to rectify a mistake and to prevent any subsequent repetition.

BEECHAM RESEARCH LABORATORIES
BETCHWORTH, SURREY

The Application of Rheological Methods to the Paint Industry

By P. S. WILLIAMS

I SHALL describe briefly the processes involved in paint manufacture and the desirable rheological properties of a paint, before discussing some of the control viscometers and research methods used in the paint industry. In preference to dealing in detail with some small aspect of paint rheology, I propose to give a general impression of apparatus and methods used to study the flow characteristics of paints and allied materials.

Paints consist of pigments dispersed in liquid media. The pigments used may be inorganic or organic, and of a wide variety of shapes and sizes. Fig. 1 shows four typical

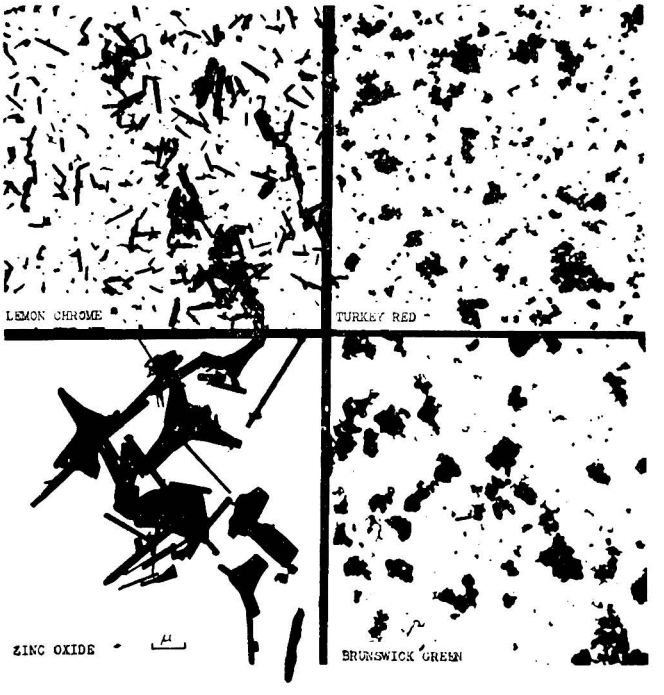

Fig. 1

paint pigments, varying in shape from acicular crystals to amorphous powder, and in size from a fraction of a micron to several microns. The medium may be a drying oil, a varnish or a nitrocellulose solution. In order to disperse the pigment in the medium, some mechanical action is necessary, and to assist in this process of dispersion—called milling—small quantities of dispersing or wetting agents are sometimes added to the paint. The milling is often carried out with only a portion of the total quantity of medium and solvent finally to be used in the paint, so that further quantities of liquid have to be added, after milling, to bring the paint to a suitable application consistency. It is this bringing of a paint to a consistency suitable for application that calls for control viscosity measurements, and it is the rather unpredictable flow behaviour of pigment suspensions in general that calls for research.

There are three main methods of applying paint to a surface: by brushing, spraying or dipping, and the requirements of a paint for application by each of these methods are not the same.

Brushing—It is necessary that the paint shall work well under the brush, that is, there shall be little drag or pull on the brush, otherwise the painter will be tired after a short time. In addition, the paint must have sufficient "flow," so that after the brush has left the surface,

the brush-marks will flow out and a smooth finish result. On the other hand, this flow must be so controlled that no sags, or tears, appear on the finished article.

Spraying—For this it is necessary for the paint to contain more solvent than is present in the brushing material. The consistency must be such that the paint can be atomised by the spray-gun, and sufficient solvent must be present to allow for loss by evaporation during transfer from the gun to the surface being painted. The film so produced must have sufficient "flow" to prevent what is known as "orange-peeling," the name given to the condition that arises when the droplets of paint, impinging on the surface being coated, remain in position instead of flowing out to give a smooth finish. On the other hand, as with brushing paints, the flow must be controlled to prevent sagging.

Dipping—In this method, as the name suggests, the articles are completely immersed in the paint, and then removed at a controlled rate. Here, the important factor is to control the flow so that films of the right thickness are produced.

It is clear that whether a paint is to be applied by brushing, spraying or dipping, its rheological properties, or more simply its viscosity, is a factor of prime importance. Unfortunately, the viscosity of a paint is not a true physical constant but depends on many factors. The types of rheological behaviour encountered in the paint industry may be classified under the main headings of Newtonian, thixotropic and dilatant. Fig. 2 shows

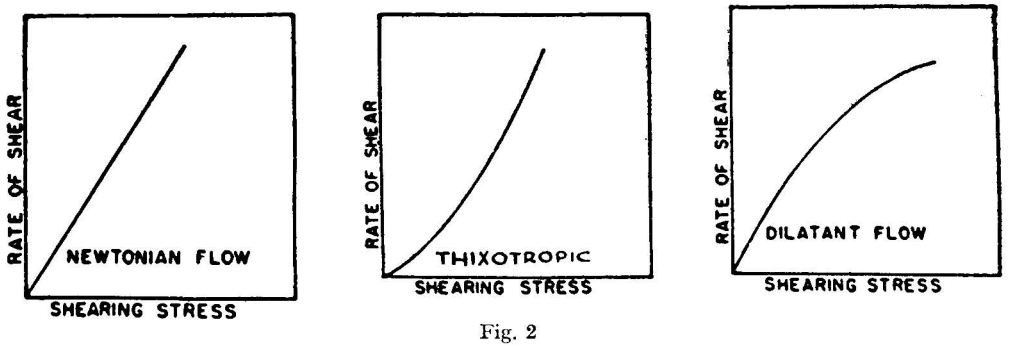

Fig. 2

the general shape of curves obtained by plotting stress against rate of strain for these types of flow. Of particular importance is the study of the flow behaviour represented by the thixotropic curve. Paints are subjected to a high rate of shear during brushing or spraying and may then appear to flow readily, yet the rate of flow under such small forces as surface tension and gravity may be very small indeed and, in fact, flow may cease altogether, resulting in brush-marks or other defects. Another complication from the rheological testing point of view arises from the time dependence of the viscosity of a paint. By time dependence, I mean that a paint, at rest in a container, will have a certain apparent viscosity, but that on stirring the paint, the viscosity will decrease and regain its former value on leaving at rest for some time, maybe hours, maybe minutes. These two factors, the dependence of flow on applied shear stress and on time, are generally grouped together under the term thixotropy. A certain degree of thixotropy is desirable in a paint, for it is the "physical" increase in viscosity that holds a paint in position against gravity forces, before the chemical drying has begun to take effect.

Many materials exhibit thixotropy and several mechanisms have been postulated to account for the phenomenon.[1,2,3,4,5] One suggests that the material is a loose network of particles interconnected at a few points, the network enclosing and immobilising dispersion medium. A second picture is that particles do not form any connected structure but are set and held in the dispersion medium by long-range forces. It is most likely that a combination of mechanisms applies to most systems, but further work must be done before any satisfactory theory can be formed.

I will now describe some of the instruments and experimental methods used to determine viscosity and to assess thixotropy. Efflux viscometers are most widely used by the industry for control purposes. There are very many types in use—a few of them standardised—and all of them are used in the following manner. The cup is filled with the paint to be tested and the time taken for all, or some specified volume, to flow through the orifice is a measurement of the viscosity. Although these cup viscometers are quite suitable for use with

Newtonian liquids such as most oils, varnishes and lacquers, they have serious limitations when some paints are tested in them, for often near the end of efflux there is not sufficient hydrostatic head to overcome the structure in the paint, and even if the time of efflux of the first 50 ml. is taken, there is often wide variation due to breakdown of thixotropic structure in filling the cup.

Another type of viscometer enjoying some popularity abroad, as a control instrument, is the Gardner Mobilometer. This consists of a cylinder containing the material under test through which a plunger is forced. The plunger consists of a metal rod passing through a guide, and on its end is screwed a disc, perforated with holes. Loads are applied to the plunger, and velocity of fall against load is plotted. A very wide range of materials can be studied using various shaped discs provided, and some qualitative estimate of degree of thixotropy can be formed by stirring with the plunger, allowing structure to reform for some set period and then making the measurement.

Turning now to the field of varnish and bodied oil manufacture, we have viscosity measurement as the control deciding how long to heat the ingredients to give the required degree of polymerisation. In making an oleo-resinous varnish, a resin and an oil are heated together for a certain time. The molecular weight of the varnish increases as the cooking proceeds, and the viscosity is measured at frequent intervals so that heating may be stopped when the material has reached the required degree of polymerisation. It is unfortunate that at the elevated temperatures used in varnish making, the differences in molecular weight have little effect on the viscosity, although at room temperature they cause large differences in viscosity. The usual method of viscosity measurement for varnishes is to test a sample by means of "body" or "bubble" tubes. These are tubes of standard size, about 10 cm. long and 1 cm. in diameter, containing mineral oils of known viscosity. A sample of liquid to be tested is put in a similar tube, leaving a bubble about the same size as that in the standard tubes. By comparing the times of rise of bubbles, the viscosity of the material may be readily estimated. This method is quick and requires only a small sample—an important point in varnish manufacture—for until the viscosity determination has been made, the material is undergoing further polymerisation and there is risk of spoiling a batch.

A method for determining the viscosity of a paint or varnish in a large container and not requiring the withdrawal of a sample would be of considerable value. The Brookfield viscometer is used for this purpose in America. This viscometer uses a synchronous motor to drive a shaft at a constant speed, one of four speeds selected by a gear box. The shaft is coupled by a torque-measuring spring to a cylinder which is dipped into the liquid under test. The drag on this cylinder is used to give a dial reading in centipoises, and by using cylinders of different sizes a wide range of viscosities can be covered.

For accurate viscosity measurements there are the well-known methods using B.S.I. U-tube viscometers or B.S.I. falling sphere viscometers. To find the viscosity of a small quantity of very viscous liquid such as a drying oil or varnish, an extension of the B.S.I. falling sphere method is very useful, and rapid. The liquid is contained in a body tube and the B.S.I. technique is followed, except that the ratio of ball to tube diameter, d/D, is greater than 0·1. Owing to the close proximity of the wall of the containing vessel, care must be taken to apply the correct wall-correction factor which Faxen[6] has derived, and which is given by the bracketed term in the expression

$$\eta = \frac{2\,\mathbf{g}r^2}{9\,v}(\sigma - \rho)\left[1 - 2{\cdot}104\left(\frac{d}{D}\right) + 2{\cdot}09\left(\frac{d}{D}\right)^3 - 0{\cdot}95\left(\frac{d}{D}\right)^5\right]$$

where d = diameter of sphere, radius r; D = diameter of cylindrical tube; v = velocity of sphere; and σ and ρ are the densities of the sphere and liquid, respectively.

I will now discuss recent research methods and their uses. Recent techniques seem to favour concentric cylinder apparatus so that the material being sheared between two cylinders may be subjected to known steady rates of shear for any duration. By measuring the torque on the inner cylinder and rotating the outer, or *vice versa*, it is possible to cover a wide range of shear stresses.

Green and Weltmann[7,8,9] in America have developed a technique for giving some quantitative measure to thixotropy. This they do by constructing and analysing hysteresis loops for their materials. Fig. 3 shows such a loop, which is obtained by plotting deflection of inner cylinder against speed of rotation of outer cylinder for increasing speeds. The down curve is obtained by quickly lowering the speed of rotation to zero. From analysis of this

loop, the authors derive two coefficients of thixotropic breakdown; one is independent of time and may be defined as the loss in shearing force per unit area per unit increase in velocity gradient for the selected time employed in making the up curve. The other gives a relation between the total length of time employed in producing the breakdown, and the breakdown itself. Application of this technique has been made by Fischer and Jerome,[10] who studied

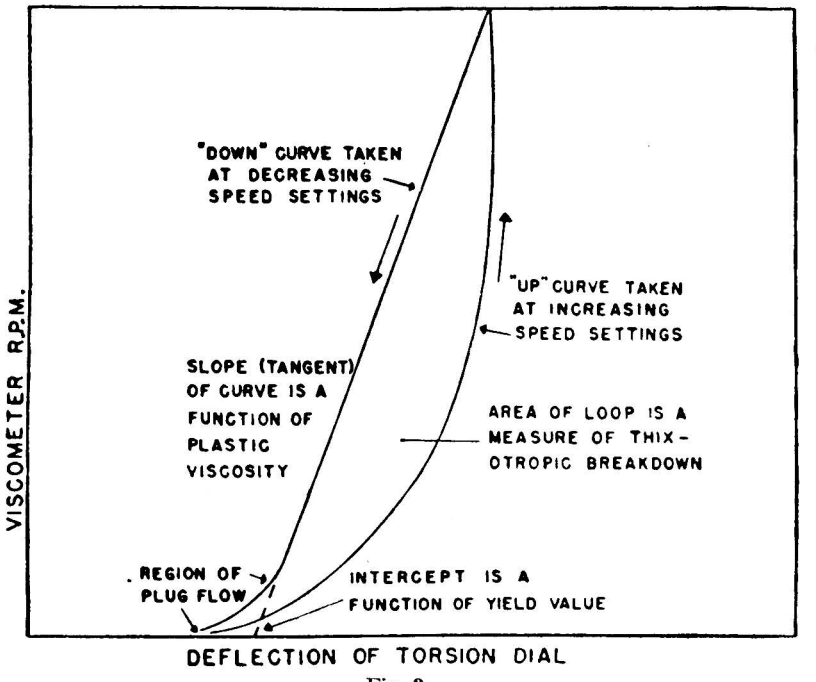

Fig. 3

the effect of milling conditions, wetting agents and variation of medium on flow properties of suspensions. Table I shows a few of the results they tabulate, and it is evident that the effect of the wetting agent is highly specific to the system being investigated.

TABLE I

EFFECT OF SURFACE ACTIVE AGENTS ON FLOW PROPERTIES

(Fischer and Jerome[10])

	Carbon black				Iron blue				Ultramarine blue			
	9·7% in glycerol		15·3% in stand oil		29·8% in glycerol		28% in stand oil		39·7% in glycerol		32% in mineral oil	
Reagent	V	*f*	V	*f*	V	*f*	V	*f*	V	*f*	V	*f*
None	3·0	3800	57	10,400	8·3	37	90	2600	41	0	46	1900
Benzidene ..	17·0	5870	53	770								
Tergitol 7 ..	4·4	820	65	10,700								
Sapamine K.W.					70	8000	81	2300				
Lecithin.. ..									65	7700	23	74
Zinc naphthenate									60	1970	35	180

V = plastic viscosity. *f* = yield value.

A new type of viscometer described by Wachholtz and Asbeck[11,12] has been used to study pigment - oil dispersions. Called a band viscometer, the instrument consists of two metal blocks, A (Fig. 4), which have a recess in the top, acting as a reservoir. The band C is drawn through the slit formed between the two faces of the blocks by thin metal spacers, B. The whole assembly is clamped together and held in a stand. At the lower end of the band, which is 60 cm. long, 3 cm. wide and 0·005 cm. thick, are hung weights, and the velocity of fall of band is plotted against load. Of particular interest is the method of plotting results. The authors use a value η_∞ which is the viscosity the material would have at infinitely large

rate of shear. This value η_∞ is obtained by plotting apparent viscosity against $\sqrt{1/D}$, where D is the rate of shear, and extrapolating to D = 0. Relationships between viscosity and pigment concentration have been examined by using η_∞, since various anomalies present at low rates of shear disappear at the very high shear rates of the band viscometer, as indicated by the statement that the curve against pigment concentration suffers no change in shape when the suspending medium is changed from a mineral oil to a vegetable oil.

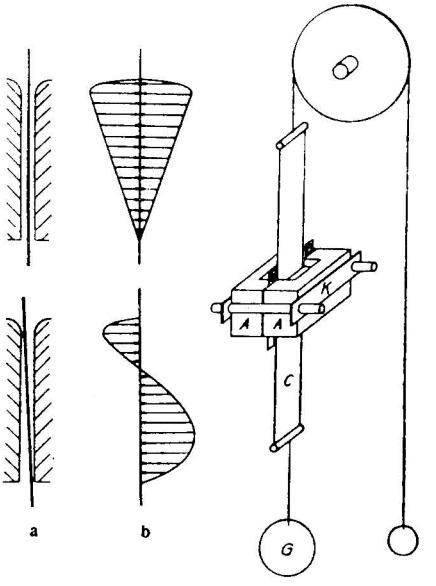

Fig. 4

Finally, I will mention alternating stress techniques. A long time ago it was realised that most paint systems are visco-elastic, and Pryce-Jones[13] made some qualitative experiments showing that the elastic component of many suspensions is quite large. Recently, techniques have been developed whereby materials instead of being subjected to a unidirectional shear stress may have alternating stresses imposed on them, or superimposed on a unidirectionally applied stress. Weissenberg[14] in England, and Sandvik and Goldberg[15] and W. P. Mason[16] in America, have developed apparatus for determining modulus of rigidity and dynamic viscosity of visco-elastic materials. Nearly all previous methods demand that the sample undergoing test suffers large deformations. By decreasing the amplitude of oscillation, in alternating stress methods, it is possible to study the rheological behaviour of a material without disturbing its state.

