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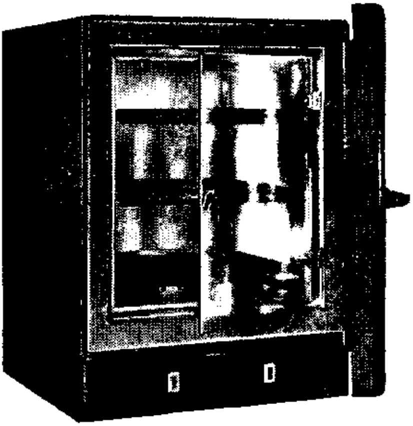

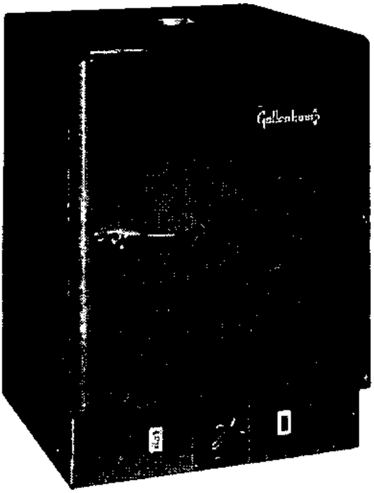
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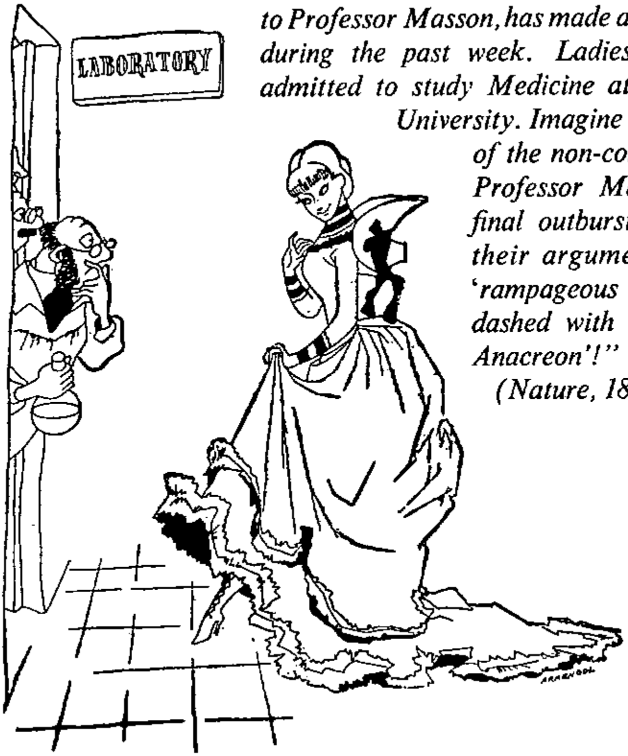
LABORATORY

JOURNAL OF THE
NEW ZEALAND INSTITUTE OF CHEMISTRY

VOL. 22. AUGUST, 1958. No. 4.

EDITORIAL

(Contributed by N. T. CLARE, on behalf of the Conference Committee.)

When Conference delegates assemble at the Hamilton Girls' High School on 27th August, they will be on ground with an historical association with the Institutes, for it was here that the first Combined Conference was held in 1935. The N.Z.I.C. was then four years old with four branches and a membership of little over 100. Hamilton was not yet a city, its population being only 15,000.

When the Conference next met in Hamilton in 1951, again at this School, the Institute had expanded to six branches, with 400 members. In Hamilton (grown to City status, but at the time possessed by Mooloonacy following very recent installation of the Ranfurly Shield), there were sufficient chemists to justify formation of a sixth Branch and the Waikato Branch was constituted early in 1951. For the third Conference in Hamilton delegates will come from the six Branches of an Institute numbering over 500 members to a City swollen, with rather painful rapidity, to an urban area population of 43,000 and now the sixth largest in the country.

The Arms of this City (devised, incidentally, by the wife of a former Associate), depict agricultural products on a shield supported by pukekos. This heraldry symbolises the development of an originally swampy district into the present highly productive grasslands, a development brought about largely by the use of phosphatic fertilisers and the ryegrass-clover mixture. It has been said that Yorkshire Fog produced the first butter that bought the first phosphate that grew the clover that fixed the nitrogen that sustains high production grasses. Members of the Institutes have played and are playing their part in the scientific aspects of this chain reaction. Appropriately, a symposium on phosphate is one of the main sessions on this year's programme.

It is fitting also that, in a year marked by a crisis in butter marketing, the main industrial symposium should be devoted to discussion of the uses of fats.

Although most Institute members resident in Hamilton are employed at the two agricultural research stations, the area covered by the Branch includes important and increasing industrial

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enterprises. Twenty miles north of the city is the North Island coalfield, assuming a new interest with the construction of the Meremere steam electricity generator. To the south and east are the great exotic forests, where two large factories are producing pulp, kraft and newsprint. Chemical aspects of both coal and pulp industries will be discussed at the Conference.

The Waikato Branch differs from its five senior sibs in that it is not (yet) associated with a University College. Its members are conscious of this lack, and have ensured that in the Conference programme the more refined odours of academic chemistry will sweeten the ordure of agriculture and the olid dusts of industry.

Not all of the proceedings will be in such a serious vein. It is noted that the Conference Chairman is chemist to the Waikato Brewery, so that the local slogan "Wherever you go, take Waikato." may be disregarded on this occasion. But any Conference Committee can only set the stage — delegates have their parts to play in ensuring enlightenment and enjoyment for all who attend.

OFFICIAL NOTICE

A General Meeting of the New Zealand Institute of Chemistry (Inc.) will be held at Hamilton Girls' High School on Wednesday, 27th August, 1958, at 4 p.m.

AGENDA

1. Apologies.
2. Confirmation of Minutes of General Meeting held in Christchurch on 27th August, 1957.

   Business arising out of the minutes will be dealt with under the appropriate heading below.
3. Presidential Remarks.,
4. Institute Prizes.
5. Sub-Committees of Council:—
   1. Membership.
   2. Journal.
   3. Examinations.
   4. Employment.
   5. Conferences.
   6. Salaries.
6. Finance.
7. Rules and Regulations.
8. Technician Training.
9. General.

W. E. HARVEY,
General Secretary.

ABSTRACTS OF PAPERS — Conference 1958

RECENT STUDIES ON THE CONSTITUTION OF MOLTEN SALTS

By H. BLOOM,

Chemistry Department, University of Auckland.

Molten salts are high temperature liquids which have physical properties similar in magnitude to those of room temperature liquids. For example their viscosity, surface tension, refractive index and thermal conductivity, are of the same order as those of water. Their extremely high electrical conductance however, establishes that they consist mainly of ions. Such ions will exert much larger electrical interactions on one another than in dilute electrolyte solutions, owing to the much closer proximity of the ions in molten salts.

Earlier work on electrical conductance, viscosity, transport number, vapour pressure, etc., has led to much useful information on interionic forces in molten salts. In simple binary mixtures there is apparently a uniform gradation of interionic forces from one pure component to the other, so that when any physical property of the mixture is plotted against molar composition, the resultant curve obtained deviates by less than ten per cent. from a straight line. Such systems are said to be practically ideal.

In another group of binary molten salt systems, the physical properties of the mixtures cannot be predicted even approximately, by a linear relation between property and molar composition. Deviations of up to ninety-five per cent. from linearity occur in practice. Such non-ideal systems are thought to contain complex ions existing in equilibrium with the simple ions of the components. Recently we have developed a new model of molten salt mixtures which enables a calculation of both the stoichiometric composition and the stability constants of complex ions.

Vapour pressures and thermal conductivities of molten salts have also been investigated. The experimental methods used and application of the results to the study of constitution of molten salts, will be discussed.

THE LIFETIME OF OPTICALLY EXCITED MOLECULES

By MISS S. PAGE.

Chemistry Department, University of Canterbury Christchurch.

Molecules absorb light energy, and after a time interval of the order of 10^{-8} sec., give it out again as fluorescence, unless it has been already lost by internal degradation or by reaction with other molecules. The average time between absorption and emission is known as the lifetime of the fluorescent molecule. This quantity can be calculated from the U.V. absorption spectrum, or measured by a method to be described.

When certain other compounds are present, the intensity of fluorescence is reduced. Such compounds are known as quenchers; they act by depriving the excited molecule of its energy before it can be emitted as fluorescence. It can be shown that the intensity of fluorescence depends on the concentration of the quencher in the following manner:—

$$f_0/f = 1 + k[Q]$$

where f_0 is the intensity of fluorescence without quencher, f is the intensity of fluorescence with quencher concentration [Q]. k, the experimental quenching constant, is the product of the specific rate constant, k_e for the quenching reaction, and the lifetime. A knowledge of the life time is therefore necessary before k_e can be determined and before the effects of the solvent and ionic strength on the quenching can be assessed.

In the method used to measure the lifetime, a beam of U.V. light is made to oscillate in intensity at 5 megacycles/sec. by passing it through a standing wave set up by a vibrating quartz crystal in a tank of water. This light beam illuminates two cells, one containing a scatterer and the other a fluorescer. The fluorescent light lags behind the scattered light by a time equal to the lifetime of the molecules. To find this time the light beams are converted into electrical signals by two photo-cells, and the signal from the scatterer is delayed by a calibrated delay circuit until it exactly balances the signal from the fluorescent cell. The amount of this delay is known, and so the lifetime of the fluorescent molecule is found.

ANALYTICAL APPLICATIONS OF ATOMIC ABSORPTION SPECTRA.

