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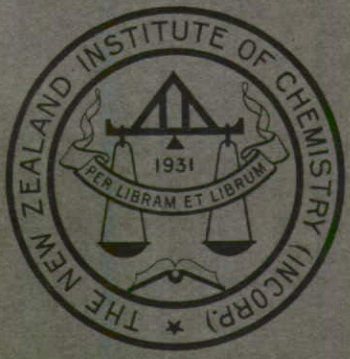
# JOURNAL

## OF THE

# NEW ZEALAND INSTITUTE OF CHEMISTR

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# JOURNAL

OF THE

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JOURNAL

*of the*

NEW ZEALAND INSTITUTE OF CHEMISTRY

## EDITORIAL

This is the first issue of a journal whose fate lies wholly in the hands of the chemists of our Dominion. We publish in this number an account of the Branches of the Institute, together with original papers and general articles. We hope to publish in the future a greater number of original papers, for much research which is done in this country finds its way abroad and some, we fear, buries its head and fails to see the light of day. Now, although it is but natural to seek the wider publicity of the great overseas journals, such journals have their own difficulties of finance and may not always welcome papers from other countries.

New Zealand has not yet forgotten that she was once a colony, and as such entitled to live on the borrowed culture of older countries. But whilst this position is understandable historically, as a permanent policy it is inconceivable. We have our part to play as a unit of world culture and sooner or later, if we are to retain our self-respect, we must play that part. A few years ago the permanence of the high import—high export policy seemed assured: to-day no well-informed section of public opinion looks to such a policy as our future. With a rapidly changing economy, the need of a strong chemical profession is great. We intend to make this *Journal* a strong point of the profession and to play our part in the Dominion of the future.

Our policy is to publish material under the following broad headings:—Papers of original research; Original notes upon analytical methods and laboratory technique; Articles or summaries of general chemical interest; Proceedings of Branches, with condensed accounts of papers read if necessary; Summarised proceedings of the annual conferences; Official notices and statements by Council; General intelligence service; Book reviews and possibly local market quotations for commodities of interest to technical chemists. In allocating space, preference will always be given to original research. It is hoped that the advertisements will serve a useful purpose to members and that members will

respond by patronising our advertisers, mentioning this *Journal* wherever possible.

Notwithstanding several handicaps and the obvious imperfections of this initial issue, the Publications Committee is firmly convinced that our Dominion is now ready to maintain a high-standard chemical journal; and this conviction is confirmed by our Council's instruction to proceed with publication. The credit for success, or the onus for failure, properly belongs to each individual member of our Institute.

We are sending copies of this and future issues to the abstracting bureaux in Great Britain, the United States, France and Germany, and are distributing also to several publishing and technical organisations overseas.

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## OBITUARY.

### PROFESSOR J. K. H. INGLIS.

The death occurred on the 19th September, 1935, of Professor J. K. H. Inglis, professor of chemistry at the University of Otago. Professor Inglis's health commenced to fail over a year ago, but he suffered a relapse, and his death occurred somewhat suddenly and unexpectedly.

Dr. Inglis was born in Christchurch on April 24th, 1877, and was educated at Christ's College Grammar School. He became a student in Canterbury College in 1894, where he had a most distinguished career. He gained the degrees of B.Sc. and M.A., with first-class honours in mathematics and mathematical physics. His papers for the M.A. were among

those that were lost in the wreck of the *Mataura*, so that he had to sit again in Edinburgh, where a special examination centre had been arranged for him. At Edinburgh he took courses in mathematics, natural philosophy and chemistry, and gained the highest award in chemistry, the Vans Dunlop Scholarship. Professor Chrystal, the well-known professor of mathematics in that university, declared him to be one of the ablest students he had ever had and expressed his disappointment that Dr. Inglis had determined to devote himself to chemistry instead of mathematics.

On leaving Edinburgh he went to Leipzig, studying there for one year under Professor Ostwald. A year later he was awarded the 1851 Exhibition Science Research Scholarship and carried out important research work in University College, London, under Sir William Ramsay; on completing the tenure of his scholarship Dr. Inglis became assistant to Sir William. In a testimonial given to Dr. Inglis when he was a candidate for the chair of chemistry in the University of Otago, Sir William Ramsay spoke in the highest terms of his ability in research.