I have indicated some of the control methods used in the paint industry and their limitations, and have outlined briefly research methods for studying paint systems. It is likely that in the future we shall see a wider use of such methods in the control of manufacture, for it is becoming increasingly important to standardise our products more rigorously.

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DISCUSSION ON THE FOUR PAPERS ABOVE

Mr. S. W. BUTTERWORTH asked Mr. Williams if alternating stresses at supersonic frequencies had been used in assessing the rheological properties of materials.

Mr. WILLIAMS replied that the maximum frequency used in mechanical alternating stress techniques was about 10,000 cycles per minute. The work of W. P. Mason, using torsionally oscillating crystals, covered the range 0 to 100 kilocycles per second, and so *did* use vibrations in the supersonic region. Although the shear waves set up in the liquid were too highly attenuated to be studied, they introduced a loading on the crystal which altered the resonance resistance and frequency of the crystal. From these values the viscosity and shear stiffness of materials might be calculated.

Mr. SYDNEY C. BEARD asked Dr. Marriott if the yield value depended on the time that elapsed while the sample was in the machine before the test began and whether a standard time had been found necessary. With cetyl alcohol emulsions, did the yield value and the viscosity depend on the degree of dispersion of the cetyl alcohol in water?

Dr. MARRIOTT said that the yield value did depend on the time that elapsed before the test was begun, but in practice it was not found necessary to take any special precautions. If it were required to determine the yield value, then a standard time must elapse before the machine was started. Regarding the effect of the degree of dispersion of the cetyl alcohol on the yield value and viscosity of emulsion made with it, the experimental figures shown were derived from emulsions made up under standard controlled conditions and they were therefore comparable with one another. The degree of dispersion of the cetyl alcohol was not known.

Mr. J. F. WOOD asked Dr. Marriott what standards were used to calibrate the revolving cup viscometer and in particular whether he could detect drifts in the characteristics of the instrument with continued use.

Dr. MARRIOTT replied that in the instrument described no calibration was employed, but it would be quite possible to use a suitable oil as a means of checking it. A number of viscometers of the design shown had been made and they were found to give similar readings when the same material was examined.

Mr. A. GELLMAN asked if Mr. Williams had anything to say about the methods of measuring the consistency of some of the heavier products of the paint industry, such as pastes and putties. Did he think some of the instruments described by other speakers might be useful for this purpose.

Mr. WILLIAMS suggested that the Institute of Petroleum testing cone-resistance penetrometer and the instruments described by Dr. Amos would deal with pastes and putties. Of the instruments he himself had mentioned, the Gardner Mobilometer would be most suitable for measurements on these materials.

Dr. C. G. SUMNER, apropos of Mr. Gellman's question, drew attention to two recent papers dealing with materials of that kind: one on "The Rheology of Stiff Pastes" by A. G. Ward and P. R. Freeman (*J. Scientific Instr.*, 1948, **25**, 387), and the other, "The Rheology of Building Mastics. I. Caulking Compounds for Gum Application" by A. G. Ward and E. L. E. Westbrook (*J. Soc. Chem. Ind.*, 1948, **67**, 389).

Studies in the Analytical Chemistry of Tungsten

IV. Separation of Tungstic and Arsenic Acids

BY D. A. LAMBIE

THIS paper, which treats of the separation and determination of tungstic and arsenic acids, continues the study of the complex-forming acid radicals begun, with the separation of tungstic and phosphoric acids, in Section II of this series.[1]

It was anticipated by analogy with phosphorus that solutions containing both tungstates and arsenates would yield on acidification arsenotungstic acid, most probably the "12" acid. This would render the precipitation of tungstic acid by means of mineral acid incomplete unless an alkaloid, *e.g.*, cinchonine, were added. The tannin phenazone procedure on the other hand, in which the precipitant is added to the alkaline solution,[1,2] would be expected to give a quantitative recovery of tungstic acid free from arsenic.

Although the main object of the investigation was to test the applicability of the tannin-phenazone method[2] to the separation of tungstic and arsenic acids, a critical examination of other methods in general use was also undertaken, as only that of Dieckmann and Hilpert[3] appears to be supported by published test analyses.

Since tungsten-bearing materials are invariably obtained in solution by means of oxidising reagents, the investigation was limited to the behaviour of quinquevalent arsenic. Also, since in practice it is usual, for simplicity of "opening up," to determine arsenic and tungsten in separate portions of material, this convenient subdivision of treatment has been adopted in the present work.

A. Separation and determination of arsenic

There is no doubt that in absence of interfering elements the classical iodimetric titration is the most accurate method for the determination of a milligram or more of arsenic. Experiments to determine the effect of tungstic acid on this method showed that the presence of a few milligrams caused significantly low results (see (*a*) below) and confirmed that separation of arsenic prior to its determination is essential.

The separation of Group II metals from tungsten by precipitation as sulphides from tartaric acid solution has been studied extensively for one of them, molybdenum, and is advocated for arsenic in standard works such as those of Schoeller and Powell[4] and Hillebrand and Lundell.[5] An examination of this method has therefore been carried out, although there is little doubt that distillation as trichloride from a solution containing excess of phosphoric acid (to retain the tungstic acid in solution as a complex) as advocated by Dieckmann and Hilpert (*loc. cit.*), provides the most satisfactory method of separating arsenic from tungsten.

(*a*) Effect of tungsten on the iodine titration of arsenite—Two series of experiments were conducted. In the first, solutions containing sodium tungstate and arsenite were rendered feebly acid to litmus paper, treated with excess of sodium bicarbonate and titrated as usual with 0·1 *N* iodine solution. As can be seen from Table I, Experiments 1 to 5, low results were obtained.

In the second series solutions of arsenite and tungstate, volume 100 ml., were treated with 10 ml. of hydrochloric acid, saturated with hydrogen sulphide, boiled and re-treated with hydrogen sulphide. The precipitates were collected on a filter, washed, "fumed" with sulphuric acid and titrated with iodine solution as usual. The tungstic acid was recovered from the filtrate by the tannin phenazone procedure and the amount of tungstic acid co-precipitated with the arsenic found by difference. Low results for arsenic (Experiments 6 to 9) were obtained as in the first series, although there is no evident proportionality between tungstic acid content and the magnitude of the error.

Table I

Expt.	Tungstic oxide taken, g.	Arsenious oxide taken, g.	Arsenious oxide found, g.	Error g.	Tungstic oxide in titrated solution g.
1	0·0798	0·1237	0·1202	−0·0035	0·0798
2	0·0798	0·0495	0·0467	−0·0028	0·0798
3	0·0798	0·0247	0·0222	−0·0025	0·0798
4	0·0200	0·1237	0·1232	−0·0005	0·0200
5	0·0200	0·0247	0·0247	nil	0·0200
6	0·0798	0·1237	0·1174	−0·0063	0·0397
7	0·0200	0·1237	0·1222	−0·0015	0·0080
8	0·0200	0·0247	0·0237	−0·0010	0·0159
9	0·0399	0·0247	0·0242	−0·0005	0·0320

(*b*) Separation of arsenic by precipitation as sulphide—Examination of the literature revealed two points requiring investigation: (i) Werz's assertion,[6] which appeared to be based on insufficient evidence, that for the formation of a stable tungsto-tartaric complex, the tungstate solution must remain or be rendered strongly alkaline after addition of the tartaric acid; (ii) the possibility that contamination of the sulphide precipitate with tungstic acid when it occurs is due to post-precipitation. An alternative explanation of Werz's results is that the final excess of mineral acid is greater when the solution is not initially strongly alkaline, and consequently leads to "tartaric hydrolysis."[7]

Stability of tungsto-tartaric complexes—To test the stability towards hydrochloric acid of tungsto-tartaric complexes produced in alkaline and in acid solution, two groups of solutions similar in content of tungstic and tartaric acids were prepared. Each solution of the first group was rendered alkaline by addition of 10 ml. of 30 per cent. sodium hydroxide solution, heated, treated with 35 ml. of concentrated hydrochloric acid, boiled for a few minutes and after addition of filter paper pulp allowed to settle overnight. Those of the second group were heated and treated with a mixture containing 10 ml. of 30 per cent. sodium hydroxide solution and 35 ml. of concentrated hydrochloric acid, boiled for a few minutes and allowed to stand after the addition of filter paper pulp as before. Each pair of solutions had the same final composition and volume, the only difference being that the first of each was strongly

alkaline before addition of the hydrochloric acid. The precipitates were collected, ignited and weighed. The more stable the complex the smaller should be the weight of tungstic oxide recovered. As is seen from Table II the stability increased (recovery decreased) with increase in tartaric acid concentration, as was of course to be expected, but no support was given to Werz's hypothesis that formation of the complex in strongly alkaline solution increases its stability.

TABLE II

Tungstic oxide taken in each experiment, 0·0998 g.

Expt.	Tartaric acid added g.	Tungstic oxide recovered, g.	
		Complex formed in alkaline solution	Complex formed in acid solution
10	1	0·0993	0·0981
11	2	0·0978	0·0993
12	3	0·0763	0·0855
13	4	0·0393	0·0253
14	5	0·0232	0·0192

Although precipitation of arsenic sulphide is most satisfactorily done from strongly acid solution, here the acidity had to be maintained as low as was compatible with the reduction of quinquevalent to tervalent arsenic, owing to the instability of the tungsto-tartaric complex in presence of excess of mineral acid. After preliminary tests the following conditions for the separation were adopted.

Procedure—Add to the almost neutral solution of tungstate and arsenate—volume about 200 ml.—tartaric acid (or its equivalent of sodium tartrate) 30 times the weight of tungstic oxide present, followed by 5 ml. of 10 per cent. potassium iodide solution and 5 ml. of diluted sulphuric acid (1 + 1). Heat to about 80° C. and pass a rapid stream of hydrogen sulphide. Repeat the heating and treatment with hydrogen sulphide until the arsenic sulphide flocculates and settles rapidly, leaving a clear colourless supernatant liquid. Collect the precipitate and wash thoroughly with 1 per cent. v/v sulphuric acid containing hydrogen sulphide. Test the filtrate for completeness of precipitation by boiling and treating with hydrogen sulphide. Return the precipitate completely to the precipitation flask, boil to fuming with sulphuric acid and sodium sulphate[8] and complete as usual iodimetrically, or if the estimated amount is less than 1 mg., use the molybdenum blue colorimetric method.[9]

In a series of experiments, the results of which are given in Table III, the solution after titration was analysed for tungsten by the tannin phenazone method (see B (*b*)).

TABLE III

Expt.	Tungstic oxide taken, g.	Arsenic oxide taken, g.	Arsenic oxide found, g.	Error, g.	Tungstic oxide in arsenic solution, mg.	Tartaric acid added, g.	pH of solution
15	0·10	0·0994	0·0995	+0·0001	not detd.	3	1·0
16	0·10	0·0994	0·0995	+0·0001	0·05	3	0·82
17	0·10	0·0398	0·0400	+0·0002	0·05	3	—
18	0·10	0·0199	0·0199	nil	0·05	3	—
19	0·05	0·1988	0·1990	+0·0002	0·18	1·5	0·75
20	0·50	0·00010	0·00010	nil	—	15*	—
21	0·50	0·00099	0·00100	+0·00001	—	15*	—
22	0·50	0·00249	0·00245	−0·00004	—	15*	0·82
23	0·50	0·00020	0·00020	nil	—	15*	—
24	0·50	0·00050	0·00048	−0·00002	—	15*	—

* Added as sodium tartrate.

The colorimetric method was employed in Experiments 20 to 24 and iodine titration in the others.

It is evident that under the conditions specified a satisfactory separation of arsenic and tungsten is obtained.

In the course of the experiments with small amounts of arsenic and large amounts of tungstic acid it was observed that in the presence of the necessarily high concentrations of

tartaric acid, unless added as sodium tartrate (or tartaric acid and sodium hydroxide), the arsenic trisulphide failed to flocculate. Addition of sodium sulphate and sulphuric acid to give the same sodium concentration and pH as with sodium tartrate and sulphuric acid failed to promote flocculation. Experiments carried out with sodium arsenite solutions gave precisely the same results, proving that the phenomenon was due neither to the presence of tungstic acid nor to the necessity for the reduction of quinquevalent to tervalent arsenic prior to its precipitation. The phenomenon is so far unexplained.

Post-precipitation—There is considerable evidence to show that sulphide separations are frequently vitiated by post-precipitation. A number of tests were carried out to determine whether the proposed separation method was so affected. Solutions containing 0·1 g. of tungstic oxide as sodium tungstate and 25 ml. of 0·1 *N* sodium arsenite solution (used to avoid the complicating factor of reduction of quinquevalent to tervalent arsenic) were treated according to the above directions and the arsenic sulphide precipitates collected after various time intervals and washed thoroughly. The precipitates were ignited and the residues examined for tungsten by the tannin phenazone method B (*b*). There was no evidence of post-precipitation (see Table IV).

TABLE IV

Expt.	Time after precipitation, hours	Tungstic oxide in sulphide precipitate, mg.
25	¾	0·02
26	3½	0·05
27	19	0·09
28	26	0·04

(*c*) SEPARATION OF ARSENIC BY DISTILLATION AS TRICHLORIDE—For comparative purposes a few analyses were carried out by the distillation method. Mixtures of tungstic and arsenic acids of known composition were treated with 10 ml. of phosphoric acid (sp.gr. 1·75), 1 g. of sodium bromide and 1 g. of hydrazine sulphate (in place of cuprous chloride advocated by Dieckmann and Hilpert[3]) and distilled with hydrochloric acid, the determination being carried out according to the directions of the A.O.A.C.[10] The results are recorded in Table V.

TABLE V

Expt.	Tungstic oxide taken, g.	Arsenic oxide taken, g.	Arsenic oxide found, g.	Error, g.
29	0·10	0·0992	0·0994	+0·0002
30	0·10	0·0397	0·0395	−0·0002
31	1·0	0·0198	0·0198	nil
32	1·0	0·0080	0·0081	+0·00001
33	2·0	0·00248	0·00247	−0·00001

(*d*) HYPOPHOSPHITE METHOD—B. S. Evans has introduced hypophosphorous acid as a reagent for the separation of a number of elements, including arsenic, successful results being reported in the determination of that element in steel containing tungsten.[11]

TABLE VI

Expt.	Tungstic oxide taken, g.	Arsenic oxide taken, g.	Tungstic oxide in arsenic precipitate
34	1·0	0·0020	0·0606
35	1·0	0·0199	0·0698
36	1·0	0·0040	0·0115
37	0·5	0·0020	0·0064
38	0·25	0·0020	0·0040
39	0·10	0·0020	0·0011
40	1·0	0·0020	0·0025

A number of experiments were carried out to test the completeness of the separation of arsenic and tungstic acids by means of this reagent. Mixtures of known amounts of arsenic acid and tungsten as sodium tungstate were treated by Evans's method, and the finely divided precipitates of arsenic were collected with the aid of filter paper pulp and washed

with diluted hydrochloric acid (1 + 3) containing sodium hypophosphite and finally with ammonium chloride solution. The precipitates were then ignited to expel the arsenic. Each yielded a residue of tungstic oxide which was weighed. In Experiments 34 and 35 the tungstic oxide, which was obviously impure (contaminated with arsenic), was dissolved in sodium hydroxide solution and reprecipitated with tannin and phenazone (see B (*b*)). The results are given in Table VI.

As it was not found possible to obtain a quantitative separation of arsenic from tungsten comparable with that by the sulphide and distillation methods, no further work was carried out.

B. Separation and determination of tungstic acid

Two methods only need be considered: (i) the classical acid precipitation; (ii) tannin precipitation. The first, as stated in the preamble to this paper, would be expected to yield low results unless the arsenotungstic acid formed were precipitated by addition of cinchonine. Cinchonine arsenotungstate, unlike the corresponding phosphorus compound, would, however, be expected to lose all or most of the arsenic during ignition (in the presence of carbon from the filter paper). Precipitation by evaporation with acid and addition of cinchonine should in consequence yield satisfactory results in absence of significant amounts of alkali salts.

(*a*) *Acid precipitation*—A solution of sodium tungstate was standardised by precipitating 20-ml. aliquot portions (*a*) by evaporating with perchloric acid,[12] (*b*) by tannin and phenazone, giving the following results: 0·1003, 0·1002, 0·1005 and 0·1004 g.; adopted, 0·1004 g. of WO_3 per 20 ml. A solution of sodium arsenate was also prepared and found by reduction and iodine titration to contain 0·0994 g. of As_2O_5 per 25 ml.

Two series of experiments were carried out, in each of which mixtures of the sodium tungstate solution (equivalent to 0·1004 g. WO_3) and various amounts of the sodium arsenate solution were evaporated to about 20 ml., treated with 50 ml. of concentrated hydrochloric acid and evaporated further to about 10 ml. After addition of 10 ml. of concentrated nitric acid each was evaporated to 5 ml. and then diluted with 50 ml. of hot water; to those of the second series (Expts. 51 to 56) were subsequently added 5 ml. of 5 per cent. cinchonine solution. After standing overnight each precipitate was collected with addition of filter paper pulp, and washed thoroughly; those of the first series (Expts. 41 to 50) were washed with diluted hydrochloric acid (1 in 20), and those of the second series (Expts. 51 to 56) with a solution containing 15 ml. of hydrochloric acid and 60 ml. of 5 per cent. cinchonine solution per litre. The precipitates were then ignited and weighed.