By J. E. ALLAN,
Rukuhia Soil Research Station, Hamilton.

Following the suggestions by Walsh and his co-workers (see references below), the use of atomic absorption spectra for analytical purposes has been studied at Rukuhia for the last two years. Methods have been developed for Mg, Zn, Cu, Fe and Mn, and have been successfully applied to the determin of these elements in agricultural materials. In general, the solution to be analysed is sprayed into a flame, and by using a lamp which emits the line spectrum of the element to be determin as a light source, the absorption by the unexcited atoms of the element in the flame, at the wave length of the resonance line is measured. The method of measurement and the apparatus used will be described, and the factors affecting sensitivity, reproduceability and accuracy will be discussed.

References:

Walsh, A., (1955), Spectrochimica Acta 7, 108.
Russel, B.J., Shelton, J.P., and Walsh, A., (1957), Spectrochimica Acta, 8, 317.

PESTICIDE RESIDUES IN FRUIT.

By H. M. STONE,
Dominion Laboratory, D.S.I.R., Wellington.

Organic mercurials and organic phosphorus compounds used in horticultural sprays are discussed from the angle of residues. The use of organic mercurial spray formulations for the control of fungus diseases on glass-house tomatoes and on apple crops, necessitated an investigation into the mercury content of sprayed and unsprayed fruits. Mercury sprays were found to increase the mercury content. To minimise the risk of residues becoming excessive and constituting a hazard to the consumer, it may be necessary to restrict the numbers of applications. Modifications of digestion and analysis techniques have produced a very sensitive method capable of determining 0.1 micrograms of mercury or 0.001 p.p.m. of mercury in fruit.

Organic phosphate insecticides are characterised by r acute toxicity to plant mites, aphids, young caterpillars and many other types of insects. They are very toxic to mammals due to their capacity to inhibit the action of cholinesterase in the blood, with subsequent acetyl choline poisoning. Parathion and Schradan have been used in New Zealand and residue investigations have been carried out. More recent compounds such as Malathion and Metasystox are claimed to be safer to handle, and due to rapid degradation in the plant tissue, less likely to constitute hazardous residues. Work on determination of Metasystox residues is at present being carried out.

ARSENIC CONTAMINATION OF BACON BY USE OF TREATED SAWDUST IN SMOKING.

By C. C. WATSON,
Dominion Laboratory, D.S.I.R., Wellington.

An examination of the volatility of arsenic was undertaken to determine the possible contamination of bacon during smoking caused by the use of sawdust from timber containing arsenical preservatives.

8.6% of the arsenic from the sawdust was volatilized and amounts were determined in the smoke, bacon and on the walls of the smoking chamber.

The maximum amount found in the bacon was 2.3 p.p.m. Smaller amounts penetrated the meat to a depth of 3 centimeters from the surface.

CHROMATOGRAPHY AND PHARMACOLOGICAL ACTIVITY OF FOOD COLOURS AND RELATION TO STRUCTURE

By L. WILKINSON,
Dominion Laboratory, D.S.I.R., Christchurch.

Although Rowes Colour Index (1924) describes over 1,300 colouring substances, only about 10 per cent. of these have been considered, at some time, as suitable for use in foods.

Until recently Great Britain, with 5 exceptions which were specifically prohibited, allowed the addition of any coal-tar colour to food, provided it was not injurious to health. In the United States, however, legislation was passed in 1907 which prohibited the use of coal-tar colours in food with the exception of 7 certified colours which were specifically permitted. Later the number of these certified colours was increased to 19.

Since 1945 the toxicology and carcinogenity of many synthetic colours formerly used in England, on the Continent and in America have been reassessed by modern techniques. Three colours, formerly permitted in U.S.A., were removed from the list of certified dyes about 1956 and the remainder are being carefully scrutinised. The Supplementary Report (1955) of the English Food Standards Committee, which investigated 98 coal-tar dyes, recommended 32 colours as now suitable for use in food. The Pharmacological Panel of the Committee placed only 11 of these 32 in Class A, i.e., colours, which, from the available evidence, would seem unlikely to be harmful when consumed in foods in the customary amounts.

The restriction in many countries on the number of dyes available for foods has forced manufacturers to use two or more of the permitted dyes in order to obtain a satisfactory shade of colour. The development of chromatographic techniques has provided a most useful tool for identification of dyes when several closely-related colours are present. Much information is now available on the effect of different developing solvents on the movement of dyes on paper.

A comparison of pharmacological activity with R_f values shows a marked correlation in the case of butanol developing solvents. In this paper an attempt will be made to explain this correlation on the basis of structure. As the majority of dyes permitted in foods belong to the azo-class, the discussion is confined to this structural configuration.

SOME AGRICULTURAL AND MANUFACTURING CHARACTERISTICS OF PHOSPHATE ROCKS.

By P. J. GALLAHER,
Fertiliser Manufacturers' Research Association, Auckland.

Phosphate rocks from different sources differ markedly in their phosphate availability when applied directly as fertilisers. North African rocks are relatively efficient, while those from Nauru and Ocean Islands have low nutrient value, regardless of the fineness of grinding. The composition of the apatite constituent of the phosphate rock is considered to be the reason for this difference in properties, since all the readily available rocks have a relatively high proportion of apatite bound carbonate and low elementary granule size. Agronomic studies on acid soils fertilised with uniformly ground samples of phosphate rock indicate that there is good agreement between these properties and crop response. Solubility of the rock phosphate in 2% citric acid also shows good correlation with phosphate availability.

When phosphate rock is mixed with sulphuric acid in the manufacture of superphosphate fertiliser, the initial reaction is mainly between tri-calcium phosphate and sulphuric acid to form free phosphoric acid and calcium sulphate. On the disappearance of free sulphuric acid, the phosphoric acid reacts with further tri-calcium phosphate to form monocalcium phosphate. The composition of the final product is determined by the relative proportions of rock and acid used, and by the concentration of the acid; while the speed of the reaction is dependent on particle size of rock, and on acid concentration and temperature. Work is in progress to obtain data on the reaction for the types of phosphate rock used for superphosphate manufacture in New Zealand.

DETERMINATION OF PHOSPHATE

By K. F. HOY,
Rukuhia Soil Research Station, Hamilton.

A brief review of traditional methods for determining phosphorus is given. Results by the present official method for fertilisers is compared with the Lorenz gravimetric method. Fertiliser extracts to which have been added various amounts of P_2O_5 (as KH_2PO_4) are assayed by three methods, viz, Lorenz, quinoline-citric-molybdate, and the colorimetric vanado-molybdate procedures.

THE SIGNIFICANCE OF PHOSPHORUS AS A FACTOR IN THE ACCUMULATION OF ORGANIC MATTER IN SOILS

By T. W. WALKER and A. F. R. ADAMS,
Canterbury Agricultural College, Christchurch.

The hypothesis is presented that the phosphorus content of the parent materials from which soils are derived plays a major role in determining the levels to which the soil organic matter may accumulate.

This paper presents the results of a quantitative pedogenic study, designed to test this hypothesis. This is done under the following headings:—

1. By studying the relationship between the phosphorus content of a single parent material (greywacke) and the organic matter content of soils derived from it, under widely varying conditions of leaching and weathering;
2. By similarly studying soils formed under comparatively uniform weathering and leaching conditions but from differing parent materials of varying phosphorus content.

A simple fractionation of soil phosphorus into organic and inorganic has enabled a composite idealised picture of the situation under 1 to be presented in graphical form. In a broad sense, the practical implications of the results of this work are outlined and an example given of the effect actually produced by supplying phosphate to a phosphate deficient soil.

PHOSPHORUS IN NEW ZEALAND SOILS

By W. M. H. SAUNDERS and N. WELLS,
Soil Bureau, D.S.I.R., Wellington.

A survey has been made in New Zealand of the effect of the soil processes on the amount and the nature of the phosphorus in the topsoils. The survey included an evaluation of the relative levels of available phosphorus using the phosphorus content of sweet vernal *(Anthoxanthum odoratum)* and the fractionation of the total soil phosphorus into organic phosphorus, inorganic phosphorus and phosphorus soluble in 1 N H_2SO_4.

The amount of phosphorus in a soil is first governed by the phosphorus content of the parent material. Weathering and leaching result in a decrease in the concentration of phosphorus in the topsoil. For example, the total phosphorus content of the weakly weathered brown-grey earths of Central Otago is 0.135 % P but this has fallen to 0.015% P in the strongly leached podzol soils of North Auckland.

Accompanying the fall in total phosphorus concentration the availability of the soil phosphorus also decreases. This is best exemplified by the soils from basalt and andesite but is also shown by the zonal soils on greywacke. In the latter group, however, the process of podzolisation tends to increase the availability of the small residue of inorganic phosphorus.

This study has shown the dominating influence of soil processes in determining the phosphate fertiliser requirements of our soils.

THE UPTAKE OF PHOSPHORUS BY PASTURES

By R. H. JACKMAN,
Grasslands Division, D.S.I.R., Palmerston North.

Pastures are grass-legume associations. These components compete for room, light, moisture and nutrients including phosphorus.

The immediately useable phosphorus is probably $H_2PO_4^1$ in the soil solution which commonly contains about 0.1 p.p.m. or less phosphorus (10^{-6} to 10^{-8}M). In a 3in acre there is about 0.01 lb. P in this form. A rapidly growing pasture may withdraw 0.3 — 0.9 lb. of phosphorus per acre per day. The soluble soil phosphorus is thus very dilute and equilibrium is regained relatively rapidly after withdrawal of phosphorus.