In 1906 Dr. Inglis was awarded the degree of D.Sc. by the University of Edinburgh, and was appointed lecturer and head of the chemical laboratory in the University College, Reading. A year later he was raised to the status of professor and remained in the position for another four years.

In 1912 he returned to New Zealand as professor of chemistry in the University of Otago, and soon attracted to himself a band of eager and enthusiastic students. To these he was a sympathetic and inspiring teacher. Exact, methodical and conscientious, yet invariably courteous and kindly, he elicited their best response and gained their affection and esteem. Notwithstanding drawbacks in regard to staffing and accommodation, he built up a distinguished School of Chemistry in the University of Otago. As a colleague he was most considerate of the claims of others and scrupulously fair. Shrewd and clear in his judgment, he was tenacious when he had made up his mind in regard to a subject, but he had always the highest respect for the opinions of others. In an administrative capacity he was unsurpassed. He saw almost instinctively the correct method of procedure, he could express himself clearly and tersely, could grasp the essentials of a financial question, and was an invaluable member of any committee or administrative body to which he was appointed. The spirit and tradition which he created in his own department in the past twenty-four years are a worthy monument to his ability and character, and a legacy of incalculable value to the University.

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# OFFICIAL NOTICES.

*Unemployment Register:* The General Secretary is keeping a register of all applications received by Branches, and copies are to be posted to Branch Secretaries every three months. Secretaries will also receive a supply of official forms setting out the qualifications of applicants. Members who know of vacant positions may assist their less fortunate fellow-members by acquainting their Branch Secretary with particulars.

*Transfers:* Transfers from one Branch to another can be effected only after the member desiring transfer has paid his current subscription.

*Examinations:* Examination requirements for the Associateship are now being drafted and will be published in the next issue of this *Journal.*

*Change of Address:* Members are earnestly requested to acquaint the General Secretary directly with any change of address.

*Code of Ethics:* The drafts of the Code have been fully considered and a copy of the completed Code has been distributed.

*Branch Meetings:* Attention is drawn to the value of members bringing points of general chemical interest to the notice of Secretaries before each Branch meeting or before the paper for the evening is read.

*This Journal:* All communications regarding this *Journal* are to be made direct to *The Editor.*

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# NOTICE TO AUTHORS.

Members and others are invited to contribute papers of original research, articles or summaries of general interest to chemists, or original notes upon laboratory technique and methods—in this order of preference.

Unless all material submitted for publication is in typescript or very legibly written, the Publications Committee can accept no responsibility for inaccuracies and may reject the manuscripts.

References to the literature are to be arranged as shown in this issue of the *Journal.* Titles of reference-books must be given in full, with edition and date. As to current periodicals, the abbreviations acceptable are both those of the (British) Bureau of Chemical Abstracts or of the American Chemical Society. Lists of these official abbreviations may be found either in the annual index of British Chemical Abstracts or in the 1931 volume of (American) Chemical Abstracts.

Extra copies of authors' papers will be made available if application is made when submitting manuscript and if an undertaking is made by the author to cover the slight extra cost.

The date of the second issue of this *Journal* depends entirely upon the number and quality of papers received in the period immediately following this initial issue. These may be received at any time; a ready response will ensure the early appearance of the second number. Our first objective is to publish half-yearly and, as soon as possible, quarterly.

# THE ESTIMATION OF FLUORINE.

W. DONOVAN.

Fluorine is a very abundant element in nature. Clarke[1] estimates that the terrestrial matter in the half-mile crust of the earth and including the sea, contains 0.1 per cent. fluorine. The number of determinations on which this is based is admittedly small. The best-known fluorine containing minerals are fluorspar, $CaF_2$, cryolite, $3NaF,AlF_3$, and fluo-apatite $Ca_5(PO_4)_3F$. Fluorine is present in the bones and teeth of animals. Authorities quoted by Mellor[2] give 0.20 to 0.65% calcium fluoride in human bones, and 0.33 to 0.19% of fluorine for teeth, the enamel containing up to 2 per cent. of calcium fluoride. Fluorine is also present in brain, blood, and milk of animals. Many mineral waters contain fluorine, e.g., that from White Island, Bay of Plenty (New Zealand). It is also present in fumaroles of volcanic districts.