After weighing, the precipitates were dissolved in sodium hydroxide solution and analysed for arsenic, using the sulphide separation (see A (*b*) above) and colorimetric determination by the molybdenum blue method.

Table VII

In each experiment, 0·1004 g. of WO_3 was taken

Expt.	Arsenic oxide taken, g.	Tungstic oxide found, g.	Error, g.	Arsenic oxide in ignited precipitate, mg.
		First Series		
41	0·0994	0·0231	−0·0773	0·02
42	0·0994	0·0911	−0·0093	0·14
43	0·0994	0·0554	−0·0450	0·03
44	0·0398	0·0339	−0·0665	0·02
45	0·0199	0·0863	−0·0141	0·15
46	0·0199	0·0750	−0·0254	0·03
47	0·0080	0·0927	−0·0077	0·12
48	0·0080	0·0911	−0·0093	not detected
49	0·0020	0·0995	−0·0009	0·02
50	0·0010	0·0998	−0·0006	0·02
		Second Series		
51	0·0994	0·1000	−0·0004	0·26
52	0·0398	0·0994	−0·0010	0·18
53	0·0398	0·0995	−0·0009	0·10
54	0·0199	0·1000	−0·0004	not detected
55	0·0080	0·0999	−0·0005	not detected
56	0·0020	0·1001	−0·0003	0·06
57	0·0010	0·0998	−0·0006	not detected

The results, given in Table VII, show that, as was to be expected by analogy with phosphoric acid, the presence of arsenic acid prevents the complete precipitation of tungstic acid by mineral acids. Addition of cinchonine improves the recovery. In most experiments the amount of arsenic retained by the tungstic oxide after ignition was insignificant, owing to the reduction of the arsenic compound by the heated carbon and subsequent volatilisation.

To confirm that the cinchonine acts by precipitating cinchonine arsenotungstate, the clear filtrate, after removal of the tungstic acid precipitate in Experiment 45, was treated with cinchonine solution and the precipitate collected and washed. The precipitate was dissolved in ammonia, the solution filtered to remove cinchonine and the arsenic precipitated from tartrate solution with hydrogen sulphide and determined colorimetrically as above (A (*b*)): found, 0·00054 g. of As_2O_5. The tartaric acid was destroyed in the filtrate by wet combustion with sulphuric and nitric acids and the tungstic acid recovered by the tannin phenazone method: found, 0·0127 g. of WO_3, equivalent to 0·00052 g. of As_2O_5 in $24WO_3.As_2O_5$. These results are in good agreement with the hypothesis that the soluble compound produced when a solution of arsenate and tungstate is treated with mineral acid is 12-arsenotungstic acid which is thrown down as its insoluble cinchonine salt on addition of the alkaloid.

(*b*) *Tannin precipitation*—Mixtures of known weights of tungstic oxide and arsenic pentoxide, obtained in solution by fusion with sodium carbonate and dissolution of the melt in hot water, were analysed for tungsten by the tannin cinchonine method.[2] The precipitate, after being ignited and weighed, was analysed for arsenic as above, B (*a*). The results are summarised in Table VIII and show that the tannin phenazone method provides a satisfactory separation of tungstic and arsenic acids.

TABLE VIII

Expt.	Tungstic oxide taken, g.	Arsenic oxide taken, g.	Tungstic oxide found, g.	Error, g.	Arsenic oxide in tungstic oxide, mg.
58	0·1027	0·11	0·1031	+0·0004	0·05
59	0·0519	0·14	0·0522	+0·0003	0·05
60	0·0205	0·18	0·0205	nil	0·10
61	0·0111	0·20	0·0116	+0·0005	0·10
62	0·1518	0·05	0·1519	+0·0001	0·10
63	0·0090	0·50	0·0089	−0·0001	0·05
64	0·0040	0·50	0·0038	−0·0002	0·05
65	0·0998	0·10	0·1008	+0·0010	0·07
66	0·0998	0·10	0·0997	−0·0001	0·10

SUMMARY

A critical study of the methods available for the separation and determination of tungstic and arsenic acids has been made. The distillation method of Dieckmann and Hilpert is considered to be the most satisfactory for the separation of arsenic, although precipitation as sulphide from tartrate solution is capable of yielding equally accurate results. The tannin phenazone method has been shown to give satisfactory results for tungsten in presence of arsenic, whilst the classical acid precipitation method gives low results even when cinchonine is added to the solution.

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January, 1949

Notes

CONDITIONS UNDER WHICH MITES RAISE MOISTURE CONTENT OF FOODSTUFFS

In a recent note, Amos[1] states that mites in flour raised its moisture content from 15·14 to 28·10 per cent. within a period of 18 months, in a jar which was hermetically sealed.

It is readily demonstrated, however, that mites in any appreciable concentration cannot long remain active in a gas-tight container. If samples of mite-infested flour, etc., are enclosed in glass tubes sealed by drawing off the open ends over a flame, the mites become inactive within a few days. Hughes[2] has shown that concentrations of carbon dioxide above 30 per cent. of the atmosphere induce anaesthesia in *Tyroglyphus farinae*, and that 3 days' exposure to pure carbon dioxide kills it. On the assumption that the respiration of the mites can be represented as the complete combustion of polysaccharides to carbon dioxide and water, one can make an estimate of the maximum amount of water the mites could produce under the conditions described by Amos, if the jar were hermetically sealed; the carbon dioxide would be sufficiently concentrated to stop further activity before the moisture content of the flour had been increased by 0·1 per cent. of the flour weight. Although the basis of the calculation is over-simplified, it serves to show the order of magnitude of the maximum change which mites could be expected to bring about under gas-tight sealing.

It seems therefore that the wax seal on the jar used by Amos must have been imperfect.

I have discussed this matter with Dr. Amos, and also with Mr. T. A. Oxley, of this Laboratory, and we are agreed that the correct interpretation of his observations is probably as follows. Mites were able to remain active in a container which was tightly though not hermetically closed, because diurnal and other changes in temperature and atmospheric pressure caused the escape of excess carbon dioxide and the replenishment of the supply of oxygen, even though the fissures in the seal may have been minute. The moisture presumably did not escape to the same extent as the carbon dioxide because much more of it was held by physical sorption by the flour. Had the flour become saturated the accumulation of water could have continued by condensation, which takes place at a relatively low vapour concentration.

Thus, with the proviso that it would not apply to instances of real hermetical sealing, I agree with the submission made by Amos[1], "that the excess moisture was the natural outcome of the metabolic activity of the mites proceeding in an enclosed space." He has demonstrated the important fact that, if mites are present, good but imperfect sealing up of materials may shut in much more moisture than it keeps out.

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M. E. Solomon
March, 1949

THE RECOVERY OF URANIUM FROM SODIUM ESTIMATION RESIDUES

The Board of Trade have recently stated[1] that no further quantities of uranium compounds can be supplied to dealers for many months to come; workers in laboratories using uranium compounds must therefore conserve any quantities they may already have.

In laboratory routine, uranyl acetate is often used for determining sodium as sodium zinc (or magnesium) uranyl acetate. During the war a method of recovering uranium from residues and liquors left after sodium determinations with zinc uranyl acetate was developed in the Chemical Inspection Department of the Ministry of Supply. This method may be of interest to other users of uranium compounds at the present time. Although it was used only for residues from estimations in which zinc uranyl acetate was employed, it could presumably be applied to those obtained with magnesium uranyl acetate.

The principle of the method is the precipitation[2] of hydrated uranium peroxide, $UO_4.2H_2O$, which is converted into uranium trioxide, UO_3, by ignition.[3,4,5] The trioxide dissolves readily in acetic acid, forming uranyl acetate, the salt required for preparing the precipitating agent for sodium. Liquid and solid residues are collected and treated separately; the liquid residues are collected in Winchester bottles and, in order to prevent photo-reduction to green uranous salts, are stored in the dark until required for treatment.

Method—For the treatment of liquid residues, separate the lower, aqueous layer from the upper layer comprising organic solvents, and filter it through a Buchner funnel. Transfer 500 ml. of the filtrate to a 2-litre beaker and heat on a water-bath until most of the ether is removed. Add about three times the volume of hot water and transfer the beaker to a hot plate.

For solid residues, dissolve 20 g. of the solid in about 1½ litres of hot water in a beaker.

To the hot solution thus obtained, whether from liquid or from solid residues, run in slowly from a pipette about 100 ml. of 10-vol. hydrogen peroxide and stir constantly. A heavy yellowish-white precipitate

of $UO_4.2H_2O$ is formed. Boil the liquid for 10 minutes and then transfer the beaker to the water-bath and allow the precipitate to settle. If the supernatant liquid is colourless, precipitation of the uranium is complete, but if it is yellow, add more hydrogen peroxide and repeat the boiling and settling.

Remove the clear supernatant liquid from the beaker by suction. Wash the heavy precipitate in the following manner. Add about 1 litre of hot water, boil for a few minutes, and allow to settle. Almost the whole of the precipitate settles in about 2 or 3 minutes, but without waiting for complete settling suck off the supernatant liquor. Continue washing the main bulk of the precipitate until the zinc has been removed, as shown by testing the washings with ammonium sulphide. About 4 or 5 washings are required. The slightly cloudy supernatant liquid washings may be collected and the precipitate suspended therein allowed to settle.

Dry the washed hydrated uranium peroxide precipitate as far as possible by placing the beaker containing it on a water-bath or low-heat hot plate. Transfer the nearly dry solid to a silica dish and, after crushing the lumps, heat it on a high-heat hot plate, with occasional stirring, until it is of a uniform orange colour and a test portion is completely soluble in dilute acetic acid. The orange solid is uranium trioxide, UO_3; the heating takes ½ to 1 hour, and if care is exercised it may be carried out entirely in the original beaker. If the mass begins to turn green the temperature is too high; reduce the heat and see that there is free access of air. The green colour is that of urano-uranic oxide, U_3O_8, which is insoluble in acetic acid and therefore of little use in the recovery process. However, it is not likely that U_3O_8 will be formed, even at the temperature of a high-heat hot plate.

Uranium trioxide recovered by the above method will, if the washing has been carried out efficiently, be completely free from zinc. Very small quantities of uranium peroxide and of the oxide U_3O_8 may be present, but these remain insoluble when the trioxide is dissolved in dilute acetic acid and are removed by filtration.

The author wishes to record his thanks to Messrs. R. F. Callen and T. Moodie for their assistance in working out the method; also he thanks the Chief Scientist, Ministry of Supply, for permission to publish this note.

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F. CLARK
MINISTRY OF SUPPLY
April, 1949

THE TUNGSTIC ACID PRECIPITATION OF PROTEIN FROM PHYSIOLOGICAL FLUIDS

(1) It has been found that in order to precipitate proteins from the blood of patients who have been treated with alkaline mixtures for a month or more it is necessary to use more than 1 ml. of 2/3 *N* sulphuric acid per 1 ml. of 10 per cent. sodium tungstate solution with 1 ml. of blood and 7 ml. of water. As a rule, 0·2 ml. of extra sulphuric acid, with 6·8 ml. of water, are sufficient.

(2) One ml. of tears with 8·4 ml. of water, 0·25 ml. of 10 per cent. sodium tungstate solution and 0·35 ml. of 2/3 *N* sulphuric acid, shaken and filtered through a Whatman No. 1 paper, give a clear solution in which urea plus ammonia can be estimated by the Lieboff method.

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49 HANUMAN ROAD
NEW DELHI, 1
INDIA

MISS S. RAM
November, 1948

Erratum : June (1949) issue, p. 362.

Equation (iv), line 14 from the bottom of the page, should read

$$W = \frac{ap}{T_2} - bD \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(iv)}$$

Order in Council

STATUTORY INSTRUMENT*

1949—No. 1047 (S. 68). **The Transfer of Functions (Food and Drugs) (Scotland) Order, 1949** Price 1d.

This Order, which applies only to Scotland and came into force on June 20th, 1949, transfers to the Secretary of State for Scotland acting jointly with the Minister of Food the powers of the Secretary of State under the Food and Drugs (Adulteration) Act, 1928, to make regulations as regards the qualifications of public analysts, and under the Food and Drugs Act, 1938, to make regulations concerning food, other than meat from home-fed animals and milk, its composition and the conditions under which it is imported, prepared, transported, stored or sold.

The Order also transfers to the Minister of Food (a) *the power of the Secretary of State to make regulations under the Food and Drugs (Adulteration) Act, 1928, as regards the presumptive evidence of adulteration of condensed milk, cream, butter or cheese*; (b) *the power of the Secretary of State to make regulations as regards dried or condensed milks, including in particular their composition and the labelling of receptacles containing them*; *and* (c) *certain administrative functions exercised at present by the Secretary of State under the Food and Drugs (Adulteration) Act, 1928, and the Food and Drugs Act, 1938, relating to food, including in particular functions relating to margarine, margarine-cheese and milk-blended butter and the importation of food.*

Ministry of Food

STATUTORY INSTRUMENTS*

1949—No. 1378. The Soft Drinks (Amendment) Order, 1949. Price 1d.

This Order, as from July 31st, 1949, prescribes specifications for ingredients of "lime juice and soda."

—No. 1497. The Shredded Suet Order, 1949. Price 1d.

In this Order, "shredded suet" includes flaked suet but does not include any product which is of vegetable origin or any product having fibrous tissues.

The Order provides (a) *that all manufacturers and pre-packers of shredded suet must be licensed*; *and* (b) *that shredded suet must not be sold at a price exceeding the price stated upon a label attached to the wrapper or container.*

—No. 1498. The Manufactured and Pre-packed Foods (Revocation) Order, 1949. Price 1d.

As from August 7th, 1949, this Order revokes the Manufactured and Pre-packed Foods (Control) Order, 1942, as amended (S.R. & O., 1942, Nos. 1863 and 2073; 1944, No. 167; 1945, No. 250; 1946, No. 1486; and S.I., 1948, No. 131), *but without prejudice to any proceedings in respect thereof.*

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Grading of Raw Milk by Means of the Resazurin Test. T. E. Galesloot (*Ned. Melk Zuiveltijdschr.*, 1948, **2**, 70–90)—Because of the increasing interest in the use of the resazurin test as a means of grading raw milk, a comparison of this test and the methylene blue test was undertaken. The author concludes that the resazurin test is not a satisfactory method of determining the quality of raw milk.

The resazurin test was carried out by adding to 10 ml. of milk 1 ml. of a 0·005 per cent. resazurin solution, and standing the tubes in a water-bath at 37° C. The colour of the sample was estimated after 1 hr. for summer milk and after 2 hr. for winter milk; the English colour scale was used, in which 6 indicates a sample in which no colour change has occurred, 5 to 2 indicate shades between blue and pink, 1 is pink, and 0 is white. The methylene blue test was conducted in the usual way, the tubes being inverted after each hour. The catalase number was also determined for the winter samples, as a measure of cell activity. The cell content was estimated by means of a plate count, using meat extract - tryptone - glucose - skim milk - agar, and incubating the plates for 3 days at 30° C.

540 samples of winter milk were examined, 180 of morning milk, 180 of 12-hr. old evening milk, and 180 of mixed milk. Very poor agreement was found between the resazurin numbers and the methylene blue reduction times. The resazurin test appears to be very considerably affected by the tissue cells in the milk, and the author does not agree that milks with a high cell activity are always pathologically or physiologically abnormal, as mastitis seldom occurred in the herds from which the milk samples were taken.

Storage at 20° C. for 5 hr., followed by 16 hr. in the ice-box, shortened the methylene blue time, whilst the resazurin test showed variable results, some samples having the same resazurin number, others greater and others smaller, than before storage. With samples that had the same resazurin number before and after storage, there was a

* Obtainable from H.M. Stationery Office.

relationship between the catalase values and the resazurin numbers before storage, and there was also a correlation between the catalase numbers and the alteration in resazurin number on storage.

Agreement between plate counts and resazurin results was much worse than between plate counts and methylene blue reduction times, although after storage there was a better agreement between plate count and resazurin value.

184 samples of summer morning milk were investigated, though not in as great detail as the winter milk. The agreement between methylene blue reduction times and resazurin values was better than with winter milk, this being explained by the fact that in summer milk there are fewer tissue cells and more bacteria, but again, the results obtained with the resazurin test are unduly affected by the cell activity of the milk. Storage for 4 hr. at room temperature (above 20° C.) reduced the methylene blue times and generally reduced the resazurin values, but the results for the latter test were variable. The agreement between plate count and methylene blue reduction time was better with summer milk than that between plate count and resazurin test results, samples with low plate counts often showing low resazurin numbers, so that milk of good quality could not be detected by this latter test.

The effect of temperature on the two tests was seen by comparing the results for winter and summer milk. With both warm and cold milk there is no great difference in the relation between plate count and methylene blue reduction time. With the resazurin test, the temperature of the milk has a much greater influence on the values obtained, and the relationship between plate count and resazurin number is also affected by temperature.