The soil/root system under a pasture can be considered as three cation exchanging colloids of differing cation exchange capacities (C.E.C.) — soil, grass and legume. Each colloid has cations in its micellar solution which are not able to diffuse freely into the intermicellar solution. This fact produces a Donnan system in which the activity of the cations from the exchange sites is much greater than that of $H_2PO_4^1$. This cation activity is a function of the C.E.C. While precipitation reactions may determine the level of $H_2PO_4^1$ activity the distribution of $H_2PO_4^1$ between the above three colloids is probably according to a Donnan system. Generalisations can be made.

(1) The greater the C.E.C. the lower will be the $H_2PO_4^1$ activity in the micellar solution.

(2) The higher the valency of the associated cation or other anions the greater the micellar $H_2PO_4^1$ activity.

(3) The greater the overall activity the greater the micellar anion activity. The greater the C.E.C., the greater the overall activity must be to achieve comparable micellar anion activity.

(4) The valence effect of cations is greater the lower the overall activity and the higher the C.E.C.

In the root/soil colloid system the prediction is that that colloid having the lowest C.E.C. will contain in its micellar solution the greatest $H_2PO_4^1$ and there is presumptive evidence that this mechanism does operate in the field.

The C.E.C.'s of pasture plant roots do differ, legumes being higher than grasses, e.g. white clover 42, ryegrass 20, browntop 14 m.eq./100gm. root tissue. Donnan distribution of $H_2PO_4^1$ predicts the eventual dominance of browntop when phosphorus becomes limiting, that organic matter, with a high C.E.C., should increase the supply of available phosphorus, that low soil pH values should be accompanied by lower phosphorus supply due to a decreased C.E.C. and that potash fertiliser should sometimes decrease and sometimes increase phosphate availability depending upon the relative C.E.C.'s of plant root and soil. These phenomena have been observed.

Experimentally it has been shown that salts, especially those of divalent cations, have increased the uptake of phosphorus by peas, that potash is preferentially taken up by grasses rather than associated clovers, as would be predicted, that if phosphate or sulphate is in short supply but plenty of nitrogen is present then browntop becomes dominant but if nitrogen, phosphate and sulphate are adequate then ryegrass is dominant. Nitrogen applied to a pure stand of subterranean clover did not reduce growth or phosphorus content but did both if ryegrass was planted with the clover.

Donnan distribution of phosphorus suggests a weakness in our grass/clover pastures. The aim is to grow grass; the means is phosphate to stimulate clover growth with the resulting high supply of fixed nitrogen to feed the grasses. But the better the grass the greater the grass competition for the phosphate. The means tend to be automatically blocked. One solution is to use fertiliser nitrogen and dispense with the clover as in Denmark. Another possibility is that plant breeders produce a clover with a root C.E.C. the same or less than that of the associated grasses.

UTILISATION OF PHOSPHORUS BY THE ANIMAL

By E. W. WRIGHT,

Animal Research Station, Wallaceville.

In discussing utilisation of phosphorus, the distinctions between availability, absorption and retention must be kept firmly in mind.

Phosphorus undergoes a cycle of excretion and reabsorption in the gastro-intestinal tract being particularly secreted in the saliva and absorbed in the abomasum and ileum. Work on excretion must be carefully interpreted in view of the possible unphysiological nature of injected phosphate.

The absorption of dietary phosphorus may be measured by labelling, with radiophosphorus, the endogenous phosphorus appearing in the faeces. This has produced results varying from 60 to 90% under the same conditions. The factors causing this variation are not known.

WOOL WAX.

By J. FUTTER,

H. W. Lawrence & Son, Ltd., Johnsonville, Wellington.

Wool wax is the lipid present in the fleece of the sheep. It is a complex mixture of esters together with minor amounts of acids, alcohols and hydrocarbons. Industrially, wool wax is recovered from spent wool scouring liquors and several New Zealand scouring works recover wool grease, i.e., a crude form of wool wax. The amount recovered, however, is only a small percentage of that scoured from the wool.

The uses of wool wax are numerous, large quantities being used in the manufacture of lubricants and lesser quantities in cosmetics, rust preventatives, leather dressings, adhesive plasters and sheep branding fluids.

Various aspects of wool wax will be discussed including methods of extraction, chemical nature and uses.

TALL OIL

By R. P. HANSEN,

Fats Research Laboratory, D.S.I.R., Wellington.

Tall oil is a by-product of the sulphate process employed in the production of paper pulp from pinewood. It comprises a mixture of fatty and rosin acids together with small proportions of sterols, higher alcohols and other unsaponifiable material.

Among the many uses for tall oil overseas, are the manufacture of linoleum, oilcloth, paint, varnish, soap, detergents, printing ink and core oil. It is also used extensively as an emulsifier. In 1955 whole tall oil production in the United States alone amounted to approximately 245,000 tons, and it is anticipated that within a few years its output will exceed that of linseed oil. Economically its main advantages are its low cost and regular supply from dependable domestic sources.

At the New Zealand pulp mills tall oil is not recovered, the frothy tall oil soaps and black liquor being evaporated and burnt as a means of reclaiming the sulphate.

American tall oils vary considerably in composition, depending on the species and age of pine being pulped and the factory procedure adopted. American crude tall oil samples analysed by Anderson and Wheeler (Oil and Soap, 22, 137, 1945), ranged from 36% to 45% fatty acids, 38% to 46% rosin acids, and from 9% to 23% unsaponifiable matter. Investigations on the composition of New Zealand tall oil are in progress and the analysis of one sample prepared by acidification of soap skimmings showed it to contain approximately 43% fatty acids, 50% rosin acids and 7% unsaponifiable material. Of the fatty acids, oleic and octadecadienoic preponderate, the latter being present in both conjugated and unconjugated (linoleic) forms. The hexabromide test failed to establish the presence of linolenic acid. Investigations on the minor constituents of New Zealand tall oil have revealed the presence of trace quantities of the C_{17} *anteiso* acid (+) - 14 - methylhexadecanoic acid. Branched-chain acids had not formerly been found in vegetable fats. Minor amounts of palmitic acid and stearic acid have also been shown to be present.

The industrial potential of tall oil in New Zealand has not as yet been fully explored, but it is apparent that its utilisation will be determined by its cost of recovery, cost of refining, and the extent of the industrial uses to which it can be economically applied.

THE USE OF DRYING OILS IN PAINT.

By R. M. SINCLAIR,

Dominion Laboratory, D.S.I.R., Wellington.

The recorded use of drying oils in paint dates back to the second century but it was not until the 19th century that they became of industrial importance.

The drying oils used in paints may be classified into five groups according to the nature of the fatty acids present:—

1. Linoleic	e.g.	Soya, safflower
2. Linoleic-Linolenic	e.g.	Candlenut
3. Linolenic	e.g.	Linseed
4. Conjugated	e.g.	Tung, dehydrated-castor
5. Miscellaneous	e.g.	Tall, Fish.

For many years linseed has been the most widely used oil while tung has been an important constituent of varnishes particularly before the advent of synthetic resins. Linseed is the only drying oil that has been produced in quantity in New Zealand. Between 1921 and 1931 one to two hundred thousand gallons were produced annually which amounted to about one third of the total consumption. When production was resumed in 1944 some four hundred thousand gallons were produced annually, about half this being expressed from locally grown seed. Fluctuations in world supplies and prices have made it difficult to establish a stable industry.

Traditionally paint was made from raw or processed oils. Comparatively little oil was used in varnishes. The trend today is to use the oil as a modifying agent in a synthetic resin, as for instance in alkyd resins.

Improvement of the essential drying properties has been sought in many ways:—

1. Treatment of the triglycerides by molecular distillation or solvent fractionation to remove the more saturated constituents.
2. Replacement of the glycerol by an alcohol of higher functionality, e.g. pentaerythritol.
3. Treatment affecting the fatty acid component:
   - (a) Dehydration as in the case of castor oil.
   - (b) Isomerisation particularly conjugation.
   - (c) Addition or partial replacement of fatty acids e.g. heat treatment of a mixture of tung and soya oils.
   - (d) Reaction with various chemical compounds e.g. maleic anhydride, cyclopentadiene.

Although drying oils have successfully withstood competition in the past from synthetic resins such as nitrocellulose and have remained the principal binding medium of paints, it appears that consumption of oils as such will tend to diminish and will be replaced by oils incorporated as part of the structure of a complex resin. Thus they will be better able to meet the challenge provided by the straight synthetic resins such as Polyvinyl acetates and acrylics.

PLASTIC FATS (Acetoglycerides)

By R. M. DOLBY,
The Dairy Research Institute (N.Z.), Palmerston North.

New fat and oil products having unique properties can be produced by substituting acetic acid for a portion of the fatty acids occurring in ordinary fats and oils so as to obtain either diaceto-triglycerides or monoaceto-diglycerides or combinations of these. Such products are known as acetoglycerides. The recognition of their useful properties comes from work done during the last five years in the United States by Baur and others of Procter and Gamble Co., and by Feuge and co-workers in Southern Regional Research Laboratory, New Orleans.

Aceto-stearins are of particular interest as they are stable fats which solidify to non-greasy yet waxy and flexible solids. Some aceto-stearins can be stretched as much as 800 per cent. before breaking. Films of aceto-stearins have a reasonably low permeability to water vapour and gases so that these substances should have distinct possibilities as coatings for food products.

Tests of edibility of acetoglycerides have not yet reached the point where these substances are approved by the Food and

Drug Administration for use in foodstuffs but the extensive trials done already have not shown any harmful effects.

Three samples of different aceto-stearin products made by a British firm have been used in The Dairy Research Institute to determine their suitability as an alternative to wax for coating cheddar cheeses. Results with these have have been rather disappointing but experiments are to be continued with samples of American origin.