The conclusion to be drawn is that the tissue cells affect the reduction of resazurin to such an extent that there is no satisfactory agreement between the resazurin values and the quality of the milk. E. M. POPE

Estimation of Milk Proteins in Milk. E. Gorffon (*Le Lait*, 1948, **28**, 449–454)—The method is based on the colour developed with Folin and Ciocalteu's reagent (*J. Biol. Chem.*, 1927, **73**, 629) by the tyrosine and tryptophan contained in milk proteins. To calibrate the colorimeter or photo-colorimeter employed, commercial casein is not used as it is not wholly soluble under the conditions of the test, especially if old. A phenolic body that can be obtained pure and dry and is readily soluble is preferred, and by the method described a 0·048 per cent. resorcinol solution gives the same colour as a 1 per cent. solution of milk proteins. The method is as accurate as available macro-methods. Since lactalbumin as well as casein is determined, there will be an error of about 1 in 15; this is negligible in an industrial method such as is proposed. The determination can be made in 20 to 25 min.

Procedure—Shake 1 ml. of milk with 4 ml. of alcoholic sodium hydroxide (0·5 g. in 100 ml. of alcohol at 60° C.) and then with 5 ml. of ether until the characteristic opalescence of the milk has disappeared. Add water dropwise and with constant shaking until the aqueous phase measures 10 ml.; withdraw 1·5 ml. of this and dilute it with 25 ml. of water. Add 1 ml. of alcoholic sodium hydroxide followed rapidly by 3 ml. of Folin and Ciocalteu's reagent and water to 50 ml. After 5 to 10 min., measure the blue colour on a colorimeter or photo-colorimeter, using a red filter.

A. H. ADAMS

Component Acids and Glycerides of Whale Oil. T. P. Hilditch and L. Maddison (*J. Soc. Chem. Ind.*, 1948, **67**, 253–257)—The component acids of a specimen of Antarctic whale oil, previously (*Ibid.*, 1942, **61**, 169) separated by means of their lithium and lead salts before ester-fractionation, have now been separated by low-temperature crystallisation from solvents. The results agree well with those obtained by the other method. Six groups of component glycerides were separated by crystallisation from acetone from −60° C. upwards. The results were generally similar to, but with some numerical difference from, those by the lithium - lead salt method (*loc. cit.*); the oil contains approximately 16 per cent. of di-saturated and 2·5 per cent. of trisaturated glycerides, about 30 per cent. of tri-unsaturated glycerides and about 50 per cent. of glycerides containing one saturated acid, one unsaturated C_{18} acid, and one of the other homologous unsaturated acids. Acids of the C_{20} and C_{22} series are contained in about 45 per cent., and oleic groups in over 90 per cent., of the oil. Iodine values of the different oil fractions are: insoluble at −10° C., 29·1; soluble at −10° C., 63·2; soluble at −20° C., 82·7; soluble at −40° C., 118·3; soluble at −60° C., 215·2; soluble at −60° C. (recrystallisation), 192·9.

Component acids are calculated as:—

	By lithium and lead salt method per cent. (wt.)	By low-temperature crystallisation (present work)	
		(*a*)	(*b*)
Lauric	0·2	Trace	0·3
Myristic	9·3	9·2	9·3
Palmitic	15·6	15·6	15·6
Stearic	2·8	1·9	2·3
Arachidic	0·3	0·6	0·2
Unsaturated C_{14}	2·5 (— 2·0)	2·5 (−2·6)	2·6 (−2·0)
" C_{16}	14·4 (— 2·1)	13·9 (−2·1)	13·8 (−2·1)
" C_{18}	35·2 (— 2·5)	37·2 (−2·4)	36·9 (−2·4)
" C_{20}	13·6 (— 7·2)	12·0 (−7·1)	12·2 (−7·0)
" C_{22}	5·9 (−10·1)	7·1 (−9·4)	6·8 (−9·8)
" C_{24}	0·2 (−10·4)	—	—

E. B. DAW

Investigations of Some New Sudan Seed Oils. D. N. Grindley (*J. Soc. Chem. Ind.*, 1948, **67**, 230–231)—The seed oils of members of the families Ulmaceae {(i) *Celtis integrifola*, (ii) *Chaetacme microcarpa*, (iii) *Trema guuneensis*}; Capparidaceae {(iv) *Boscia octandra*}; Rhamnaceae {(v) *Zizyphus Spina-Christi*}; Tiliaceae {(vi) *Grewia villosa*}; Euphorbiaceae {(vii) *Chrozophora plicata*}; and Salvadoraceae {(viii) *Dobera roxburghii*} were examined.

Results:—

Species	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
Wt. of 100 seeds, g.	31·8	22·1	0·65	20·89	4·29	5·34	1·98
Oil in material, %	6·12	6·39	28·08	0·91	29·37	0·81	38·47
Oil constants:							
Sapon. value	187·1	189·7	191·4	175·2	188·0	184·6	195·2
Unsaponifiable, %	2·09	2·58	2·68	9·96	1·11	3·90	0·70
Insol. F.A. + unsap. (Hehner)	—	96·59	95·08	—	94·80	—	95·0
Fatty acids constants:							
Iodine value (g. I/100 g.)	144·0	152·6	116·8	76·5	89·28	113·4	112·5
Thiocyanogen value (g. I/100 g.)	82·1	83·8	72·3	54·0	69·1	78·2	71·4
Mean mol. wt.	280·9	280·7	276·3	275·7	281·3	279·5	272·8
Saturated acids, %	13·6	12·4	23·3	41·8	24·9	15·9	24·0
Mean mol. wt. of sat. acids	285·0	284·8	262·9	268·4	281·0	271·2	250·0
Composition of fatty acids:							
Linoleic acid, %	73·7	82·0	53·0	26·8	24·0	41·8	48·9
Oleic acid, %	12·7	5·6	23·7	31·4	51·1	42·3	27·1
Stearic acid, %	13·6	12·4	6·2	41·8	22·6	15·9	2·04
Palmitic acid, %	—	—	17·1		2·3		

Petroleum spirit extraction of kernels of (viii) yielded 0·63 per cent. of oil; further extraction with chloroform gave 1·0 per cent. more—of very bad odour. The first extract had a saponification value 130·6, and contained 30·0 per cent. of unsaponifiable matter. The mean mol. wt. of combined fatty acids was 288; the iodine value of the petroleum spirit extract was 54·5. This oil differs greatly from those of seeds of *Salvadora persica* and *S. oleoides* (of the same family), which contain high percentages of oils characterised by large amounts of acids of low molecular weight, especially myristic.

E. B. Daw

The Roeder Method for Determining Fat in Cheese. M. J. Bernaerts (*Ned. Melk Zuiveltijdschr.*, 1948, **2**, 99–107)—Following the appearance of a new type of cheese butyrometer, marketed by the Gerber firm, and described as the *Käsebutyrometer nach Dr. Roeder*, an investigation was made of the Roeder method of fat determination in cheese (Gerber, *Traité pratique des Essais du Lait et du Contrôle des Produits Laitiers*, 9th Edn., revised by Charles Schneider, Berne, 1941, p. 105). This method is as follows. Weigh out 2·266 g. of cheese into a small beaker with perforated walls, place the beaker in the butyrometer, and cover the cheese with 15 ml. of solvent; this solvent is prepared by dissolving 43 g. of stannous chloride in 700 ml. of concentrated hydrochloric acid and diluting to 1 litre with water. Heat for 10 to 15 min. in boiling water, shaking the butyrometer several times. Add 1 ml. of amyl alcohol and sufficient of the reagent to bring the meniscus to the upper part of the graduated portion of the neck. Shake vigorously once more and centrifuge at 1000 revolutions per min. for 5 min. Read the percentage at 65° to 70° C. The results obtained by this method were always too high, compared with those obtained by the Van Gulik and Weibull methods; particularly high figures were obtained with highly fermented cheeses. The cause of the deviations was found to be the formation of amyl ether and of amyl esters of lower fatty acids; these reactions proceed much more rapidly in presence of the stannous chloride solution than in presence of the dilute sulphuric acid used in the other two methods. Better results were obtained by (i) cooling the butyrometer to 65° C., after the cheese had dissolved and before adding amyl alcohol, as the formation of amyl ether and esters is quicker at the boiling-point, and (ii) by weighing out a smaller quantity of cheese, 2·09 g. The centrifuging must be done immediately after the amyl alcohol is added and the butyrometer shaken.

E. M. Pope

Component Acids of Rape Seed Oil. M. N. Baliga and T. P. Hilditch (*J. Soc. Chem. Ind.*, 1948, **67**, 258–262)—For preliminary separation of rape and similar cruciferous seed oil fatty acids before ester-fractionation, crystallisation from 10 per cent. solution in ether at −40° C. for 5 hr. was followed by recrystallisation (as before) of the deposited acids. Fractions are distinguished as (*A*) insoluble at −40° C., (*B*) soluble at −40° C., and (*B*^{1}) soluble at −40° C. (from recrystallisation of (*A*)). This method permits the approximate determination of the three unsaturated minor component acids—hexadecenoic, eicosenoic, and docosadienoic—and five saturated ones—palmitic, stearic, arachidic, behenic, and lignoceric—besides the four major component acids—erucic, oleic, linoleic, and linolenic. The average percentage fatty acid composition of four rape seed oils—Indian (Toria, Guzerat), Polish (Danzig), and Argentine (Plate) is palmitic 2·5, saturated C_{18}, C_{20}, C_{22}, and C_{24} (together) 5, hexadecenoic 2, oleic 15, linoleic 13·5, linolenic 8, eicosenoic 5, erucic 48, and docosadienoic 1 (wt.). Ravison (Black Sea) seed oil (*A*) and Jamba (Indian) rape seed oil (*B*) had the following percentage (wt.) composition: palmitic (*A*) 4, (*B*) 4·5; saturated

C_{18} to C_{24} (*A*) 5, (*B*) 5; hexadecenoic (*A*) 0·5, (*B*) 1·5; oleic (*A*) 15·5, (*B*) 24; linoleic (*A*) 21, (*B*) 9; linolenic (*A*) 10, (*B*) 6·5; eicosenoic (*A*) 4, (*B*) 11·5; erucic (*A*) 39, (*B*) 37·5; docosadienoic (*A*) 1, (*B*) 0·5.

E. B. DAW

Biochemical

Separation of Acidic Amino Acids by Means of Synthetic Anion Exchange Resin. R. Consden, A. H. Gordon, and A. J. P. Martin (*Biochem. J.*, 1948, **42**, 443–447)—A chromatographic method is presented for separating glutamic from aspartic acid after their separation together from a protein hydrolysate, the synthetic anion-exchange resin Amberlite IR4 being used.

*Method—Preparation of Amberlite IR*4 (Resinous Products and Chemical Co., Pa.)—Alternately grind the resin wet in a ball mill and sieve with a jet of water. Use $-90 + 200$ grading for the preparation of absorption columns. Wash free from ammonia, treat with hydrochloric acid until the supernatant liquid is permanently acid to thymol blue (pH <1), and wash with water. Treat alternately a number of times with acid and water.

Preparation of columns—(1) Stir and wash the resin by decantation with water until the supernatant liquor is less than 0·001 *N* with respect to alkali. Transfer the slurry to a glass tube of 0·5 cm. internal diameter, forming a column 20 cm. in height and containing about 2 g. of air-dry resin. Wash overnight with water at about 15 ml. per hr. This does not significantly raise the pH of the eluate, the acid concentration of which should be checked by titration before the next stage. (2) Prepare the second column (height 30 cm.) from about 3 g. of Amberlite and adjust the pH accurately to 2·5 by equilibration with dilute acid and water until the acidity of the supernatant fluid is slightly above 0·003 *N*. Transfer the material to a 0·5-cm. diameter tube and wash overnight with 0·003 *N* hydrochloric acid. Finally, check the acidity of the eluate by titration. The columns should not be allowed to run dry and remain so for any length of time or extensive cracking may occur.

Procedure for the estimation of glutamic and aspartic acids—Prepare the hydrolysate, containing up to 15 mg. of acidic amino acids, with hydrochloric acid, repeatedly evaporate *in vacuo* by rotating manually in a warm water-bath, allow to stand overnight *in vacuo* over potassium hydroxide, and quantitatively transfer in a small volume to the first column. Pass water down the column and elute the neutral and basic amino acids in the first 25 ml. The next 5 ml. should be free from amino acids. To test the eluate concentrate a portion of the first 25 ml. and all of the second 5 ml. fraction separately *in vacuo* to a very small bulk and test separate portions of each by partition chromatography on a strip of Whatman No. 4 paper, using phenol-ammonia, developing for 5 hr. or more, with a suitable control (*cf. Ibid.*, 1944, **38**, 224). After development and treatment with ninhydrin, basic and neutral but no acidic amino acids are found in the first eluate, whilst the second eluate should contain no amino acids. If cystine is present, oxidise the eluate sample with an excess of bromine water before chromatography; the cysteic acid thus produced occupies a position on the chromatogram not overlapping the positions of aspartic and glutamic acids (*Ibid.*, 1946, **40**, 580) if these are present. Next transfer the material remaining on the column to the second column by either of the following methods.

Method 1—Elute the column with *N* hydrochloric acid, causing the pigment to run down in a sharp band. When this has run out, stop washing, and repeatedly evaporate the eluate *in vacuo* and allow to stand overnight *in vacuo* over potassium hydroxide to remove the excess of hydrochloric acid. Transfer quantitatively to the second column, which is eluted with 0·003 *N* hydrochloric acid. Collect 10-ml. eluates and concentrate each *in vacuo* to 1 to 2 ml. and test a 4-μl. sample as described above.

Method 2—Wash the column with 3 ml. of *N* hydrochloric acid, causing the pigment to travel about halfway down, and testing that the eluate is free from amino acids by chromatography. Fix the column to the top of the second column, and continue the elution with water. The acid already added is sufficient to cause the pigment band to continue to travel down and eventually to pass into the lower column. When the pigment has travelled a few centimetres into the second column, remove the top column and continue the elution with 0·003 *N* hydrochloric acid. If no pigment is present elution may be followed by the change in shade of the resin, which is orange when strongly acid. Collect the eluates and test as in Method 1.

Method 1 gives more consistent results than Method 2. In proteins where the ratio of glutamic acid to aspartic acid is of the order of 2 to 1, the glutamic acid is eluted from the second column in the first 20 ml., and aspartic acid in the next 30 ml. In Method 2 the stages at which the acids begin to appear is less certain. Method 2 is quicker than Method 1, but requires more attention.

Evaporate each eluate *in vacuo* to dryness and add to the crystalline residue a known volume (5 to 10 ml.) of copper phosphate buffer suspension (*Ibid.*, 1939, **33**, 1070). Titrations (20 to 50 μl. of 1·0 *N* sodium thiosulphate) are carried out on 1-ml. portions after filtering and addition of the other reagents. Neutralisation before the addition of the copper phosphate is unnecessary.

Recoveries of glutamic and aspartic acids from a synthetic mixture by this technique varied from 88·8 to 97·6 per cent.

A method for isolating cysteic acid from wool hydrolysates is also presented. J. S. HARRISON

Chromatographic Separation of Amino Acids and Peptides. I. Chromatography of Neutral Peptides in 10 per cent. Formol. E. Lederer and Tchen Pau Kium (*Biochimica et Biophys. Acta*, 1947, **1**, 35–41)—Neutral di- and tripeptides can be separated quantitatively from other neutral non-adsorbed amino acids in 10 per cent. formol solution by adsorption on acid-activated alumina. The adsorbed amino acids are quantitatively eluted in an alkaline medium.

β-Alanine can also be separated quantitatively from its α-isomer and a method is described in which *o*- and *p*-aminobenzoic acids are adsorbed on activated alumina in absence of formol.

Peptides—The apparent acid dissociation constant (pKa′) of amino acids is displaced by addition of formol. For example, the pKa′ of glycine in water is 9·60, and 5·92 in 9 per cent. formol solution, and that of serine is 9·15 in water, and 5·63 in formol. Dunn and Loshakoff (*J. Biol. Chem.*, 1936, **113**, 691) found that certain peptides resembled glycine and serine in respect of their pKa′ in formol solution, *e.g.*, the pKa′ of glycyl-glycine is changed from 8·13 in water to 4·27 in 9 per cent. formol solution. It was therefore likely that neutral peptides would, like glycine and serine, be adsorbed on acid-activated alumina. This was confirmed and it was found that neutral di- and tripeptides also were adsorbed. This provides a method for the quantitative separation of the amino acids and neutral peptides, although its usefulness is diminished by the fact that glycine, serine, threonine, and cysteine are adsorbed with the peptides. The only other practical method, that of E. Fischer and E. Abderhalden (*Z. Physiol. Chem.*, 1905, **46**, 52), is not suitable for quantitative application.

β-Alanine—As the effect of formol on the acidity of glycine is probably due to the presence of an $-NH_2$ group attached to a primary carbon, similar effects can be expected with all the ω-amino acids. This effect was verified. β-Alanine in 10 per cent. formol solution is quantitatively retained on an acid-activated alumina column and can be separated quantitatively from the α-isomer. The pKa′ of β-alanine is 6·41 in 10 per cent. formol solution, compared with 7·26 for α-alanine. γ- and δ-Amino acids containing the $-CH_2NH_2$ group behave in a similar way to β-alanine.

Aminobenzoic acids—Both *o*- and *p*-aminobenzoic acids can be adsorbed on acid-activated alumina, even in absence of formol.

General procedure—Essentially, the technique of Schramm and Primosigh (*Ber.*, 1943, **76**, 373) is followed. Dissolve 3 to 30 mg. of amino acid or peptide in 5 ml. of 10 per cent. formol solution, purified by distillation of commercial formaldehyde: the distillate, free from nitrogen, contains about 30 per cent. of formol. Make a convenient dilution and neutralise just to the rose colour of phenolphthalein (pH about 8·5). Pass the solution of the substance to be tested through a column of 20 g. of acid-activated Merck alumina, prepared according to Wieland (*Z. physiol. Chem.*, 1942, **273**, 24; *Ber.*, 1942, **75**, 340 and 1001), and previously washed with 75 ml. of 10 per cent. formol solution. After the 5 ml. of solution have penetrated into the column, pour thereon about 50 ml. of 10 per cent. formol solution. The filtrate contains the substances that pass through the column without being adsorbed. Elute the adsorbed substances by washing the column with dilute alkali; use about 20 ml. of 0·5 *N* potassium hydroxide for neutralising the acid in the column, followed by 30 ml. of 0·1 *N* potassium hydroxide to effect the elution in feebly alkaline solution. Collect the alkaline liquid in an excess of dilute sulphuric acid. The elutions can also be carried out with aqueous baryta, as this facilitates subsequent treatment of the eluate after precipitation of the baryta with sulphuric acid (*cf.* Wieland, *loc. cit.*).

The recoveries of glycine, DL-serine, β-alanine and all the di- and tripeptides tested were between 95 and 102 per cent., whereas α-alanine and DL-leucine were not retained on the column. It was considered unnecessary to try other neutral amino acids, which were known to pass through the column without being adsorbed. Where 5 ml. of an aqueous solution containing 4·4 mg. of *p*-aminobenzoic acid at pH 6·5 was passed through 20 g. of acid-activated alumina and washed with 75 ml. of water, followed by 50 ml. more of water, all the acid was retained, but could be eluted quantitatively with dilute alkali. Anthranilic acid behaved similarly.

J. S. HARRISON

Photometric Estimation of Purine and Pyrimidine Nucleosides by Means of the Reaction with Orcinol. L. Massart and J. Hoste (*Biochimica et Biophys. Acta*, 1947, **1**, 83–86)
A method is described for estimating pyrimidine nucleosides by means of the reaction of Bial, as modified according to Barrenscheen and Peham (*Z. physiol. Chem.*, 1942, **272**, 81), in presence of purine nucleosides. In the normal condition of the reaction with orcinol the purine nucleosides are not hydrolysed. Treatment with bromine water or catalytic reduction diminishes the resistance to hydrolysis.

Estimation of pure pentoses and pure purine nucleosides—Mix equal volumes (3 ml.) of the solution to be tested and an orcinol reagent prepared at the time of the determination by dissolving 0·2 g. of orcinol in 100 ml. of a solution of *M*/2500 cupric chloride in hydrochloric acid. (This reagent is stable for several hours.) Allow to stand for 10 min. in vigorously boiling water and cool as quickly as possible in running water. Measure the extinction in a 1-cm. cuvette, using a Leitz photometer with filter 620, or a Zeiss instrument with filter 610.

Results—Extinction coefficients determined for xylose, arabinose, adenosine, and adenosine triphosphoric acid agreed well with those of Barrenscheen and Peham, except that the values for xylose were slightly greater than those for arabinose, and the values for adenosine, freed from pentose, were slightly high, but those for adenosine triphosphoric acid agreed well.

Hydrolysis—The method of hydrolysis used by Barrenscheen and Peham was not satisfactory for the hydrolysis of pyrimidine nucleoside unless preceded by treatment with bromine. The bromine must not be allowed to act for too long or the colour produced is unsuitable for colorimetric estimation. The following method was adopted for adenosine and cystidine: add 0·01 ml. of bromine to 3 ml. of a solution containing the nucleosides, place in an oil-bath at 105° C., and stir mechanically with a glass stirrer. After 2 min., remove the excess of bromine by a current of air and then replace in the oil-bath for 38 min. After this time add an equal volume of the orcinol reagent and

allow to react for 10 min. in the oil-bath at 105° C. Cool quickly in running water and measure the extinctions. This method gave reproducible results.

Extinction of pyrimidine nucleoside in presence of purine nucleosides—On one portion of the sample measure the purine nucleoside by the method of Barrenscheen and Peham to obtain a value *a*, corresponding to an extinction *b* for the bromine method described, using a graph constructed by joining the points 100 μg. of nucleoside against 0·20 extinction, and 300 μg. against 0·38 extinction, by a straight line. On a second portion of the solution determine the extinction by the bromine method described, thus obtaining a value *c* for pyrimidine nucleosides + purine nucleosides. The content of pyrimidine nucleoside is obtained by subtracting *b* from *c*. This method can be applied to the quantitative measurement of mixtures of pyrimidine nucleosides and purine nucleosides in extracts of animal organs. J. S. HARRISON

Determination of Peptide-Amino Nitrogen by the Copper Method. H. K. Kerkkonen (*Acta Chemica Scandinavica*, 1948, **2**, 518–522)—Solutions of partially hydrolysed proteins give too high results for amino-nitrogen by Pope and Stevens's method (*Biochem. J.*, 1939, **33**, 1070), indicating that the soluble compounds formed by copper with peptides are not similar to those formed with amino acids.

Experiments with glycyl-L-leucine, glycyl-glycine, L-leucyl-L-tyrosine and L-leucyl-glycyl-glycine, alone or in admixture, showed that the Van Slyke method gave about 50 per cent. of the total nitrogen (33·3 per cent. with L-leucyl-glycyl-glycine) as would be expected, whereas the Pope and Stevens method gave 97·2 to 98·5 per cent. (66·6 per cent. for L-leucyl-glycyl-glycine). Confirmatory evidence was also obtained in examining a pepsin-digested zein solution, an acid digest of zein plastein (Virtanen and Kerkkonen, *Nature*, 1948, **161**, 888) as well as with experiments on pentaglycine ethyl ester and glycyl-tyrosine methyl ester.

Woiwod (*Biochem. J.*, 1948, **42**, xxviii) has reported results for the α-amino-N/copper ratio of a number of amino acids, using a colorimetric copper determination, the ratio being twice that found for the dipeptide alanyl-glycine.

When titrating the peptide-copper compound, therefore, 1 ml. of 0·01 *N* sodium thiosulphate is equivalent to 0·14 mg. of amino-nitrogen and not to 0·28 mg. as for amino acids. D. C. M. ADAMSON

Colorimetric Estimation of Hexoses with Carbazole. G. Holzman, R. V. MacAllister, and C. Niemann (*J. Biol. Chem.*, 1947, **171**, 27–35)—Hexoses and pentoses, heated with sulphuric acid, produce a colour in presence of carbazole. The optimum conditions of this reaction for estimating hexoses have been found.

Reagents—Purify the carbazole by precipitating it three times with cold water from a solution in concentrated sulphuric acid. Dry the product and crystallise from toluene. To obtain low blanks, heat sulphuric acid under reflux with potassium persulphate (20 mg. per litre) until a negative test for oxidising agents is obtained with starch-iodide. *Carbazole reagent*—To 300 ml. of 84 weight per cent. sulphuric acid, add 10 ml. of a 1 per cent. solution of carbazole in absolute ethanol. This reagent is stable for only about 6 hr. and should be freshly prepared every day.

Procedure—Place 9-ml. aliquots of the carbazole reagent in tubes kept in an ice-bath. Add 1-ml. aliquots of hexose solution containing from 50 μg. to 150 μg. of glucose. Mix well and then heat in boiling water for 15 min. Cool in an ice-bath and determine the colour in a Klett colorimeter, using the green filter No. 54.

The accuracy of the method is 2 to 5 per cent. and duplicate samples should be taken. The colour intensity varies with the concentration of sulphuric acid used, reaching a maximum at 84 per cent. by weight. Increasing the carbazole concentration increases the colour intensity. The time of heating is not critical if it is between 10 and 20 min. Sodium nitrate, sodium nitrite, or ferric chloride (in amounts of 5 μg.) did not interfere with the determination of 100 μg. of glucose; N-acetyl glucosamine did not produce a colour.

The extinction coefficients of the colours with glucose, fructose, galactose, and mannose were different, but not so much so that a qualitative identification of the sugars would be possible.

The mechanism of the reaction is discussed in terms of the ultra-violet spectra of sulphuric acid solutions of hexoses. W. S. WISE

Colour Reaction for Glucuronic Acid. Z. Dische (*J. Biol. Chem.*, 1947, **171**, 725–730)—A colour reaction with thioglycollic acid is described for the detection of glucuronic acid.

Procedure—To 0·8 ml. of a solution containing 0·02 to 0·04 per cent. of glucuronic acid, add 0·2 ml. of a 0·2 per cent. solution of mannose. Add, with cooling and shaking, 4·5 ml. of a mixture of diluted sulphuric acid (6 + 1). Keep for 2 min. in ice-water, then in water at 20° to 25° C. and, later, keep for 3 min. in boiling water. Cool to room temperature and add 0·1 ml. of a 2·5 per cent. solution of commercial thioglycollic acid. Shake well and keep at room temperature for 20 to 24 hr. A deep pink colour is produced.

A colour is produced by hexuronic acids and other compounds when treated with thioglycollic acid and concentrated sulphuric acid. The colour produced in presence of an excess of mannose appears to be selective for glucuronic acids and polyglucuronides.

The absorption spectra of the colours produced by some hexuronic acids and polyuronides are given. W. S. WISE

Determination of *p*-Aminosalicylic Acid in Blood and Cerebrospinal Fluid. W. Klyne and J. P. Newhouse (*Lancet*, 1948, **255**, 611)—Although Lehman (*Svenska Läkartidn*, 1946, **43**, 2029) mentioned Ehrlich's reagent for the determination of *p*-aminosalicylic acid in blood, no details were given. A method based on Morris's procedure for the determination of sulphanilamide (*Biochem. J.*, 1941, **35**, 952) has given satisfactory results in

clinical trials. Recoveries of added *p*-aminosalicylic acid were about 100 per cent. for oxalated plasma and cerebrospinal fluid, and 80 to 90 per cent. for oxalated whole blood. Streptomycin (1000 μg. per ml.) did not interfere. Sulphanilamide interferes, since the reaction is a general one for primary aromatic amines.

Reagents—(*a*) *p*-Toluene sulphonic acid solution: 20 per cent. in 0·2 *N* hydrochloric acid. (*b*) 0·75 *M* Disodium hydrogen citrate: 39·4 g. of citric acid dissolved in 188 ml. of 2 *N* sodium hydroxide and diluted to 250 ml. (*c*) Ehrlich's reagent: *p*-dimethylaminobenzaldehyde, 2 per cent. in 95 per cent. alcohol. (*d*) Sodium *p*-aminosalicylate standards: 11·4 mg. of the anhydrous salt or 13·8 mg. of the dihydrate dissolved in water and diluted to 100 ml. (equivalent to 10 mg. of *p*-aminosalicylic acid per 100 ml.).

Procedure—Dilute 0·5 ml. of blood or 1 ml. of cerebrospinal fluid (both oxalated) to 7 ml. with water, shake well, and allow to lake (3 min.). Add 3 ml. of reagent (*a*) slowly and with shaking, and filter after 5 min. To 5 ml. of the clear filtrate add 1 ml. of reagent (*b*) and 2 ml. of Ehrlich's reagent (*c*). Measure the orange colour, which develops at once and is stable for some hours, photoelectrically, using a blue filter (Ilford 602), against a blank prepared from 1·5 ml. of reagent (*a*), 1 ml. of reagent (*b*), and 2 ml. of Ehrlich's reagent, made up to 8 ml. with water. Read the *p*-aminosalicylic acid content from a calibration curve constructed by carrying out the same procedure on 1·0, 0·5, and 0·2 ml. of reagent (*d*) diluted to 7 ml.

D. C. M. ADAMSON

Water Analysis

Determination of Manganese in Natural Waters. F. Koroleff (*Acta Chemica Scandinavica*, 1947, **1**, 503–506)—Variations of 0·001 mg. of manganese per litre can be estimated by precipitating as the manganese hydroxide and using magnesium sulphate as coagulant and carrier and oxidising to permanganate with alkali periodate. Halides, organic matter, and suspended material must be removed from the water.

Method—Reagents—Sodium paraperiodate, prepared by Wells's method (*J. Amer. Chem. Soc.*, 1901, **26**, 278). *Sulphuric acid*: dilute 1 part of manganese-free concentrated acid with 2 parts of water and add 15 mg. of sodium paraperiodate per ml. *Magnesium sulphate solution*: dissolve 22·5 g. of heptahydrate in 250 ml. of water to give a solution containing 9 mg. of magnesium per ml. *Standard permanganate solution*: dissolve 57·539 mg. of recrystallised potassium permangate, add 1 ml. of 2 *N* sulphuric acid, reduce by adding 0·15 g. of sodium hydrogen sulphite, boil free from sulphur dioxide, cool, and dilute to 200 ml.; dilute 1 ml. to 60 ml., boil with 10 ml. of the sulphuric acid reagent and 2 ml. of 0·2 *N* silver nitrate, add 50 mg. of sodium paraperiodate, place in a water-bath for 30 min., cool, and dilute to 100 ml.; the solution contains 0·001 mg. of manganese per ml. and should be protected from direct sunlight.

Procedure—(*A*) *Organic matter absent*—Mix 50 ml. of 0·2 *N* potassium hydroxide with 1 litre of seawater in a measuring cylinder. After setting aside for at least 2 hr., siphon off the supernatant liquid and dissolve the precipitate in 1·5 ml. of concentrated sulphuric acid; if this solution is coloured by organic matter proceed as in (*B*). Precipitate the halide ions with a slight excess of 2 *N* silver nitrate and filter through a Jena 3G4 porcelain filter. Boil the filtrate with 10 ml. of the sulphuric acid reagent, add 50 mg. of sodium paraperiodate, place in a water-bath for 30 min., cool, dilute to 50 ml. in a Nessler tube and compare with standards. (*B*) *Organic matter present*—Transfer the coloured sulphuric acid solution containing the manganese to a platinum dish, evaporate, and heat the residue to fusion. Cool, dissolve in 10 ml. of the sulphuric acid reagent, boil, cool, and filter through a Jena 3G4 porcelain filter. Dilute the filtrate to 75 ml., add 2 ml. of 0·2 *N* silver nitrate, and proceed as in (*A*).

C. F. HERBERT

Organic

Determination of Organic Peroxides. Evaluation of a Modified Iodimetric Method. C. D. Wagner, R. H. Smith, and E. D. Peters (*Anal. Chem.*, 1947, **19**, 976–979)—Many peroxycarboxylic acids, diacyl peroxides, hydroperoxides, and other peroxide compounds can be determined by iodimetric methods, although the accuracy of certain iodimetric methods with such simple peroxides as *cyclo*hexene and Tetralin peroxides has been disputed, especially on the grounds that the iodine liberated in the reaction disappears by addition to olefinic double bonds, and that in modifications requiring the use of strong acids there may be reduction of organic compounds other than peroxides, including any alkylene di-iodides formed by addition of iodine to olefines. Atmospheric oxygen is known to cause high results with most iodimetric methods, particularly in presence of strong acids, and methods employing sodium bicarbonate or solid carbon dioxide have been devised to overcome this defect.

For general use the method of Kokatnur and Jelling (*J. Amer. Chem. Soc.*, 1941, **63**, 1432; *Analyst*, 1941, **66**, 430), which is said to be uninfluenced by atmospheric oxygen, has been found the most suitable of the methods tested. Modifications found advantageous are (*a*) the replacement of potassium iodide by sodium iodide, which is much more soluble in the reaction mixture, thus tending to increase the reaction rate and to decrease the possible addition of iodine to unsaturated materials, and (*b*) the exclusion of water from the reaction mixture to avoid the low results obtained with auto-oxidised diolefines in its presence. In the experimental work the reaction mixture was kept in an atmosphere of carbon dioxide, and both sample and reaction mixture were de-aerated before analysis, but such precautions were found unnecessary for general use.

With the modified iodide method results with known hydroperoxides were accurate. Variation in reaction conditions produced little change in results with materials containing no auto-oxidised

conjugated diolefines. Results with diolefines and ascaridole showed wide variations with reaction conditions and such bridge-type peroxides are not determined accurately by the method. Under the conditions of the method, iodine is not taken up by mono-olefines nor, in absence of peroxides, by diolefines. One experiment indicated that iodine might be absorbed by diolefines in presence of diolefine peroxides. The method with sodium iodide and *iso*propyl alcohol is as useful as that with sodium iodide and acetic acid, and has the advantages of a somewhat more general applicability and comparative freedom from interference by atmospheric oxygen. The following procedure is recommended for general use.

Procedure—Into a 250-ml. Erlenmeyer flask introduce 40 ml. of dry *iso*propyl alcohol, 2 ml. of glacial acetic acid, and up to 10 ml. (usually 5 ml.) of the sample containing not more than 2 mg.-equivalents of peroxides. Heat to refluxing temperature, add 10 ml. of *iso*propyl alcohol saturated at room temperature with sodium iodide (prepared by refluxing 25 g. of sodium iodide with 100 ml. of *iso*propyl alcohol), heat under reflux for 5 min., add 5 ml. of water, and titrate with 0·1 *N* or 0·01 *N* sodium thiosulphate. Blank determinations on the reagents will be nil, unless oxidising impurities are present in the *iso*propyl alcohol, and a blank determination on each new batch of the alcohol is sufficient. Although the method is not recommended for use with conjugated diolefines, it is sometimes useful for obtaining precise empirical results, provided that an atmosphere of carbon dioxide is maintained in the flask during the analysis.