MONOGLYCERIDES AND RELATED EMULSIFYING AGENTS.

By S. G. BROOKER,
Abels Limited, Auckland.

Originally, monoglycerides were manufactured by esterifying commercial stearic acid with an excess of glycerine, hence the name usually applied to them " Glycerol (or Glyceryl) Monostearate," or, shortly, " G. M. S. " At present, this product is usually made by heating triglycerides with glycerine and a catalyst, such as caustic soda. The composition of the final product depends on the proportions of fat and glycerol used, the reaction proceeding according to the Law of Chance in a homogeneous mixture. Typical commercial products contain 40% monoester, 40% diester, 10% triester and 8% of glycerol which is roughly the proportion miscible with the glycerides in the liquid state. Self-emulsifying grades contain 2% - 5% of soap. Products containing 90% or more of monoester can be prepared by molecular distillation of the above-mentioned. There has been much discussion as to the relative merits of distilled and undistilled products. The monoester is almost entirely in the alpha form.

Monoglycerides used at the optimum amount of 0.2% improve the texture and volume of bread and soften the crumb so that staling is delayed. The theory underlying this effect will be discussed. It is usual to add the G. M. S. as an emulsion with fat and water. Monoglycerides can be employed in other baked goods, such as sponges, buns and cakes, and other uses are in cream fillings, margarine, and ice cream, where they promote smoothness and reduce " weeping." Because of their surface active properties, monoglycerides in certain cases act as foam breakers, e.g. in the evaporation of milk. They are much more plastic than the fats they are derived from and, on this account, have uses which are not connected with their emulsifying powers.

Since it has been conclusively shown that monoglycerides and diglycerides occur in natural fats and they are a normal stage in the digestion of fats, no health hazards have arisen in their use. A number of derived and related emulsifiers which are being used overseas or have been proposed, will be briefly discussed.

MANUFACTURE OF SHORTENINGS.

By S. G. BROOKER,
Abels Limited, Auckland.

Historically, lard has been used as a shortening for many years. It is an excellent fat for pastry and biscuits and, in the past, its flavour was acceptable. About 70 years ago, shortening based on cotton seed oil and oleo stearine was introduced and proved more satisfactory for cakes. From 1910, hydrogenation and deodorising provided the means of making a product of any desired melting point and consistency and with a bland flavour. In 1933, the so-called "high emulsifying" shortenings containing monoglycerides were introduced concurrently with new cake recipes including higher proportions of sugar and water. With the large usage of hydrogenated vegetable oils, the American public became used to their bland flavour while the fact that lard was unsuitable for cake making owing to its crystal structure, spurred lard producers to up-grade their product by hydrogenation, deodorising and interesterification. In 1931, the Votator, a totally enclosed system of solidifying shortenings in a plastic state, was introduced in the United States and is now used all over the world.

At one time, the trend of manufacture was towards an "all purpose" shortening but it is now recognised that different shortenings are required for different purposes such as cakes, pastries, frying, biscuits, etc., and the requirements of shortenings for these purposes will be outlined.

While shortenings have very largely captured the market for bakers' fats used in cakes and biscuits in America, margarines are holding their own in Europe because of their lower prices and the plasticity conferred on them by the water content.

THE OXIDATION OF PYRIMIDINES BY BACTERIA.

By R. D. BATT,
Medical School, University of Otago, Dunedin.

Two different mechanisms have been described in bacteria for the degradation of pyrimidines. One sequence, initiated by a reduction yielding a dihydropyrimidine, has been demonstrated in both aerobic and anaerobic bacteria, and also in animal tissues. The second type of catabolic pathway involves an initial oxidation and has been demonstrated, with certainty, only in bacteria.

The oxidative pathway for pyrimidine degradation has been studied in detail with cell-free enzyme preparations of several species and the results show that both uracil and thymine are oxidised to the corresponding barbituric acids by an induced enzyme, the uracil-thymine oxidase. This initial oxidative reaction has now been demonstrated in intact bacterial cells and factors affecting the induction of the oxidase have been studied.

The catabolism of barbituric acid (formed from uracil) has been considered to involve a hydrolytic cleavage catalysed by barbiturase and yielding urea and malonic acid. These fragments were then further degraded by urease and a malonic decarboxylase system. However, all attempts to demonstrate a barbiturase-catalysed step in intact cells have proved unsuccessful. The possibility is considered that barbiturase activity in cell-free extracts may be due to a modification, during isolation, of the enzyme present in whole cells for barbituric acid catabolism.

The general problem of demonstrating catabolic sequences in intact cells will be discussed.

THE METABOLISM OF GLYCEROL BY MYCOBACTERIUM BUTYRICUM.

By D. E. WRIGHT and N. L. EDSON,
Medical School, University of Otago, Dunedin.

A knowledge of the catabolism of glycerol by the mycobacteria is of interest in an understanding of the intermediary metabolism of the acid-fast bacteria. These micro-organisms which include the tubercle bacillus, grow readily on glycerol as a carbon source but since partially oxidised metabolites do not usually accumulate, their study has been difficult.

Mycobacterium butyricum accumulates considerable amounts of α-oxoglutaric acid along with small amounts of succinic and pyruvic acids. The occurrence of these acids in liquid culture has provided an opportunity to study the metabolism of glycerol by growing the bacteria in the presence of (1:3-$^{14}C_2$) glycerol and in the presence of non-isotopic glycerol accompanied by smaller amounts of (1-^{14}C) acetate, (2-^{14}C) acetate or $NaH^{14}CO_3$. Carbon and radioactivity balance sheets were determined for the bacteria and culture media, and the distribution of 14-carbon in the organic acids accumulating in the media found by degradative procedures.

Isotopic carbon from each labelled substrate was incorporated by the bacteria and widely distributed amongst the end products. The experiments established the fixation of carbon dioxide in the α-carboxyl of α-oxoglutaric acid as predicted by the citric acid cycle. In addition, the labelling pattern of α-oxoglutaric and succinic acids formed in the presence of (1-^{14}C) acetate, (2-^{14}C) acetate or (1: 3-$^{14}C_2$) glycerol were substantially characteristic of the citric acid cyle. The distribution of labelled carbon amongst the amino acids prepared by hydrolysis of the bacterial protein, suggests that the citric acid cycle was supplying intermediates for the synthesis of amino acids. The evidence strongly supports the view that the citric acid cycle has a major role in the metabolism of glycerol by *Mycobacterium butyricum.*

STUDIES ON THE CARBOHYDRATE METABOLISM OF STREPTOCOCCUS BOVIS

By A. E. OXFORD and R. W. BAILEY,
Plant Chemistry Division, D.S.I.R., Palmerston North.

The facultative anaerobe *Streptococcus bovis* is an ubiquitous rumen organism and is easily isolated in pure culture from rumen contents. It ferments most hexoses and oligosaccharides to lactic acid only and can also hydrolyse starch. It possesses an introcellular amylomaltase system producing bacterial starch from maltose but not glucose. It can also produce good yields of dextran from sucrose in liquid media under certain conditions, when an extracellular enzyme, dextransucrase, which is produced by the streptococci at pH 5.5 - 6.0, brings about the following transfers of glucose from sucrose to acceptor molecules:

$$\text{n sucrose } (+ \text{ glucose}) \rightarrow \text{n fructose} + (\text{glucose})_{n+1};$$

also, sucrose + fructose → fructose + leucrose, a reducing disaccharide containing both glucose and fructose units. The products from a sucrose culture are thus chiefly dextran and fructose together with some leucrose and lactic acid. Unlike *Leuconostoc* sp., *Strep. bovis* always produces an unbranched chain of isomaltose units, even at 28° the optimum temperature for the first named organism. The cultural conditions conducive to dextran formation by *Strep. bovis* are not quite the same in simple as in complex media, although provision of CO_2 gas in solution in a medium of high buffering power is always required. Lacking one of these conditions, growth may be good but little or no dextran is usually produced. In a complex medium containing yeast extract and peptone the buffer may be either phosphate (0.06 M) or acetate (up to 0.25 M), but in a simple amino-acid medium, acetate is always to be preferred for high dextran yields. Both biotin and pantothenic acid are also usually required.

Dextransucrase, as distinct from dextran itself, is secreted not only in a sucrose, but also in a glucose medium, even when the inoculum is also from a glucose culture. The purification, temperature and pH optima, and stability of *Strep. bovis* dextransucrase will be discussed.

CARBOHYDRATES IN PASTURE SPECIES UNDER NEW ZEALAND CONDITIONS

By R. W. BAILEY,
Plant Chemistry Division, D.S.I.R., Palmerston North.

Recent work on several aspects concerning various carbohydrate fractions in clover and ryegrass growing under New Zealand climatic conditions will be described.

1. Contrary to overseas reports starch is present in clover leaves (up to 5.5%, dry wt.) and ryegrass (0.7%, dry wt.) as very small granules (1-2 μ). The activity of an oligotrich ciliate in the rumen of cows appears to be governed, in part at least, by the starch content of ingested clover leaves.
2. The soluble sugars of red clover have been examined in detail and at least seven sugars identified.
3. The nature and distribution of the soluble sugars has been examined in autumn-grown samples of two ryegrass species (Perennial and Short Rotation).

NUCLEOPROTEINS OF PLANTS.

By J. W. LYTTLETON,

Plant Chemistry Division, D.S.I.R., Palmerston North.

Of recent years, ribonucleoproteins of cells have been considered to play an important part in protein synthesis. When some animal cell extracts are fractionated by centrifugation, the "microsome" fraction is found to be most active in incorporating amino-acids labelled with radioactive carbon, and the mechanism of this incorporation is considered to be closely related to that of protein synthesis. This "microsome" fraction consists of ribonucleoprotein particles in association with lipid material, from which they can be removed by treatment with detergent.