The materials used in the investigation were tetrahydronaphthyl hydroperoxide (Tetralin peroxide) prepared by air oxidation of Tetralin at 75° C. and subsequent purification by crystallisation, α,α-dimethylbenzyl hydroperoxide (cumene peroxide), prepared from cumene by a method similar to that of Hock and Lang (*Ber.*, 1944, **77B**, 257), *tert*-butyl hydroperoxide, hydrogen peroxide (30 per cent. in water), benzoyl peroxide, and ascaridole. The following substances were auto-oxidised by allowing them to stand under oxygen in diffused daylight until analysis indicated a sufficiently high peroxide content (air was used with 2-pentene): di-*iso*butylene, 2-pentene, *cyclo*hexene, Tetralin, methylpentadiene, isoprene, and diethyl ether.

Experiments, in which known amounts of a standard solution of iodine in *iso*propyl alcohol were titrated hot in *iso*propyl alcohol containing 2 ml. of glacial acetic acid and 2 g. of sodium iodide, showed that reaction between sodium thiosulphate and the tri-iodide ion is slow unless 5 to 10 per cent. of water is present in the reaction mixture. When the titre is large, the sodium thiosulphate solution will supply enough water, but when the titre is low, water must be added before titration. Investigation of the effects of varying the manipulative details of the method showed that the amount of iodide is not critical provided that a large excess is present, that reaction time and sample size are not critical except for ascaridole, which is reduced slowly, that only the ascaridole determination was affected by the presence of water during the reaction, and that, with the exception of benzoyl peroxide, the peroxides are stable towards heat. With auto-oxidised materials variations in manipulative details had little effect on results with materials containing no conjugated diolefines, whereas results with auto-oxidised isoprene and methylpentadiene were critically dependent upon the experimental conditions. The diolefine peroxides react slowly and incompletely like ascaridole and the rate of reduction depends upon the concentration of the iodide ion in the mixture rather than upon the concentration of the peroxides. Water present during the heating under reflux sometimes causes lower results and its exclusion at this stage is recommended. The results demonstrate conclusively that peroxides in auto-oxidised conjugated diolefines differ radically from those in other materials; the latter are now generally accepted to be hydroperoxides, whereas Bodendorff (*Arch. Pharm.*, 1933, **271**, 1) has shown that conjugated diolefines form peroxides largely by 1 : 4-addition to produce intramolecular peroxides of the ascaridole type or polymeric peroxides by intermolecular peroxy-bridging to the 1- or 4-positions of other molecules.

In absence of iodide ion a large portion of the iodine is lost, particularly in presence of water. The fact that no loss of iodine occurs in presence of iodide is undoubtedly due to the formation of unreactive tri-iodide ion and the resultant small concentration of free iodine. In an examination of the application of the method to isoprene in presence of benzoyl peroxide, no peroxide-catalysed addition of iodine was observed. Some evidence was obtained of the possible absorption of iodine (as tri-iodide) by diolefines in presence of diolefine peroxides. In presence of diolefine peroxides, simple alkyl iodides are not reduced by the iodide reagent. Exclusion of air is essential only if the method is applied to diolefine samples of low peroxide content.

The method was compared with two methods in which the solvent is acetic acid. In the reflux method, 50 ml. of glacial acetic acid and 5 ml. of sample were subjected to a stream of carbon dioxide for 2 min. and the mixture was then heated to refluxing temperature. After the addition of 2 ml. of saturated aqueous sodium iodide solution, the mixture was heated under reflux for 15 min., the passing of carbon dioxide was resumed, 100 ml. of water were added, and the cooled mixture was titrated at room temperature with sodium thiosulphate to the disappearance of the yellow colour, the carbon dioxide stream being maintained during the titration. The result was corrected by means of a blank determination. The other method follows the same procedure except that after carbon dioxide has been passed through the mixture, sodium iodide solution is added, the carbon dioxide supply is discontinued, and the stoppered flask is set aside in the dark for 15 min. at room temperature before resuming the carbon dioxide flow, adding water and titrating as before. Acetic acid as a solvent offered no advantages over *iso*propyl alcohol other than the elimination of refluxing. Disadvantages are greater

interference by air, occasional slight destruction of peroxides, the need for great dilution with water before titration, and increased tendency for diolefinic materials to polymerise to dark-coloured products. Use of a strong acid in place of acetic acid would probably accentuate these difficulties.

A. O. JONES

Determination of Organic Peroxides. Evaluation of the Ferrous Thiocyanate Colorimetric Method. C. D. Wagner, H. L. Clever, and E. D. Peters (*Anal. Chem.*, 1947, **19**, 980–982)—The colorimetric ferrous thiocyanate method of Young *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 198; *Analyst*, 1936, **61**, 502) has been tested with a variety of auto-oxidised materials and is recommended as the best for frequent analyses of materials containing only small amounts of peroxides. For materials (except diolefines) containing large amounts of peroxides, the iodimetric method is more precise and accurate. The colorimetric method is not well suited for materials containing polymers, particularly diolefines, owing to the turbidity caused by insoluble high polymers.

To prepare the ferrous thiocyanate solution, dissolve 1 g. of pure ammonium thiocyanate and 1 ml. of 25 per cent. w/w sulphuric acid in 200 ml. of de-aerated methanol and shake the resulting solution with 0·2 g. of finely powdered ferrous ammonium sulphate. Place the decanted reagent (prepared fresh daily) in a brown glass-stoppered bottle.

Procedure—Place 1 ml. of the sample, preferably containing from 0·0001 to 0·0007 mg.-equivalents of reactive peroxide, in a 25-ml. volumetric flask. If necessary use 1 ml. of a suitable dilution of the sample with methanol. Dilute to the mark with ferrous thiocyanate reagent, mix well, and fill a 1-cm. cell of the Spekker photo-electric absorptiometer, equipped with blue No. 6 and green No. 5 filters, with the mixture. At 10 min. from the time of mixing, read the optical density and convert the value, corrected by a blank determination, into terms of concentration by means of a calibration curve prepared with corresponding known concentrations of ferric chloride.

In the study of the method the materials used were those listed in the preceding abstract, and these were analysed by the colorimetric method and also by the method described in that abstract. With most of the materials agreement was satisfactory, but was poor with ether and methylpentadiene (a conjugated diolefine), and with the latter substance the reduction was slow and incomplete by both methods, the discordant results being thus only of empirical value. Benzoyl peroxide also reacted only slowly with the reagent. Since good results (considering the low precision of the colorimetric method) were obtained with the pure hydroperoxides, the colorimetric method is probably fundamentally accurate when applied to auto-oxidised materials containing only isolated double bonds.

The hydroperoxides react quickly, the optical density increases rapidly during the first 2 min., and thereafter remains constant. However, the peroxides in methylpentadiene, which, presumably, are of the bridge-type described by Bodendorff (see the preceding abstract), react very slowly. Sample size does not affect results appreciably with any of the materials tested. The absence of an effect of sample size with methylpentadiene is noteworthy in view of the pronounced effect of this variable on results with conjugated diolefines by the sodium iodide method.

To study the effect of oxygen concentration, dissolved oxygen was removed from the sample and reagent before mixing by means of oxygen-free nitrogen in an apparatus similar to that of Lea (*J. Soc. Chem. Ind.*, 1945, **64**, 106; *Analyst*, 1945, **70**, 308). Lea's observation that much lower results are obtained in absence of oxygen was confirmed. When air was added after mixing the de-aerated sample and reagent, no deepening of colour occurred. This shows that the peroxide (non-diolefine) is completely and rapidly destroyed in presence of ferrous ion by both reduction and decomposition. In presence of molecular oxygen the reduction reaction proceeds much more rapidly than the decomposition reaction; in absence of oxygen the reverse is true, and only a small amount of ferrous thiocyanate is formed. Use of oxygen in place of nitrogen gives approximately normal values, thus verifying that a certain amount of oxygen is necessary to obtain quantitative results and that the effect is not one of oxidation of ferrous ion by molecular oxygen. In absence of oxygen lower values are also obtained with methyl pentadiene, although the lowering is less marked. The presence or absence of oxygen seems to have no influence on the rate of reduction of those peroxides remaining after mixing, since the optical density after mixing increases slowly and at about the same rate whether oxygen is present or not. This suggests that the hydroperoxides are destroyed rapidly upon mixing reagent and sample, leaving only the bridge-type peroxides intact.

A. O. JONES

Determination of Organic Peroxides. Evaluation of the Ferrous-Titanous Method. C. D. Wagner, R. H. Smith, and E. D. Peters (*Anal. Chem.*, 1947, **19**, 982–984)—Yule and Wilson (*Ind. Eng. Chem.*, 1931, **23**, 1254) reported that peroxides in gasolines could be quickly and conveniently determined by reducing them with ferrous thiocyanate in aqueous acetone and titrating the resulting ferric thiocyanate with standard titanous solution. Although recognising that the results did not represent actual peroxide content, they used them chiefly as a measure of the gum-forming tendencies of the gasoline. Their choice of the ferrous-titanous method rather than of iodimetric methods was based on its greater sensitivity compared with that of the Marks and Morell method (*Analyst*, 1929, **54**, 503), with which high and variable "blanks" are obtained.

The sodium iodide - *iso*propyl method and the ferrous thiocyanate colorimetric method (see the two preceding abstracts) are both basically accurate for the determination of peroxide in auto-oxidised materials that contain no conjugated diolefines. Both methods give only empirical results with

conjugated diolefine samples owing to the slow rate at which such peroxides are reduced and possibly owing to side reactions. Since the method of Yule and Wilson (*loc. cit.*) is widely used particularly in the petroleum industry, its fundamental accuracy for determining peroxides in auto-oxidised materials was investigated. The prescribed correction factors, being admittedly arbitrary, were not applied.

Procedure—To prepare the ferrous thiocyanate solution dissolve 5 g. of ferrous sulphate and 5 g. of ammonium thiocyanate in 500 ml. of water and add 500 ml. of acetone. Add about 1 g. of pure iron wire and 5 ml. of concentrated sulphuric acid, and expel air by passing hydrogen or carbon dioxide through the solution. Store the product in an all-glass system under hydrogen and use it when the red colour has disappeared.

To prepare 0·01 *N* titanous sulphate, heat a mixture of 20 ml. of concentrated sulphuric acid and 80 ml. of water to 70° C. and add in small portions 0·6 g. of titanium hydride powder (Metal Hydrides, Inc., Beverly, Mass.; trade name "Altertan"). When the reaction subsides, boil the liquid on a hot-plate for 2 min., then pour it into about 900 ml. of water, freshly de-aerated with carbon dioxide. After the undissolved matter has settled, siphon the supernatant liquid into a dark storage bottle previously filled with carbon dioxide. Store the solution under hydrogen, dispense from an all-glass system and standardise daily against standard ferric chloride solution in presence of thiocyanate ions.

Measure 50 ml. of ferrous thiocyanate solution into a 250-ml. glass-stoppered Erlenmeyer flask and discharge any red colour with the least amount of titanous sulphate solution. Adjust the temperature to 25° ± 2° C., add the sample containing up to 5 mg.-equivalents of peroxide, stopper the flask, shake vigorously for 5 min. ± 5 sec., and titrate with 0·01 *N* titanous sulphate to the disappearance of the red colour.

The materials tested were as before (see the two preceding abstracts) and the method was applied to several of the known peroxides to check its accuracy. With hydroperoxides the results were far below the theoretical values or below those of the sodium iodide and *iso*propyl alcohol method. Of the peroxides tested only Tetralin peroxide and cumene peroxide were formed by natural auto-oxidation, but the results obtained with these showed that the ferrous-titanous method is inaccurate with even the simplest peroxides, whereas the iodimetric method of the preceding abstract gives satisfactory results. The fact that the results of the ferrous-titanous method are dependent upon sample size indicates, however, that it may be possible to obtain theoretical results on samples containing only very small amounts of peroxides.

Results obtained with non-diolefinic samples showed considerable similarity to those obtained with pure hydroperoxides, as might be expected. Diolefine peroxides react slowly with ferrous ions as well as with the iodide ion, the results with both methods being purely empirical. Ascaridole, a pure monomeric, 1 : 4-bridge-type peroxide, behaves in the same way, reacting slowly and incompletely with both iodide ion and ferrous ion.

In order to test the oxygen effect noted by Lea (*J. Soc. Chem. Ind.*, 1945, **64**, 106; *Analyst*, 1945, **70**, 308), experiments were made in which carbon dioxide or oxygen was passed through the reagent for 2 min. before adding the sample and shaking the mixture, and also during the titration. The results, compared with those obtained with an air atmosphere, showed a very evident dependence upon oxygen concentration, but, although those obtained with oxygen were higher in some instances than those obtained when carbon dioxide or air was used as the purging gas, they were considerably below the theoretical values. When an auto-oxidised non-diolefine has been reduced under carbon dioxide, titrated, and then air or oxygen is passed into the mixture, no further coloration appears. This indicates that the peroxides have been entirely destroyed, although they have been reduced only partly by the ferrous ion. Apparently oxygen either catalyses the reduction or inhibits the decomposition reaction. If it is assumed that the concentration of oxygen necessary for quantitative reduction of the peroxide depends upon the peroxide concentration, the low results obtained are understandable, since the ratio of dissolved oxygen to peroxide in the ferrous-titanous method is only one-hundreth of that in the colorimetric method.

The ferrous-titanous method thus appears to be empirical and useful only if values obtained by it are reproducible and can be correlated with some significant property of the test material, *e.g.*, explosion hazard or gum-forming tendency. To test the dependence of precision on the experimental conditions of the method, various materials were analysed with variations in the time of shaking, sample size, and reaction temperature. Peroxides in conjugated dienes react slowly and results are affected by sample size, temperature, and oxygen concentration. Peroxides in the other materials react almost instantaneously and results depend only upon oxygen concentration and, to a less extent, upon sample size. These results are consistent with the fact that peroxides in mono-olefines and probably those in ethers are the rapidly reacting alkyl hydroperoxides, whereas those in conjugated diolefines are the slowly reacting bridge-type peroxides. With the latter, precise results are obtainable only if the variables of the procedure are closely controlled. Benzoyl peroxide is a special instance reacting fairly rapidly with iodine ion but only slowly with ferrous ion. Ascaridole, although it is a typical diolefine peroxide monomer, seems to react rapidly in contrast with auto-oxidised diolefines. The slowly reacting diolefine peroxides may be the polymeric peroxide types mentioned by Bodendorff (*vide supra*) rather than the monomeric bridge-type forms. [NOTE—Tanner and Brown (*J. Inst. Petrol.*, **1946, 32, 341**; *Analyst*, **1946, 71**, 444) report a method, accurate to within ±4 per cent., which is based on the oxidation of ferrous salts, avoids the tedium of titanous chloride titrations, and needs no special colorimetric apparatus.] A. O. JONES

Direct Titration of Mercaptans in Gasoline. G. E. Mapstone (*Australian Chem. Inst. J. Proc.*, **1948**, **15**, 236–241)—An alkaline nitroprusside solution is a sensitive reagent for detecting mercaptans in gasoline. Owing to the insolubility of silver mercaptides, the reaction is reversed and the colour discharged on adding silver nitrate. The reaction is made the basis of a method for the direct titration of mercaptans in gasoline. As the indicator is alkaline, addition of ammonia or some other complex-forming substance (*e.g.*, pyridine) is necessary to prevent precipitation of silver oxide. Silver mercaptides are practically insoluble even in 15 *N* aqueous ammonia.

The intense violet colour formed with nitroprusside rapidly changes on standing to pale green by oxidation of the nitroso group with some further breakdown to Prussian blue. To retard this irreversible reaction, it is necessary to keep the alkali concentration as low as possible. Mercaptans have a low water-solubility and are only very slightly dissociated, so that it is necessary to add substances such as amyl or butyl alcohol to maintain a significant mercaptan concentration in the aqueous phase.

Method—To 100 ml. (or other suitable volume) of the gasoline, freed, if necessary, from hydrogen sulphide by washing with 5 per cent. cadmium sulphate solution, in a 250-ml. flask, add 1 ml. each of pyridine, sodium cresylate solution (prepared by dissolving 15 ml. of re-distilled cresylic acid, free from hydrogen sulphide and mercaptans, in 85 ml. of 10 per cent. sodium hydroxide solution), and freshly prepared 0·5 per cent. sodium nitroprusside solution and then 10 ml. of amyl or butyl alcohol. Shake well and titrate with 0·05 *N* silver nitrate until the purple colour of the lower layer is discharged. Add a further 0·5 to 1 ml. of the nitroprusside solution, and, if the colour reappears, continue the titration, repeating the procedure until addition of more nitroprusside fails to regenerate the colour. If much silver mercaptide is precipitated during the titration, it can be coagulated by adding a pinch of fuller's earth. The percentage of mercaptan sulphur by weight is given by $3{\cdot}2\,NV/vs$, where N is the normality of the silver nitrate solution, V is the number of millilitres used in the titration, v is the volume of the sample, and s is its specific gravity. The pyridine and sodium cresylate solution may be mixed before use. The pyridine concentration is not important, but enough sodium cresylate must be added to maintain the alkalinity of the aqueous-alcoholic phase and to neutralise the acid liberated by precipitation of silver mercaptide. A suitable reagent can be prepared by adding pyridine to the sodium cresylate solution until it is cloudy and then adding enough cresylate or cresol to dissolve the excess of pyridine. Two to 4 ml. of this reagent are used in each titration.