When a similar fraction is prepared from plant cells, ribonucleoprotein particles are obtained directly in a form free from lipid. Thus plant tissue is a good starting material for studying these particles, and good preparations can reproducably be made from etiolated pea shoots, wheat roots, or yeast cells. In these preparations, the ultracentrifuge reveals a single ribonucleoprotein component, with molecular weight of the order of five million.

Leaf cells seem to differ from those studied hitherto in that they contain more than one type of ribonucleoprotein particle. The difficulties encountered in the study of these particles will be described, and some ideas put forward as to their location in the leaf cell.

METABOLISM OF BUTYLATED HYDROXYTOLUENE IN THE RABBIT

By J. C. DACRE,

Toxicology Research Unit, Medical School, Dunedin.

The compounds butylated hydroxytoluene (BHT, 2:6-di-*tert.*-butyl-4-methylphenol) and butylated hydroxyanisole (BHA, a mixture of 85% of 2-*tert.*- and 15% of 3-*tert.*-butyl-4-methoxyphenol) are used extensively overseas as antioxidants in edible fats. Although acute and chronic toxicity studies of the conventional type have been reported, very little is known about their metabolism in the animal body. The metabolism of BHA in the rabbit was reported on at the Palmerston North Conference in 1955 (see also Biochem. J., 1956, *64*, 777-782); this paper describes a similar study of the metabolic fate in the rabbit of large doses of BHT and the isolation and structure of some of the major metabolites from the urine.

In the 3 days after 1.28 g. of BHT dissolved in olive oil had been given to a rabbit by stomach tube, about 60% of the dose is excreted in the urine. About 31% of the dose appears as phenolic ether-type glucuronides, 10% as free unconjugated phenols, 10% as ethereal sulphates and about 8% as an ester-type glucuronide. The excretion of these metabolites is not greatly altered following the administration of five daily doses of 1.20 g. of BHT.

Paper chromatographic examination of the urine and ether extracts of urine from rabbits receiving repeated doses of BHT indicates the presence of two phenolic glucuronides as well as small amounts of 3:5-di-*tert.*-butyl-4-hydroxybenzoic acid. One of the glucuronides was isolated as a crystalline triacetyl methyl ester and analysis indicates that it is an oxygenated derivative of a monoglucuronide of BHT. Enzymatic hydrolysis of urine with β-glucuronidase liberates two phenolic aglycones, one of which was identified as 3:5-di-*tert.*-butyl-4-hydroxybenzoic acid. Recent work on the isolation and structure of these glucuronide conjugates will be discussed.

CHEMISTRY OF WEEDKILLERS

By F. B. THOMPSON,
Rukuhia Soil Research Station, Hamilton.

The discovery in 1942 that phenoxyacetic acid compounds had a toxic effect on some plants opened up an entirely new field of weed control. Subsequent intensive research led to equally fundamental and important discoveries regarding the weedkilling properties of other selective (i.e. toxic to certain types of plant, only), and non-selective (toxic to all plants) chemicals.

This knowledge has been rapidly and extensively applied in agricultural countries. An important chemical industry has developed in New Zealand, as a result of the use of weedkillers.

The selective action of weedkillers on plants varies greatly according to the chemical nature of the material. The principal types of weedkillers grouped according to composition, and their main uses are:—

(1) Mono- and dichlorophenoxy acetates—toxic to broad-leafed weeds and legumes.

(2) Mono- and dichlorophenoxy butyrates—toxic to broad-leafed weeds, but not to legumes.
(3) Trichlorophenoxy acetates—toxic to brush weeds.
(4) Chlorine substituted fatty acids—toxic to grasses and/or selectively kill broad-leafed weeds in crops.
(5) Substituted carbamates—as (4).
(6) Substituted phenols—contact action, non-toxic to legumes.
(7) Substituted methyl ureas—non-selective.
(8) Chlorates, borates, and arsenicals—non-selective.

Derivates of the following materials are used for special purposes; endoxophthalate, triazine, and triazole.

Examples of the various types of materials and their practical applications are discussed.

THE SPONTANEOUS COMBUSTION OF COAL

By W. G. HUGHSON,
Dominion Laboratory, D.S.I.R., Wellington.

Statistics are quoted to show that coal is still the world's greatest source of heat and power, and in New Zealand even after due allowance has been made for efficiency (or lack of it) coal is first equal with imported oil and produces twice as much energy as hydro-electricity. The overall conclusion is that coal is well worth conserving and therefore spontaneous combustion which is responsible annually for much economic loss merits more attention than is generally given to it.

Many underground tragedies have been due to gas explosions or coal dust explosions which have been initiated by fires due to the spontaneous heating of coal. Heatings are responsible for the shutting off or closing down of large areas of economically valuable coal. On the surface, spontaneous combustion is the main hazard in storing coal either in the open or in bins. Earlier in the century, fires in steamship cargo coal were responsible for huge losses. Knowledge is still insufficient to safeguard present day cargoes of coal as was shown recently when a shipment of Australian coal had to be off-loaded at Wellington because of spontaneous combustion.

Quite a wide field has been covered in the investigation of the causes which lead to the heating and ultimate firing of coal and much information is now available which enables coal to be handled and stored in such a way as to obviate loss from this cause. There are chemical factors, the chief of which is the tendency of all coals when freshly mined to oxidise with the generation of heat. The oxidation of pyrites is an auxiliary factor and not the main cause as was at one time popularly supposed.

Then there are physical factors such as the fine sub-division of coal giving an increased surface area for oxidation and the ways and means of limiting or, if possible, preventing the access of air to a coal pile or a bin. Access of air must either be prevented (and there are many ways of doing this) or ventilation must be sufficient to remove all heat during the oxidation stage.

The dangerous stage varies with different coals but if temperatures are observed over a month, and more particularly over the first week, the initial rise may give way to a falling temperature before the firing temperature is reached.

Some work has been done in New Zealand at the Otago School of Mines but very much more requires to be done on the spontaneous heating of coal.

THE IMPORTANCE OF PULP AND PAPER TO NEW ZEALAND.

By D. L. STACEY,

New Zealand Forest Products Ltd., Tokoroa.

This paper shows that the vicissitudes currently plaguing our primary exports have been paralleled in the pulp and paper fields over the last century. It then quotes a recent long term forecast made for the latter field which would seem also to apply to the former.

A brief historical survey of the paper making art is given from the origin in China along the routes of travel, and war, to the West.

The four major methods by which the world's current 67,843,773 tons of pulp are made is given together with three tables showing:—

(a) New Zealand's annual per capita consumption (9th out of 90 nations).

(b) Her ranking position in paper manufacture (30th out of 70).

(c) Her pulp manufacturing output (16th out of 51).

Slides also show how production rose 268% between 1953 and 1956 and in 1957 made this field the fourth greatest exporter following the three primary industries.

The current usage, predicted expansion and unfulfilled requirements in Oceania by 1962 are tabulated. The future is shown to be bright.

The paper concludes detailing some revolutionary developments and predicts their probable effects in our lifetime.

THE USE OF 8-HYDROXYQUINOLINE IN THE NON-DESTRUCTIVE TESTING OF ENGINEERING MATERIALS.

By E. F. HUBBARD,

Laboratory, New Zealand Railways, Hutt Workshops, Woburn.

In the testing of engineering materials it is frequently necessary to examine a component intact. Tests may be required for its chemical composition, physical state, the presence or absence of discontinuities such as cracks and porosity, also for the detection of welding and its extent. In this kind of testing the component is returned to service if satisfactory.

Several kinds of non-destructive testing will be described. Attention in particular will be paid to the use of fluorescent materials.

Metallic compounds of 8-hydroxyquinoline are employed in electro-magnetic examination. A description will include the preparation of several metallic quinolinates, their fluorescent properties and the conditions governing their use.

Specimens of these materials will be exhibited. The testing technique will be demonstrated.

POLYURETHANES.

By G. SMITH,

Henry H. York & Co. Pty., Ltd., Christchurch.

Long-chain addition products of high molecular weight, so-called "polyurethanes" are formed from compounds with two isocyanate groups which are reacted with an alcohol containing two hydroxyl groups. This is the type of polyurethane compound which has been investigated since 1937 and which today is used for fibres, bristles and thermoplastic materials.

The polyurethanes offer great advantages in very many fields of application, as a result of their large variety of synthesis potentialities, which so far are unequalled by any other type of plastics. In thin films, polyurethanes are used as high-quality paints, adhesives and textile spread coatings.

By means of certain polyisocyanates and compounds of accurately pre-determined chain length which contain hydroxyl groups, it is possible to produce elastomers of high molecular weight. which in some characteristics are similar to natural rubber, while being superior to the latter in many properties.

If the polyaddition, which produces the polyurethane, coincides with the reaction of further isocyanate groups with water, the resulting carbon dioxide expands the plastic being formed to a material consisting of an infinite number of cells, i.e., a polyurethane foam.

If the starting products contain a higher number of hydroxyl groups, the resulting foams are rigid instead of elastic.

THE APPLICATION OF GAS CHROMATOGRAPHY TO THE ANALYSIS OF GASES

By Miss J. B. ROSS,

Dominion Laboratory, D.S.I.R., Wellington.

By the use of the new technique of gas liquid partition chromatography, knowledge of the composition of mixtures of hydrocarbon gases has been greatly increased. In this paper, some general comments are made about this method of analysis, which both separates and identifies the components of a mixture. Details of the particular instrument in use at Dominion Laboratory are given and the analyses of about 30 gases determined in this way.

SEASONAL CHANGES IN THE CHEMICAL COMPOSITION OF HOP MATERIAL

By R. J. MONK,

Cawthron Institute, Nelson.

Samples of hop roots taken at intervals during a season were analysed for water-soluble and for acid-soluble reducing materials, estimating them as glucose. The data obtained show some correlation with the stages of growth. Analytical data for water-soluble reducing substances, estimated as glucose, from hop cones taken at intervals during each season for five seasons give curves similar in shape at approximately the same calendar dates. They show a sharp increase in sugar content followed by a sharp decrease over a period of a few days.

THE NON-PROTEIN NITROGEN FRACTION OF RYEGRASS HERBAGE

By G. W. BUTLER, N. O. BATHURST and BERIS G. BUTLER,

Plant Chemistry Division, D.S.I.R., Palmerston North.

There are appreciable gaps in the complete characterisation of the nitrogenous compounds extracted from ryegrass herbage by 80% (v/v) ethanol. Particularly is this so when the plants are rapidly growing and are supplied with mineral nitrogen as nitrate. The scheme we follow at present for analysis of such extracts is:—

Total Nitrogen

The Dumas micro-combustion method is used and is found to be highly satisfactory. The microkjeldahl method with pre-reduction of nitrate is erroneous, giving low and variable results — the errors appear to arise from incomplete determination of organic forms of oxidised nitrogen.

Nitrate

The phenoldisulphonic acid method is used after alkaline peroxide oxidation of organic matter. Unless prior chromatographic separation is carried out, organic forms of oxidised nitrogen are measured along with nitrate.

Paper-chromatography

Two-dimensional paper chromatography gives an excellent separation of the components of the non-protein-nitrogen fraction, which can then be detected by the use of suitable reagents.

(i) Amino acids are quantitatively determined using a ninhydrin reagent. Bound amino acids can be estimated by determining the amino acids formed on hydrolysis of the extracts with 6N-HCl. Inorganic nitrate must first be removed.

(ii) Many nitrogenous compounds can be detected by formation of N-chloro-derivatives with tertiary butyl hypochlorite followed by starch/iodide reagent.

(iii) Ureido and guanido-compounds, betaine, choline and perloline can be detected using suitable reagents.

(iv) Organic forms of oxidised nitrogen are suspected to be present and attempts are being made to reduce them catalytically to amino-derivatives, which could be detected by paper chromatography.

Results from typical analyses of samples of rapidly-growing ryegrass herbage will be presented and their interest from animal nutritional and plant biochemical standpoints will be discussed.

THE CHROMATOGRAPHIC ISOLATION OF EGG PHOSPHOLIPIDS

By J. C. HAWKE,

Fats Research Laboratory, D.S.I.R., Wellington.

More progress has been made in working out the composition of the phospholipid in egg yolk than of the phospholipids found in other biological material. A contributing factor has been the less divergent nature of its principal components, which are phosphatidylcholine and phosphatidylethanolamine. These are mixed with small proportions of lysophosphatidylcholine, lysophosphatidylethanolamine, sphingomyelin and inositol phospholipid.

Countercurrent methods have not proved very successful in separating phospholipids because the nature of the fatty acids appears to affect the solubility of the phospholipids more than the nitrogen-containing alcohol which is esterified to the phosphate group.

Silicic acid and alumina columns have been used successfully to isolate the major constituents of egg phospholipid, thus allowing a detailed examination of the composition of the individual phospholipids.

Chromatographic analysis of the methyl esters obtained from phosphatidylethanolamine and phosphatidylcholine has revealed marked differences in composition. Of the total acids in phosphatidylethanolamine 39.5% is saturated C_{18} and 20.1% is unsaturated C_{18}, whereas in phosphatidylcholine 14.2% is saturated C_{18} and 44.7% is unsaturated C_{18}. The larger proportion of unsaturated C_{18} acid in phosphatidylcholine is attributed to oleic acid.

It is estimated that in phosphatidylcholine all the fatty acids esterified in the α' position are unsaturated but in phosphatidylethanolamine one-third are saturated.

The significance of the findings in the biological synthesis of phospholipids will be discussed.

CONCENTRATION OF THE FACIAL ECZEMA POISON

By E. P. WHITE,

Ruakura Animal Research Station, Hamilton.

Work aimed at isolating from pasture the poison responsible for "facial eczema" has been going on for some years, using the guinea pig as test animal.

The minimum of 4 weeks' feeding is a limitation to rapid progress, but the main limitation until recently has been a restricted supply of highly toxic grass.

A routine has been worked out for preparation of concentrates containing one seventy-thousandth of the weight of the grass and at least half the poison. The procedure will be outlined, and difficulties associated with some of the steps mentioned.

Many alternative but less effective concentration techniques are known, and much of the work has not produced results of practical value. Only steps which confine the position to a small part of the weight of a fraction are of value, and such steps must be simple and capable of repetition as a routine with different grass samples.

Possible short-cuts to the systematic concentration have been tried, such as absorption studies in the visible and ultra-violet, comparison of pigments by resolution on paper chromatograms, and weight difference studies, without as yet revealing any feature associated with toxicity, even in the best concentrates.

On occasions it has been possible to obtain concentrates containing one two-hundred to one four-hundred-thousandth of the weight of the grass, and half the poison. Even at these high concentrations it is possible to get fractions of similar weight and appearance from non-toxic grasses. A few milligrams of concentrate from 900 g. dry-weight of grass can produce severe liver damage.

Many properties of the poison are known — for example its neutrality, and generally non-characteristic chemical and physical properties. The best concentrates are slightly yellow coloured syrups or resins, and the poison may well be one of a series of high boiling point colourless liquids. Insolubilities in water and petroleum ether provide a limitation to techniques applicable. Work is continuing mainly along the lines of finer adsorption chromatography, partition chromatography on columns and paper and counter-current distributions.

During the course of the work two compounds were obtained, each in pasture at 1 in 50,000 or less. One substance, m.p. 149° C., $C_{20}H_{30}O_6$ is in toxic and non-toxic pasture. It contains two alcoholic $-OH$ groups, and an intense peak in absorption at 215 mμ, and infra-red peaks are consistent with an $\alpha\beta$ unsaturated $\delta-$lactone or unsaturated ester.

The other substance, of which a major component has a m.p. 260°C., $C_{26}H_{45}O_7N_3$ is responsible for the " beaker test." This substance and the poison generally occur together in pasture, but there is no evidence for chemical alliance between the two. Drastic acid hydrolysis gives leucine and valine in a 1:1 ratio, and probably another amino acid, and saponification gives a complex acid, capable of hydrolysis to the above amino acids. The infra red evidence shows many bonds of the ester and amide (peptide) nature, and there is considerable chemical and physical alliance to amidomycin and allied antibiotics. Amidomycin consists of alternate amino and hydroxy acid residues linked in a large ring, and our substance could be similar.

Formononetin, an isoflavone of red clover can also appear in concentrates, and amorphous material from pennyroyal and other labiates is in some properties similar to the beaker test substance.

CO-ORDINATION OF TRIMETHYLAMINE BY HALIDES OF SILICON, GERMANIUM AND TIN.

By C. J. WILKINS,

Chemistry Department, University of Canterbury, Christchurch.

Trimethylamine forms crystalline 1:1 adducts with halides of silicon and germanium. Mono-amine adducts may also be obtained from stannic halides in nitromethane solution, but contain solvent of crystallisation. The trends in the dissociation pressures and heats of formation of these complexes may be correlated with polar and steric influences. When these are sufficiently favourable a second molecule of amine may be co-ordinated. Tetramethylethylenediamine, which also forms 1:1 adducts, differs from trimethylamine in not causing disproportionation of chlorofluorosilanes. The bearing of this and other observations on the structures of the trimethylamine adducts will be discussed.

NITROUS ACID EQUILIBRIA IN PERCHLORIC ACID.

By T. A. TURNEY and G. A. WRIGHT,

Chemistry Department, University of Auckland, Auckland.

Nitrous acid exists in equilibrium with the nitrosonium ion and dinitrogen trioxide in aqueous perchloric acid. Thermodynamic calculations of these equilibria have been made. The equilibrium constant for the equilibrium between nitrous acid and the nitrosonium ion has been determined spectrophotometrically. The reactivity of nitrous acid is then discussed in terms of these equilibria.

THE EXCHANGE OF LABELLED CYANIDE WITH POTASSIUM CHROMICYANIDE.

By R. F. C. CLARIDGE and R. W. OLLIFF,

Chemistry Department, University of Auckland, Auckland.

The exchangeability of co-ordinated ligands with free ligands has been used as a criterion of bond type within a complex ion. Thus $Fe(C_2O_4)_3^{3-}$ exchanges rapidly with free oxolate ions and is said to be 'ionic' or 'outer,' whereas $Fe(CN)_6^{3-}$ exchanges very slowly with free cyanide ions and is therefore said to be 'covalent' or 'inner.'

The major problem is to distinguish the originally free ligands from the originally co-ordinated ligands. This can be done by using isotopically labelled ligands, either free or co-ordinated, and measuring the distribution of isotope after a period of time.

Potassium chromicyanide was found to exchange with free cyanide ions, labelled with radioactive C^{14}, at a very slow rate. The rate was found to be first order in complex, and independent of cyanide concentration. The effect of varying acidity was small. The reaction has been interpreted as pseudo-unimolecular, the rate determining step being attack by a water molecule.

The results are similar to those for potassium manganicyanide, and it would appear that both reactions proceed by the same mechanism.