With raw gasoline samples containing tar bases, 10 per cent. sodium hydroxide solution can be substituted for the sodium cresylate and 2 *N* aqueous ammonia for the pyridine. With dyed and discoloured gasolines, the colour remains in the upper layer and does not interfere with the end-point in the lower phase. With highly oxidised raw gasoline, a faint purplish colour remains, but with a little practice this can be recognised and does not then interfere.

The method compares favourably in accuracy and reproducibility with the method of Borgstrom and Reid (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 186; *Analyst*, 1929, **54**, 767) and has the advantage that tar bases do not interfere and need not be removed. A. O. Jones

Analysis of Sulphite Waste Liquor and Lignosulphonates. Determination of Neutralised Solids, and Wet Oxidation for the Determination of Total Sulphur and Cations. J. R. Salvesen and D. Hogan (*Anal. Chem.*, 1948, **20**, 909–911)—*Neutralised solids*—Pipette 10 ml. of sample into 125 ml. of water, and titrate with 0·2 *N* sodium hydroxide to pH 8·5 to 9·0, using a glass electrode (x ml.). Weigh a weighing bottle, having a ground-glass stopper, add 10 ml. of sample, and re-weigh. Add x ml. of 0·2 *N* sodium hydroxide, evaporate, dry the residue at 105° C. (usually for 48 to 72 hr.), cool in a desiccator, and weigh. Correct the weight of the residue for the weight of alkali added, and so obtain the total solids. The method gives results that are reproducible to within 0·2 g. per litre, and it minimises losses of sulphur dioxide and organic acids on drying.

Total sulphur and cations—Transfer 10 ml. of sample (or 1 to 2 g. of dried sulphite liquor) into a Kjeldahl flask and rinse the neck of the flask with 10 to 15 ml. of water; add 10 to 15 ml. of concentrated nitric acid and 5 ml. of perchloric acid. It is important that sufficient nitric acid should be present to prevent an explosion. A sudden darkening of the solution indicates insufficient nitric acid. Place the flask on a steam-bath until red-brown fumes are no longer apparent, heat gently over a burner until the solution is colourless and dense white fumes appear, add 5 ml. of concentrated hydrochloric acid to the cool solution, and again heat until white fumes appear. Allow to cool, add 60 ml. of water, and heat to dissolve the salts present. Filter off and determine any silica present in the usual way, precipitate the iron and aluminium present in the filtrate as hydroxides with aqueous ammonia solution, wash the precipitate with hot 1 per cent. ammonium chloride solution, and finally dilute the filtrate to exactly 250 ml. Pipette out 100 ml. of the filtrate, make just acid to methyl orange with dilute hydrochloric acid, and precipitate the sulphate present with barium chloride. The remaining 150 ml. of the filtrate are used for the determination of calcium (as oxalate) and magnesium (by the bromometric 8-hydroxyquinoline method). The uranyl acetate method is used for the determination of sodium in the filtrate from the silica determination. The method gives results at least as precise as those obtained by the Carius method; and losses of sulphur dioxide from the sample are minimised. No hazard from the perchloric acid was experienced with sulphite waste

liquors, but precautions should be taken when applying the method to other types of samples.

J. GRANT

Analysis of Primary Cellulosic Materials used in Paper-making. A. Roudier (*Chimie Analyt.*, 1948, **30**, 244–249)—Notes are given on the effects of variations in the state of subdivision of the sample and in the working details of sampling and of determinations of the moisture content, ash, water- and solvent-soluble constituents, and cellulose content of pulping woods, with special reference to the French standard methods. The moisture content is determined by pre-drying the sample at 40° to 50° C. overnight and then drying at 100° C. for 5 hr.; this gives higher results than immediate drying at 100° C. J. GRANT

Analysis of the Primary Cellulosic Materials used in Paper-making. A. Roudier (*Chimie Analyt.*, 1948, **30**, 276–280)—Of the known methods for the determination of secondary polysaccharides ("hemi-celluloses"), that of Kullgren and Tyden (*Ing. Vetensk. Acad. Handl.*, Stockholm, **1929**, Vol. **94**), in which the furfural is oxidised to pyromucic acid by 0·05 *N* bromide - bromate (the excess of which is determined by titrating the iodine liberated from potassium iodide with 0·05 *N* sodium thiosulphate), gives good results. The acidity during the bromate titration should be 0·2 *N*, and the time of oxidation must be exactly 5 min.; the ammonium molybdate catalyst recommended by some workers is useless, or even harmful. The method of Unger and Jäger (*Ber.*, 1903, **36**, 1222), in which barbituric acid is used to precipitate the furfural, gives good results, but is inconvenient because the reagent must be recrystallised from water, its 1 per cent. solution in 12 per cent. hydrochloric acid is unstable, and the precipitate is difficult to filter. The only drawback of the Simon method (*Biochem. Z.*, 1932, **247**, 171), in which the furfural is precipitated by 2 : 4-dinitrophenylhydrazine, is that it is a gravimetric method. The colorimetric aniline acetate method (Duffau, *Bull. Soc. Chim. biol.*, **1946**, **28**, 873) is very sensitive for small quantities, but its accuracy (±5 per cent.) is less than that of the three other methods.

J. GRANT

Inorganic

New Method for the Determination of Water. M. Pesez (*Bull. Soc. Chim.*, 1948, 1108–1109M)—Lead tetra-acetate is decomposed by water, with the formation of lead dioxide, thus—

$(CH_3COO)_4Pb + 2H_2O \rightarrow PbO_2 + 4CH_3COOH$

Iodimetric determination of the lead dioxide then affords a measure of the quantity of water originally present. The method is suitable for the examination of solvents.

Lead tetra-acetate reagent—Shake 20 g. of minium with 80 ml. of acetic acid (m.p. 16° to 16·6° C.) for 15 min. at 40° to 50° C., and then heat at 70° to 80° C. until dissolution is complete. Cool quickly, and filter off the crystallised lead tetra-acetate, wash it with 50 ml. of acetic acid and then with 100 ml. of light petroleum, without allowing it to become dry. Dry *in vacuo* at 40° C. and store out of contact with air and moisture. Dissolve 3 g. of the tetra-acetate in 100 ml. of dry benzene in a stoppered flask. Some lead dioxide is formed through the hydrolytic action of residual traces of water in the crystals. This is removed by sedimentation or by centrifuging.

Aceto-iodide reagent—To 50 ml. of acetic acid add, slowly with cooling, 50 ml. of sodium hydroxide solution ($d = 1·4$) and then 7·5 g. of potassium iodide dissolved in 50 ml. of water. Store in the dark.

Detection of water—To 5 ml. of the tetra-acetate reagent add 1 to 2 ml. of the liquid for test. If water is present a yellow-brown colour and then a brown precipitate of lead dioxide, are formed. The sensitivity is 1 in 200,000 when testing non-hydroxylic solvents. With methyl and ethyl alcohols the sensitivity is of the same order, but the lead dioxide does not precipitate. The colour generated can be used for the estimation of traces of water in these alcohols by comparison with standards.

Determination of water—Place 5 ml. of the liquid for test, or 5 ml. of a suitable dilution in benzene, in a stoppered centrifuge tube. Add 10 ml. of the tetra-acetate, allow to stand for 30 min. in the dark, and then centrifuge. Confirm the presence of an excess of lead tetra-acetate in the supernatant liquid by adding it to 5 ml. of acetone containing 1 per cent. of water. Suspend the centrifuged lead dioxide in 5 ml. of benzene, centrifuge, and decant. Suspend the dioxide in 1 ml. of acetone, dissolve in 20 ml. of aceto-iodide reagent, and titrate with 0·02 *N* sodium thiosulphate. 1 ml. of 0·02 *N* sodium thiosulphate is equivalent to 0·00036 g. of water.

The operations must be carried out rapidly with special care for the exclusion of moisture.

W. C. JOHNSON

Colour Reaction of the Alkaline Earths. A. Okáč and J. Pech (*Coll. Czech. Chem. Comm.*, 1948, **13**, 400–406)—In alkaline solution the alkaline earths give an intense violet colour, or at higher concentrations a blue precipitate, with pyrogallol carboxylic acid, which can be prepared by the method of Thiele and Jaeger (*Ber.*, 1901, **34**, 2842) or Konstanecki (*Ber.*, 1885, **18**, 3205).

The neutral test solution is made alkaline with sodium hydroxide and filtered if a precipitate forms, and a freshly-prepared, saturated, aqueous solution of the reagent is added.

The reaction is inhibited by strong reducing agents capable of energetic action in alkaline media (*e.g.*, stannites), and by anions such as phosphate, fluoride, oxalate, and carbonate which reduce the cation concentration in the solution. The solubilities of the alkaline-earth sulphates are such that addition of sulphate lowers the concentration of barium and strontium below the sensitivity of the reaction for these cations, and calcium may be detected in a mixture of the three by acidifying the test solution with sulphuric acid, boiling, rendering the solution alkaline, and adding an

aqueous solution of the reagent. Filtration of the acid solution is advisable as the colour is adsorbed on the precipitate.

In general, the hydroxides of other metals should be precipitated and filtered off; the use of tartrate or cyanide to limit precipitation renders the colour produced by the alkaline earths unstable. The permanence of the colour depends on pH, reagent concentration, and atmospheric oxidation of the solution. The use of ammonia instead of sodium hydroxide gives a finer colour, but the reaction is less sensitive and the colour less permanent.

Procedure—On a micro scale, treat 0·1 ml. of solution in a micro test tube with 1 drop of 2 *N* sodium hydroxide and 2 drops of a 1 per cent. ether solution of the reagent. Remove any precipitate produced by the alkali by centrifuging before adding the reagent. In this volume the reaction is sensitive to 1 part of barium in 10,000, 1 part of strontium in 20,000, and 1 part of calcium in 200,000. The test is not suitable for use on a drop-reaction plate, or on drop-reaction paper, as the large surface exposed leads to immediate oxidation of the alkaline reagent to a dark brown solution. M. E. DALZIEL

Polarographic Copper, Zinc, and Manganese Determinations in Aluminium and Zinc Alloys. M. Spálenka (*Z. anal. Chem.*, 1947, **128**, 42–51)—*Procedure for the determination of copper in aluminium or zinc alloys and of zinc in aluminium alloys containing little copper*—Warm 0·3 g. of alloy with 10 ml. of 5·0 *N* hydrochloric acid and dissolve any residue by adding 1 drop of concentrated nitric acid. Dilute to approximately 50 ml. with water and add 25 ml. of 10 *N* aqueous ammonia. Cool to room temperature, transfer to a 100-ml. volumetric flask and, after adding 1 ml. of saturated sodium sulphite solution and 1 ml. of gelatin solution (0·5 g. of gelatin and 3 ml. of concentrated hydrochloric acid in 100 ml.), dilute to 100 ml. with water. Record a polarogram from 0 to −0·6 v. for copper determinations, or from −0·8 to −1·4 v. for zinc determinations.

This procedure can be used for alloys containing between 0·03 and 10 per cent. of copper or between 0·1 and 15 per cent. of zinc.

Procedure for the determination of zinc in aluminium alloys that are rich in copper—Dissolve 0·5 g. of alloy, containing between 0·007 and 4·0 per cent. of zinc, in 10 ml. of 3·5 *N* sodium hydroxide, dilute with 10 ml. of water, cool, and add 15 ml. of the ammonium chloride solution (4·5 g. of ammonium chloride and 350 ml. of concentrated aqueous ammonia solution in 1 litre), 1 ml. of saturated sodium sulphate solution, and 2 ml. of gelatin solution. Dilute to 500 ml., and examine a portion of the solution polarographically between −0·6 and −1·6 v.

Procedure for determining manganese in aluminium alloys—Warm 0·5 g. of alloy with 8 ml. of 5·0 *N* hydrochloric acid until all the aluminium has dissolved. Heat to boiling and then add sufficient 30 per cent. hydrogen peroxide (5 to 20 drops) to dissolve the copper. Cool slightly and add 2 ml. of saturated sodium sulphite solution and 3 ml. of Metol solution (0·1 g. of Metol, 2 ml. of a saturated solution of sodium sulphite, and 5 ml. of concentrated hydrochloric acid in 100 ml.), stirring well after each addition. Add 15 ml. of tartrate solution (500 g. of Rochelle salt and 10 ml. of a saturated solution of sodium sulphite in 1 litre) and 10 ml. of 2·5 *M* potassium cyanide solution (164 g. of potassium cyanide, 200 g. of sodium hydroxide, and 10 ml. of a saturated solution of sodium sulphate in 1 litre), stir, and cool to room temperature. Add 1 ml. of gelatin solution, dilute to 50 ml. with water, and examine the solution polarographically from 0 to −1·2 v.

Procedure for determining manganese in zinc alloys—Follow the procedure for determining manganese in aluminium alloys as far as the addition of the Metol solution. Then add 10 ml. of aqueous ammonia solution containing sodium sulphite (500 ml. of concentrated aqueous ammonia solution and 20 ml. of a saturated solution of sodium sulphite in 1 litre), stir and, after cooling to room temperature, add 15 ml. of 5·0 *M* potassium cyanide solution (326 g. of potassium cyanide and 20 g. of sodium hydroxide in 1 litre), 5 ml. of 10 *N* sodium hydroxide solution containing 5 per cent. by volume of a saturated solution of sodium sulphite, and 1 ml. of gelatin solution. Dilute to 50 ml. with water and examine a portion of the solution polarographically between 0 and −1·2 v.

The last two procedures can be used for alloys containing between 0·04 and 4·0 per cent. of manganese.

The copper, manganese, or zinc concentrations are calculated by adding a known amount of a standard alloy to the sample under examination, and comparing the height of the step given by the sample alone with that of the step given by the sample plus standard alloy. J. G. WALLER

Masking of Molybdenum, Tungsten, and Vanadium Reactions by Fluoride. F. Feigl (*Analyt. Chim. Acta*, 1948, **2**, 397–401)—The reactions of molybdate with silver nitrate, potassium ferrocyanide, potassium thiocyanate under reducing conditions, hydrogen peroxide, 8-hydroxyquinoline, rhodamine B, alkali xanthogenate, or benzoinoxime do not occur in presence of sufficient amounts of fluoride. Similarly, tungstates give no reaction with mineral acids, silver nitrate, stannous chloride, zinc and hydrochloric acid, benzidine, diphenyline, cinchonine, 8-hydroxyquinoline, or rhodamine B if sufficient fluoride is present. Fluoride also masks the reaction of vanadate with zinc and hydrochloric acid, silver nitrate, or hydrogen peroxide, but does not affect the reaction with cupferron; potassium ferrocyanide gives a yellow precipitate, benzidine a violet precipitate, and 8-hydroxyquinoline a blue-green colour in the presence of fluoride, as against a green precipitate, a green precipitate, and a brown precipitate, respectively, in its absence.

The reason for these effects lies in the formation of complex "fluorised" molybdic, tungstic, and vanadic acids; this depends on equilibrium reactions. Treatment with boric acid has a "demasking effect" by removing fluoride as hydrofluoboric acid.

These effects can be demonstrated by treating

a solution of molybdate in acetic acid with an excess of silver nitrate and dissolving the precipitate by adding potassium hydrogen fluoride. Treat a third of the solution with saturated boric acid solution, and the precipitate reappears; add 8-hydroxyquinoline acetate to another third, and a yellow oxine precipitate appears; add potassium hydrogen fluoride and 8-hydroxyquinoline and no precipitate appears, proving that the masking effect depends on the quantity of the masking ion.

M. E. DALZIEL

Colorimetric Determination of Traces of Gold. E. B. Sandell (*Anal. Chem.*, **1948**, **20**, 253–256)—Quantities of gold from 0·1 to 10 μg are isolated by precipitation with stannous chloride, with tellurium as collector, and estimated colorimetrically or photometrically with *p*-diethylaminobenzylidenerhodanine as reagent. A colloidal solution of a red-violet compound is formed by adding an alcoholic solution of the reagent to a weakly acid, auric gold solution. The sensitivity of the reaction decreases as the mineral acid concentration is increased, but the reproducibility of results is better with 0·12 *M* hydrochloric acid than with a 0·075 *M* solution.

METHOD — *Apparatus* — Several flat-bottomed, glass-stoppered tubes, about 1·2 × 8 cm. and graduated at 5 ml. or 4·5 ml.

For the filtration, use a small, wide-mouthed bell-jar resting on a piece of ground-glass and fitted with a two-hole rubber stopper carrying a small funnel. Use a rubber ring to fit the filter-crucible into the funnel.

Reagents — *p-Diethylaminobenzylidenerhodanine solution*, containing 0·05 g. in 100 ml. of absolute ethyl alcohol. *Stannous chloride solution*—Dissolve 20 g. of the dihydrate in 100 ml. of 2 *N* hydrochloric acid. *Tellurium tetrachloride solution*—Add 1 to 2 ml. of nitric acid to 100 mg. of precipitated tellurium and evaporate to dryness. Dissolve the residue in 10 ml. of concentrated hydrochloric acid and dilute to 100 ml. *Standard gold solution*—Prepare a solution containing 0·001 per cent. of gold as chloroauric acid in 0·10 *M* hydrochloric acid.

Procedure—Prepare a solution of the sample containing 0·1 to 10 μg. of gold in about 50 ml., and not containing any strong oxidising agents. Make the solution 2·5 *N* with respect to hydrochloric acid and add 0·2 ml. of the tellurium solution. Add 5 ml. or more of the stannous chloride solution to produce a brown colloidal precipitate of tellurium and add an excess of 3 to 5 ml. Heat to the boiling-point and keep at this temperature for 30 min. to coagulate the precipitate. Collect the precipitate in a 7-ml. porous, porcelain filter-crucible and wash the beaker and filter with five 5-ml. portions of diluted hydrochloric acid (1 + 4). Add 1 ml. of *aqua regia* to the beaker used for the precipitation, heat the contents almost to boiling-point, and pour into the crucible. Bring the acid into contact with the tellurium on the walls of the crucible and when all or most of the precipitate has dissolved, draw the solution through the crucible into a 20-ml. Pyrex beaker. Repeat the operation with a further 1 ml. of *aqua regia*. Wash the beaker and crucible with two small portions of water. Evaporate the solution to dryness, avoiding prolonged heating of the residue. Add 0·01 ml. of *aqua regia* to the cold residue and with the aid of a stirring rod moisten the walls of the beaker with the acid. Allow the acid to evaporate at room temperature.

Prepare standards containing 0, 0·2, and 0·4 μg. of gold by transferring quantities of standard gold solution to the glass-stoppered tubes, adding 0·3 ml. of 2·0 *M* hydrochloric acid, and diluting with re-distilled water to nearly 4 ml. Add 0·25 ml. of 1 per cent. sodium fluoride solution and mix.

Add 0·3 ml. of 2·0 *M* hydrochloric acid to the dry tellurium residue, moistening all the residue with the acid. Add 1 ml. of water and stir. If the solution is clear, transfer to a tube and rinse the beaker with re-distilled water to bring the volume in the tube to 3·5 ml. If the solution is turbid, filter through a small, porcelain filter-crucible into a tube and wash with small portions of water to bring the total volume to 3·5 ml.

Add 0·25 ml. of 1 per cent. sodium fluoride solution to the sample and standard tubes, and mix. Add 0·3 ml. of the rhodanine reagent to each tube and mix by inverting three times. Dilute to the mark and mix by inverting three times. After a few minutes, compare the colour of the sample with the standards and if it is less strongly coloured than the 0·4-μg. standard, find the gold content by visual comparison. Otherwise, transfer the sample solution to a dry absorption cell and, using a green filter, measure the extinction exactly 10 min., or other fixed time, after the addition of the rhodanine reagent. To obtain the standard extinction curve take 0, 0·5, 2·5, 5, 7·5, and 10 μg. of gold, add 2·0 *M* hydrochloric acid to make the total volume 0·3 ml., treat with sodium fluoride solution and rhodanine reagent as described above, and dilute to volume. A graph of extinction against concentration should be a straight line. Extinction measurements should be reproducible to within 0·001.

Silver, iron, copper, lead, and arsenic do not interfere, and small amounts of mercury, thallium, platinum, molybdenum, titanium, tungsten, uranium, vanadium, zirconium, bismuth, and germanium are without effect. Palladium reacts with the rhodanine reagent. Up to 3 μg. of palladium in the final volume of 5 ml. can be made harmless by adding 0·05 ml. of a 1 per cent. alcoholic solution of dimethylglyoxime to the acid sample solution before the addition of the rhodanine reagent. For the estimation of gold in biological material the procedure must be modified to ensure the removal of carbon.

Procedure for biological material—Ash the sample in a porcelain dish at low red heat. Transfer 1 to 2 g. of the ash to a small porcelain dish, add a few millilitres of water, followed by 2 ml. of nitric acid added in portions. Evaporate to dryness and heat gradually to dull red heat. Keep at this temperature for about 15 min., or until brown fumes cease to be evolved. Add 5 ml. of diluted hydrochloric acid (1 + 1) and evaporate to dryness. Add another 5-ml. portion of the acid and repeat the evaporation. Take up the residue in a mixture

of 5 ml. of concentrated hydrochloric acid, 5 ml. of water, and 2 ml. of saturated bromine water. Heat nearly to the boiling-point, with stirring, and filter through a sintered-glass crucible. Wash with 10 ml. of diluted hydrochloric acid (1 + 1) and a few portions of water. Transfer the filtrate and washings to a 100-ml. beaker, dilute to 50 ml., and add 0·2 ml. of tellurium solution and 5 ml., or more, if required, of stannous chloride solution. Continue as in the above procedure.

B. ATKINSON

Reviews

QUALITATIVE ANALYSIS BY SPOT TESTS: INORGANIC AND ORGANIC APPLICATIONS: FRITZ FEIGL. Third English Edition, translated by RALPH E. OESPER. Pp. xvi + 574. New York and Amsterdam: Elsevier Publishing Company, Inc. London Distributors: Cleaver-Hume Press Ltd. 1947. Price 43s. net.

Everyone who has any acquaintance with modern analytical methods is familiar with the name of Dr. Fritz Feigl, and with the place that he has made for himself in the inception and development of the technique and methods of analysis by the use of spot tests. Most will also be familiar with one or other of the earlier editions of this work, translated by Dr. Matthews, which appeared in 1937 and 1939.

Since the appearance of the third German edition, on which the second English edition was based, a vast mass of additional material on this branch of microchemistry has appeared in the literature, and for some time it was clear to the author that a new edition, incorporating a critical selection of the fresh material, was necessary. Owing to difficulties of communication during the war, it was necessary to choose a translator in the Western Hemisphere. Those chemists familiar with Dr. Feigl's research publications are also well acquainted with the name of Dr. Oesper in this, among other capacities.

There is much new material of value in this edition. There are detailed descriptions, not included in earlier editions, of a wide range of techniques used in spot analysis. Many new spot reactions, both inorganic and organic, are described with full working directions, whilst the text carried over from previous editions has been completely revised. The bibliography has been extended to include many additional references, and, indeed, the author, to quote his own intentions, "has tried to assemble and present the entire literature on spot test analysis in such a form that the reader will be able to secure here a rapid survey of the available spot tests and their application." Some idea of the comprehensiveness of the book can be given by noting that there is an eight-page author index in addition to the excellent 56-page subject index.

The reviewer has nothing but admiration for the contents of the book, and can only add that he considers it to be an essential part of the library of every up-to-date analytical chemist. The production—binding, printing, illustration—also is excellent, subject only to the criticism that the paper is hardly sufficiently opaque, so that the ghost of the printing on the reverse side can be seen. This is a trifle tiresome: it may, however, be the result of an attempt to reduce somewhat the bulk of a volume covering so comprehensively all practical aspects of a fascinating and invaluable branch of microchemistry. CECIL L. WILSON

THE PLANT ALKALOIDS. By T. A. HENRY. Fourth Edition. Pp. xxiii + 804. London: J. and A. Churchill, Ltd. 1949. Price 63s. net.

There is a small and select number of scientific books, a new edition of which one opens with a sense of pleasurable anticipation. Henry's "Plant Alkaloids" is one of this class. It stands unchallenged as the classic work on alkaloids, and one knows in advance that the information given will be full, accurate, up-to-date and lucidly expressed. The new edition does not disappoint.

Very much has been re-written and the size has been expanded from 689 to 804 pages. A rough calculation shows that some 2,000 different alkaloids are mentioned. The labour of keeping such a book up to date must be great indeed, and Dr. Henry is to be congratulated on the care and accuracy with which it has been done. The method of arrangement and classification of the earlier edition has been maintained, though the author finds it increasingly difficult to adhere to the system of classification based on nuclear structure for many of the more complex alkaloids. As he characteristically writes, "Nature does not produce alkaloids to meet the needs of either botanical or chemical systematists."

The structural formulae, which occur in great numbers, are admirably drawn and reproduced,—a protracted search has failed to discover a single tervalent carbon atom.

From the medicinal standpoint, the vast amount of work carried out on alkaloids since the last edition of this book was published is disappointing. No new alkaloid has been found possessing outstanding pharmacological properties. The British Pharmacopoeia 1948 contains sixteen of the alkaloids described in this book, and all of these have been known for many years. Ergometrine, the most recent, was discovered in 1935. Tubocurarine, not in the B.P., has recently found a valuable use in medicine but already seems likely to be replaced by synthetic compounds. One wonders for how long alkaloids will retain a place in medicine. Cocaine is falling out of use, quinine faces powerful competition from synthetic rivals and even morphine is threatened. But old remedies die hard and many more editions of this book will surely be required before the last alkaloid is omitted from the B.P.

Interesting developments have occurred in the elucidation of the structure of alkaloids. The discovery that certain alkaloids of *Aconitum*, *Delphinium*, *Veratrum* and *Solanum* species contain a tetracyclic system

identical with, or closely related to, that of the steroids and that the alkaloid solanine is a glycoside, is of great interest in relation to the biogenesis of alkaloids in the plant. In fact, great interest is now being shown in the problem of biogenesis, particularly in devising methods of synthesis that might occur in the plant itself.

The book is, of course, indispensable to the drug analyst. Although no attempt is made to describe methods of analysis except in general terms, a great deal of information on methods of detection and identification is given and the comprehensive lists of references guide the reader to the original sources.

NORMAN EVERS

MICROCHEMISTRY GROUP

A JOINT Meeting of the Group with the East Midlands Section of the Royal Institute of Chemistry will be held in Nottingham on Thursday, September 22nd, 1949. In the afternoon a limited number of members will visit the laboratories of Boots Pure Drug Company at Beeston and Nottingham.

At 6.30 p.m. a meeting will be held at Nottingham Technical College, at which the following papers on Microbalances will be read and discussed:

"Microchemical Balance Design," by George F. Hodsman, B.Sc., Ph.D., A.Inst.P.
"Maintenance and Precision of Microbalances," by David W. Wilson, M.Sc., F.R.I.C.
"The Ultra Microbalance," by Cecil L. Wilson, M.Sc., Ph.D., F.R.I.C.

In an adjoining room an Exhibition of Microbalances will be on view from 5 p.m. to 9 p.m.

PHYSICAL METHODS GROUP

A MEETING of the Group, organised by its Polarographic Discussion Panel, will be held in Sheffield, on Friday, October 7th, 1949.

At 2·30 p.m. there will be a visit to the Bragg Laboratory, Naval Ordnance Inspection Department, followed by tea in the Laboratory.

At 6.30 p.m., a Joint Meeting with the Sheffield Section of the Royal Institute of Chemistry and the Sheffield University Chemical Society, on "Polarographic Analysis," will be held in the Chemical Lecture Theatre of Sheffield University. The following papers will be read:

"The Use of Polarographic Methods for the Analysis of Fine Chemicals," by G. H. Osborn, A.R.I.C.
"Applications of Mercury Drop Control to Differential and Derivative Polarography," by L. Airey, B.Sc., A.R.I.C., and A. A. Smales, B.Sc., A.R.I.C.
"Diffusion Current Measurement with the Tinsley Polarograph," by W. Furness, B.Sc., F.R.I.C.

The following further meetings of the Physical Methods Group have been arranged:

November 29th, 1949: At the Imperial College, London, S.W.7, the Annual General Meeting of the Group, followed by an address on "The Mass Spectrometer, a Survey of its Applications in Analysis," by Dr. J. G. A. Griffiths.

January 3rd, 1950: At the Imperial College, London, S.W.7, a discussion in Spectroscopic Analysis.

February 1st, 1950: In London, a discussion on Modern Methods of Moisture Determination.

CROWN AGENTS FOR THE COLONIES

SCIENTIFIC OFFICER (ANALYTICAL CHEMIST) required by the East Africa High Commission for the East African Industrial Research Board for one tour of 4 years with prospects of permanency. Commencing salary will be between £760 and £935 a year, according to qualifications and experience, in a scale rising to £1,320 a year. Free passages. Candidates, preferably under 45, must possess a University Degree with Honours in Chemistry or an equivalent qualification. They should have had good experience in chemical analysis, particularly of clays, rocks and mineral ores. Apply at once by letter, stating age, whether married or single, and full particulars of qualifications and experience, and mentioning this paper to the Crown Agents for the Colonies, 4, Millbank, London, S.W.1, quoting M/N/22686/3E on both letter and envelope.

The Crown Agents cannot undertake to acknowledge all applications and will communicate only with applicants selected for further consideration.

MINISTRY OF SUPPLY invites applications from CHEMISTS for unestablished posts in Experimental Officer Class in Research and Development Establishments, mainly in South England.

Candidates must possess Higher National Certificate or Higher School Certificate or equivalent. General chemical experience, particularly in fields of physical chemistry and chemical engineering, is required. Special knowledge or interest in any of the following fields would be an advantage:

Modern analytical methods.
Thermo-chemistry and combustion.
Stability and sensitivity of explosives.
Instrumentation.
Plastics (with special reference to aircraft materials).
Chemical plant development, or
Library and information work.

Grade and starting pay assessed on age, qualifications and experience. Salary ranges:—

Senior Experimental Officer	£705–£895.
Experimental Officer	£495–£645.
Asst. Experimental Officer	£220 (at age 18)–£460.

Rates for women somewhat lower above age 21.

Write, quoting F. 563/49A, to Technical and Scientific Register (K), York House, Kingsway, London, W.C.2, for application forms, which must be returned by 17th September, 1949.

MINISTRY OF SUPPLY (CHEMICAL INSPECTORATE) invites applications from CHEMISTS for appointment in following grades for analytical work offering scope and opportunity for advancement and extended scientific experience:—

Experimental Officer, £495–£645 (men), £405–£520 (women).
Assistant Experimental Officer, £220 (age 18)–£460 (men), £220–£380 (women).

London rates somewhat higher.

Candidates must possess at least Higher School Certificate with chemistry as principal subject or equivalent qualification; experience in general analytical work desirable. For the Experimental Officer grade applicants must also have experience in application of physico-chemical methods and must normally be at least 28 years of age.

Posts are unestablished and are mainly in N.W. England, with a few in S.E. England. Starting pay will be assessed within the above ranges.

Write, quoting F.542/49A, to Technical and Scientific Register (K), York House, Kingsway, London, W.C.2, for application forms, which must be returned by 10th September, 1949.

REQUIRED an Analytical Chemist of A.R.I.C. standard to work under Chief Analyst mainly on development of new methods and techniques of inorganic analysis. Applicants must have industrial experiences of analytical work and a sound theoretical background. Applicants to Secretary, Magnesium Elektron, Ltd., Clifton Junction, Manchester.

CHEMIST (A.R.I.C. or equivalent) required to take charge of analytical and research work in one of the S.C.W.S. Cereal Laboratories under the direction of the Chief Chemist. The work is related to wheat, flour and feeding stuffs. Experience in some branch of Food Technology will be an advantage, but a sound scientific training and ability to organise work will be of more importance than specialised knowledge. Applications, stating qualifications, experience and salary required, to be addressed to The Secretary, S.C.W.S., Ltd., 95, Morrison Street, Glasgow, C.5. Envelopes to be endorsed "Chemist."

METROPOLITAN BOROUGH OF STEPNEY

APPOINTMENT OF ASSISTANT ANALYST, PUBLIC HEALTH DEPARTMENT

APPLICATIONS are invited for appointment to the position of Assistant Analyst at a salary of £520–£570 per annum, plus appropriate London Weighting Allowance.

Candidates must possess an appropriate University Degree or the Associateship of the Royal Institute of Chemistry, and should have had experience in the analysis of food and drugs.

The appointment will be subject to the approval of the Minister of Food, the National Scheme of Conditions of Service as adopted by the Council, and to the Council's bye-laws and Superannuation Acts.

Applications, on forms which are obtainable from the undersigned, should be delivered to these offices by the first post on the 12th September, 1949.

J. E. ARNOLD JAMES,
Town Clerk.

5th August, 1949.
Municipal Offices,
London Fruit Exchange,
Duval Street, E.1.

ANALYST—qualified assistant required in Analytical Department, Glaxo Laboratories, Barnard Castle (Co. Durham). Chiefly concerned with antibiotics, including chemical analysis, biological assay and sterility testing. Applications are invited from suitably qualified persons with experience in an industrial (preferably pharmaceutical) controlled laboratory, or with Public Analyst. Experience of antibiotics, biological methods of assay, and of bacteriology is desirable but not essential. Salary according to qualifications and experience. Staff pension scheme. Write giving full details to—Personnel Department, Glaxo Laboratories, Ltd., Greenford, Middlesex.

CHEMIST, required by firm with modern works recently established in South Wales, to supervise metallurgical laboratory. Previous experience in the analysis of aluminium alloys is essential. Reply stating age, qualifications and salary required to Box No. 3715 THE ANALYST 47 Gresham Street, London E.C.2.

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