ISOTOPIC STUDIES ON THE LABILITY OF CO-ORDINATED AMMONIA

By Miss C. J. BISHOP, D. R. LLEWELLYN and A. L. ODELL,
University of Auckland, Auckland.

The lability of ammonia co-ordinated to transition metal ions has been studied in aqueous solutions using ammonia labelled with N-15 isotope.

Tetrammine copper II cation has been shown to equilibrate with isotopically labelled ammonia within the time required for separation of the species.

Hexammine cobalt III cation shows no detectable exchange with labelled ammonia in aqueous solution at pH 9.9 and 2.4 even after 130 days at 24.8°C.

Bjerrum (1) has published successive dissociation constants for the $Co6NH_3^{3+}$ ion; the sixth of these being given by log $K_6 = -4.41$. If this figure is correct, we would expect a concentration of free ammonia in a 1M solution of $Co6NH_3^{3+}$ of approximately 10^{-2}M.

Isotopic dilution analysis methods were employed in an attempt to detect such free ammonia but none was detected even after the solution had stood at 24.8°C for 162 days.

Bjerrum's value for the first hydrolysis constant of the hexammine cobalt III cation has been confirmed by ultra-violet spectrophotometric methods—the hydrolytic equilibrium being established in the presence of activated charcoal or platinum black. It was noticed, however, that no hydrolytic equilibrium is established unless free ammonia is present; the presence of excess hydrogen or hydroxyl ions did not induce aquotisation in the absence of free ammonia. This unexpected result may be explained by supposing that the equilibrium is established through a preliminary reduction of CoIII to CoII and that a reducing agent (such as ammonia) is necessary.

Tri-nitro tri-ammino cobalt III (trans.) has been found to undergo exchange with labelled ammonia at a measurable rate. First order rate constant at 24.8°C is $2.01 \pm 0.5 \times 10^{-2}$ day $^{-1}$. The rate of the exchange reaction has been shown to depend on the first power of the concentration of the complex and to be independent of the concentration of free ammonia.

These kinetic results are in accord with the view that the nitro groups will weaken the covalent metal-ammonia bonds.

Ammonium tetra-nitro di-ammino cobalt III (Erdman's Salt) was found to exchange with labelled ammonia in aqueous solution to the extent of 30% in 50 days at 24.8°C.

Hexammine chromium III tri-nitrate was found to show no ammonia exchange in 7 hours, and after longer periods extensive aquotisation was observed.

Reference:

(1) Bjerrum " Metal Ammine Formation in Aqueous Solution" (Haase — 1941).

CONFERENCE PROGRAMME

WEDNESDAY, 27th AUGUST

MORNING—

9.00—Registration, etc.
10.00—Morning Tea.
10.30—Welcome by Mayor of Hamilton, and opening of Conference by President, N.Z. Section, R.I.C.
11.00—Presidential Address, President, N.Z.I.C.

AFTERNOON—Conference Sessions

A Series

2.00—Recent studies on the constitution of molten salts (H. Bloom).
2.30—The lifetime of optically excited molecules (Miss S. Page).
3.00—Analytical applications of atomic absorption spectra (J. E. Allan).

B Series

2.00—Pesticide residues in fruit (H. M. Stone).
2.30—Arsenic contamination of bacon by use of treated sawdust in smoking (C. C. Watson).
3.00—Chromatography and pharmacological activity of food colours and their relation to structure (L. Wilkinson).
3.30—Afternoon tea.
4.00—Annual General Meeting, N.Z.I.C.

EVENING—

8.00—Discussion Groups.

THURSDAY, 28th AUGUST

MORNING—Conference Sessions

A Series

9.00—Some agricultural and manufacturing characteristics of phosphate rock (P. J. Gallaher).
9.30—The determination of phosphate (K. F. Hoy).
10.00—The significance of phosphorus as a factor in the accumulation of organic matter in soils (T. W. Walker and A. F. R. Adams).
10.30—Morning Tea.
11.00—Phosphorus in N.Z. soils (W. M. H. Saunders and N. Wells).
11.30—Uptake of phosphorus by pastures (R. H. Jackman).
12.00—Utilization of phosphorus by the animal (E. W. Wright).

B Series

9.30—Wool wax (J. H. Futter).
9.30—Tall oil (R. P. Hansen).
10.00—Use of drying oils in paints (R. M. Sinclair).
10.30—Morning tea.
11.00—Plastic fats (acetoglycerides) (R. M. Dolby).
11.30—Monoglycerides and related emulsifying agents (S. G. Brooker).
12.00—The manufacture of shortenings (S. G. Brooker).

AFTERNOON—

1.30—Visits to Ruakura Animal Research Station and Rukuhia Soil Research Station Chemical Laboratory.
3.30—Afternoon tea.
4.00—Annual General Meeting, R.I.C., Continuation of visits by members not attending this meeting.

EVENING—

8.00—Social occasion.

FRIDAY, 29th AUGUST

MORNING—Conference Sessions.

A Series

9.00—Oxidation of pyrimidines by bacteria (R. D. Batt).
9.30—The metabolism of glycerol by Mycobacterium butyricum (D. E. Wright and N. L. Edson).
10.00—Studies on the carbohydrate metabolism of Streptococcus bovis (A. E. Oxford and R. W. Bailey).
10.30—Morning tea.
11.00—Carbohydrates in pasture species under New Zealand conditions (R. W. Bailey).
11.30—Nucleoproteins of plants (J. W. Lyttleton).
12.00—The metabolism of butylated hydroxytoluene in the rabbit (J. C. Dacre).

B Series

9.00—Chemistry of weedkillers (F. B. Thompson).
9.30—The spontaneous combustion of coal (W. G. Hughson).
10.00—The importance of pulp and paper to New Zealand (D. L. Stacey).
10.30—Morning tea.
11.00—The use of 8-hydroxyquinoline in the non-destructive testing of engineering materials (E. F. Hubbard).
11.30—Polyurethanes (G. Smith).
12.00—The application of gas chromatography to the analysis of gases (Miss J. B. Ross).

AFTERNOON—Conference Sessions:

A Series

2.00—Seasonal changes in the chemical composition of hop material (R. J. Monk).
2.30—The non-protein nitrogen fraction of ryegrass herbage (G. W. Butler, N. Bathurst and Beris G. Butler).
3.00—The Chromatographic isolation of egg phospholipids (J. C. Hawke).
3.30—Concentration of the facial eczema poison (E. P. White).

B Series

- 2.00—Co-ordination of tri-methylamine by halides of silicon, germanium and tin (C. J. Wilkins).
- 2.30—Nitrous acid equilibria in perchloric acid (T. A. Turney and G. A. Wright).
- 3.00—The exchange of labelled cyanide with potassium chromicyanide (R. F. C. Claridge and R. W. Oliff).
- 3.30—Isotopic studies of the lability of co-ordinated ammonia (Miss C. J. Bishop, D. R. Llewellyn and A. L. Odell).
- 4.00—Afternoon tea.
- 4.30—Conclusion of Conference.

NEWS AND NOTES

AUCKLAND BRANCH:

The retirement is announced of Mr. K. M. Griffin, Government Analyst at Auckland for the past 34 years. Mr. Griffin is a Foundation Member of our Institute and has always been a dominant figure in Institute affairs where he has won the respect of all members for his integrity and tenacity of purpose. He was President of the Institute in 1955 and a brief outline of his career was published at that time (J.N.Z.I.C. *19,* 9 and *18*, 18). All members will join in wishing Mr. Griffin a very long and happy retirement. We trust that his retirement from official duties will not lead to any relinquishment of the unofficial position he has held for so long—watch-dog of the Institute.

MANAWATU BRANCH:

Dr. H. R. Whitehead, Deputy-Director and Chief Bacteriologist, The Dairy Research Institute, has just returned from a brief trip to the United Kingdom. The object of Dr. Whitehead's trip was to arrange collaborative studies on cheese problems with the National Institute for Research in Dairying, Reading.

On two occasions last month the Manawatu Branch acted as hosts to groups of about 150 senior Post-Primary School pupils. The first visit was to the chemical laboratories of Massey College and The Dairy Research Institute and the second was to the factory and laboratories of Glaxo Laboratories (N.Z.) Ltd. Both evenings were again highly successful and members feel that the enthusiasm of the pupils and staff amply repays the effort and expense involved in arranging evenings of this sort.

WELLINGTON BRANCH:

All members will join in offering congratulations to Mr. T. A. Rafter, Director of the Division of Nuclear Sciences, D.S.I.R., who was made an Officer of the Most Excellent Order of the British Empire in the recent Birthday Honours. The award is in recognition of Mr. Rafter's services to nuclear science.

Mr. G. Maskill Smith, previously Senior Chemical Engineer at Dominion Laboratory, Gracefield, has joined the staff of Winstones Ltd., Auckland, as Technical Adviser.

The Wellington Branch is donating a lectern to be placed in the new science block lecture theatre at the Victoria University of Wellington. The lectern is of timber and was designed by the Architect to match the lecture theatre.

BOOK REVIEWS

QUANTITATIVE INORGANIC ANALYSIS, by G. Charlot and Denise Bezier (Translated by R. C. Murray). Published by Methuen and Co., Ltd., London, July, 1957. 690 pages and 211 diagrams. Price 84/-.

This book is a very valuable contribution to the literature on Quantitative Inorganic Analysis. Although the style may be for some people somewhat abrupt it has the advantage of conciseness which has enabled a very large amount of valuable discussion to be incorporated within the one volume. The book is an excellent translation from the third French edition. Subject matter is treated in two sections: General Methods of Analysis; Determination of the Principal Elements. In the section on general methods of analysis the theory on which the analytical methods are based is adequately and clearly discussed and a valuable innovation is that the level of accuracy possible using the various techniques is given with each section. There is a useful simple explanation of the place of statistical methods in the determination of the precision of various methods. All forms of titrimetry, gravimetric analysis and instrumental analysis are discussed with examples of their specialised applications and these are each adequately referenced. In the section on the determination of the principal elements the various methods available for the analysis of the particular element in its various forms and combinations are listed with working details, lists of interfering ions and any other pertinent data together with references for further information. For those interested in assessing the most suitable method of analysis under specified conditions this latter section would be most valuable. The whole book can be highly recommended.

—G.M.W.

GENERAL BIOCHEMISTRY (Second Edition), by Joseph S. Fruton and Sofia Simmonds. Published by John Wiley and Sons, Inc., New York, March, 1958. 1077 pages. Price 18 dollars.

It is just five years since the first edition of this book was published and in that time it has become widely recognised as a standard textbook of biochemistry — many, including this reviewer, consider it the finest of its kind. It is unfortunate that in a rapidly expanding field such as biochemistry a valuable text of this type is predestined to pass out of date, at least in some aspects of the subject, in a very short time. Those familiar with the first edition will therefore welcome this revised second edition. The structure of the book remains unchanged although a number of sections have been rewritten and the text and illustrations extensively altered in many places. In particular, a new chapter has been added on alternative pathways of carbohydrate metabolism, new developments in aspects such as protein structure, photosynthesis, metabolism of carbohydrates, biosynthesis of proteins and vitamins have been included and several chapters have been rewritten to give a slightly different and perhaps improved presentation of data and discussion.

" General Biochemistry " is based largely on a Ph.D. course in general biochemistry. It is undoubtedly excellent for this purpose. But it is perhaps even more valuable as a general book on biochemistry for use by chemists and biologists who, as the authors put it, " wish to examine the structure of modern biochemistry from a general point of view." In the same way this text will find increasing application in the fields of medicine and agriculture.

As in the first edition the text is well set out and clearly illustrated by figures and diagrams. References, chosen particularly as sources of further bibliographic information, are included as footnotes on each page. A particularly valuable contribution to the literature of biochemistry.

—W.A.McG.

TRACE ANALYSIS, Edited by John H. Yoe and Henry J. Koch, Jr. Published by John Wiley & Sons, Inc., New York, December, 1957. 672 pages. Price 12 dollars.

This text is based on papers presented at a symposium on trace analysis held in New York in November, 1955 and contains contributions from 24 recognised leaders in their respective fields of analysis.

The book is divided into three sections. The first, and by far the largest section (574 pages) is devoted to methodology and covers all, or most, of the methods and techniques used in trace analysis. Individual chapters deal with the following subjects: Chromatography and Electrochromatography; Ion Exchange; Extraction; Chemical Microscopy; Spot Tests; Colorimetry; Fluorimetry; Flame Spectrometry; Potentiometry; Coulometry; Polarography and Voltammetry; Amperometry; Emission Spectrochemical Analysis; Gamma-Ray Spectroscopy; Mass Spectroscopy; X-Ray Spectroscopy; X-Ray Micrography; Neutron-Activation Analysis; and Microbiological Techniques; Inorganic Ions. Two short sections, each of two chapters, deal with Instrumentation and Sensitivity, Separation, Concentration, and Contamination.

The papers deal with the theory of the methods and with their applications. Aspects such as advantages and limitations, accuracy, sensitivity, precision, sources of error, are also all well covered. Each chapter is followed by a discussion prepared by a discussion leader and many references to original papers are included in the text.

This is an extremely useful collection and critical appraisal of methods of trace analysis. It will be of value to chemists in a wide variety of fields since, whatever our particular interests, we all come up against the problem of trace analysis.

INTRODUCTION TO PROTEIN CHEMISTRY, by Sidney W. Fox and Joseph F. Foster. Published by John Wiley and Sons, Inc., New York, 1957. 459 pages. Price 9.50 dollars.

This is an extremely interesting text which will have a wide appeal to chemists, biochemists, nutritionists and food technologists. While it claims merely to be an introduction to the subject, it is by no means superficial and even specialists in the various fields should find much material of value.

The development of the subject is a logical one — amino acids, peptides, proteins and finally some special protein systems. The section on amino acids covers their physical and chemical properties, their preparation and assay, and their metabolic and nutritive significance. The naturally occurring peptides and their fractionation, the determination of peptide structure and peptide synthesis is then discussed. The chapters on proteins themselves deal with amphoteric properties, electrophoresis, other physical methods for investigating proteins, solubility, protein structure and denaturation. The particular proteins and protein systems include, blood proteins, egg white proteins, milk proteins, muscle proteins, several plant proteins, and hormonal proteins. Enzymes, and peptides and proteins as substrates are also covered.

The book is well written and well illustrated. Although specific references are not given, each chapter concludes with a set of selected references to reviews and original articles.

—W. A. McG.

ORGANIC ELECTRODE PROCESSES, by Milton J. Allen. Published by Chapman and Hall, Ltd., London, 1958. 174 pages. Price 32/-.

Electro-chemistry has not yet been fully adopted by organic chemists but it does offer most interesting methods for the preparation of organic compounds utilising oxidation and reduction techniques. This text is intended to give organic chemists the fundamental information to start investigatory work in this field and is admirably suited to this purpose.

HOUBEN-WEYL:METHODEN DER ORGANISCHEN CHEMIE, 4th Edition, Edited by Eugen Muller, Vol. 1 Part 1, General Laboratory Practice, 1048 pages. 1958, Stuttgart Georg Thieme Verlag, DM 198.

Although this is the first part of the new work several other volumes have already appeared and this one is produced at the same standard of excellence. It covers the materials used in the laboratory apparatus such as glass and porcelain and such fundamental operations as distillation, filtering, chromatography, liquid-liquid extraction, evaporation, crystallisation and electrophoresis. These subjects are treated in such detail (e.g. 180 pages on distillation and sublimation), that no other books on them would be required in most laboratories. There are over 500 illustrations comprising graphs, line drawings and photographs which are of a very high standard and contribute in no small measure to the value of this book.

—S. G. B.

The latest volumes of the eighth edition of *Gmelins Handbuch* to come to hand are Calcium Part B Section 2 dealing with calcium compounds from the hydrides to dithionate, (392 pages); Copper Part B Section 1 dealing with copper compounds from hydrides to tellurate (624 pages); and a key showing the arrangement of data on the various elements and compounds discussed. This key has an increased usefulness through being in English and German. The literature is covered up to the end of 1949 and the very large amount of information contained may be gauged from the fact that calcium chloride takes up 128 pages and copper sulphate nearly 100. These volumes are prepared by the Gmelin Institute and published by Verlag Chemie, Weinheim, Germany.

—S. G. B.

ION EXCHANGE RESINS (2nd Edition), by Robert Kunin. Published by John Wiley and Sons, Inc., New York, 1958. 466 pages. Price 11 dollars.

This second edition contributes a very valuable consolidation of facts concerning ion exchange resins. "The second edition, like the first, is designed to serve those who have not yet become interested in ion exchange technology, and, in addition, those who have been working in a narrow area of ion exchange and are curious about the overall aspects of the field." With this in view there are five chapters discussing the theory and mechanism of ion exchange, resin characteristics and synthesis. These are followed by a general consideration of their applications, and then specific applications such as water softening and deionisation, hydrometallurgy, use of permselective membranes, use in catalysis and in analytical chemistry. These are discussed with sufficient detail to obtain a working knowledge of the processes and are adequately supplemented with diagrams, tables and literature references.

For those who are interested in ion exchange, or feel they should be, this book can be recommended.

—G. M. W.

Conference Notes

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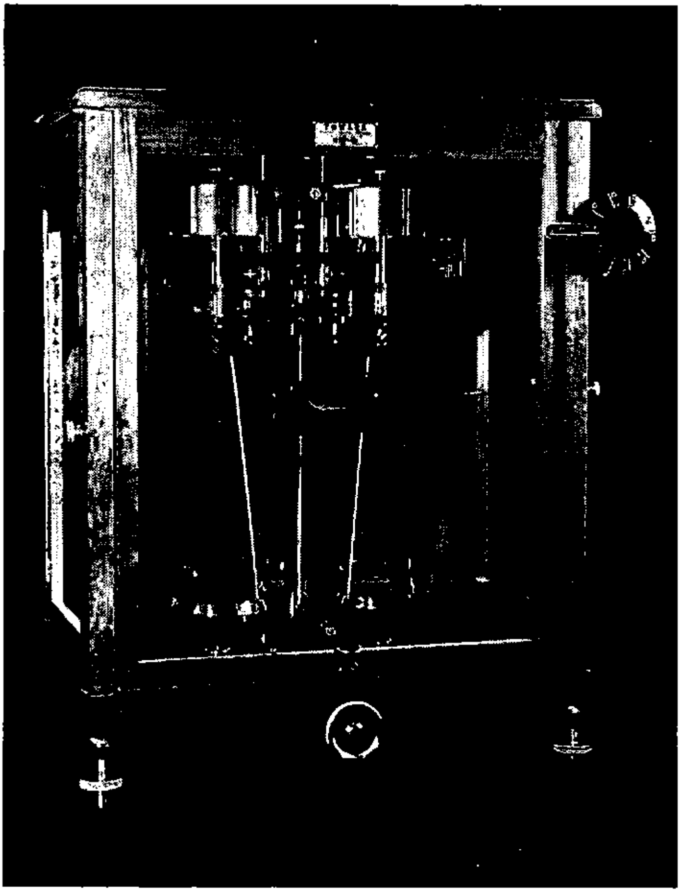

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