Methods for the estimation of fluorine are based chiefly on one of three reactions:—

(1) The precipitation as calcium fluoride by addition of calcium chloride to a soluble fluoride.

(2) The bleaching action of sodium fluoride on a solution of titanium salt and hydrogen peroxide.

(3) The production of volatile silicon fluoride when a decomposable fluoride is acted on by sulphuric acid in the presence of silica.

The method of Berzelius is based on the first of these. It is essential that no ammonium salts be present. Sodium carbonate is added to the fluoride solution, then excess of calcium chloride, and the whole boiled for some minutes. The precipitate, consisting of mixed fluoride and carbonate of lime, is ignited to convert the carbonate to oxide, and treated with dilute acetic acid which dissolves the oxide. The fluoride, which is unaffected, is filtered off and weighed. The method is applicable to rocks, and to difficultly decomposable fluorides. The fluorine is brought into solution by fusion with sodium carbonate, silica is eliminated by digestion with ammonium carbonate, and phosphorous by precipitation as silver phosphate in slightly alkaline solution. Full details are given in "The Analysis of Silicate and Carbonate Rocks" by W. F. Hillebrand.[3]

The details of the second method were worked out by Steiger, and modified later by Merwin, the method being known as the Steiger-

Merwin method. It is specially applicable to rock analysis. Alumina, which exercises a marked effect even in small quantities, must be removed. Phosphoric acid, which also bleaches the colour, does not interfere unless present in larger amounts than are likely to be encountered in rock analysis. Two grams of rock powder are fused with 8 grams mixed sodium and potassium carbonates, avoiding high heat. The melt is leached, 3 or 4 grams ammonium carbonate added, and heated on water bath until the ammonia is destroyed. Silica is thrown down by this means, and filtered out along with alumina and ferric oxide. Ammonia must be destroyed, because ammonium sulphate bleaches the final solution. Hydrogen peroxide 3-4ccs., is added and then standard $TiO_2$ containing 0.01 gram $TiO_2$. The solution is neutralised by addition of strong $H_2SO_4$—3ccs. additional $H_2SO_4$ are then added and the solution made up to known volume (100 ccs.). The colour is compared with a similar solution containing 0.01 gram $TiO_2$, 4 ccs. $H_2O_2$ and 3 ccs. $H_2SO_4$. If more than 0.004 gram fluorine is indicated, more acid is added to the test solution, and a fresh solution made for comparison. It is essential to make up a chart for each quantity of sulphuric acid used. Full details are given by Hillebrand[3]. The limit of accuracy for the method is about 0.5 mg. fluorine.

Wichmans and Dale[4], applying this method to distillates containing fluorine used HCl instead of $H_2SO_4$. They found that bleaching effect was at maximum at pH 1.5 and adjusted test solutions and standards accordingly. They claim to be able to determine as little as 0.01 mg. F. by the modified method.

The third method involves the volatilization of the fluorine as silicon tetrafluoride and passing into water, with which it reacts to form hydrofluo-silicic acid.

The fluorine can then be estimated in several ways—

(1) By direct titration.

(2) By precipitation as lead chlorofluoride, using a saturated solution of lead chloride.

(3) By bleaching effect on titanium-hydrogen peroxide solution or on ferric-thiocyanate colour.

(4) By colour reaction with alizarin, or alizarin and zirconium.

The volatilization method is the one most generally used for the determination of fluorine in phosphate rock and in organic and biological material. For these latter the determination is made on the ash. Sharples and McCollum,[5] recommend the following procedure for ashing. They point out that loss of fluorine may be caused if the sample is moist when placed in the furnace, if the ash

is acid, or if a high temperature is employed. Bones and teeth are dried, and ashed direct. Biological materials which give an acid ash (usually those containing a large proportion of phosphate) are treated with a solution of calcium acetate, plus caustic soda if necessary, and carefully dried at 80°C. If boron compounds are present, sodium carbonate must be added to prevent the formation of volatile boron-fluorine compounds. The incineration is carried out in porcelain dishes in a muffle furnace at a temperature not exceeding 500°-600°C (dull red heat).

The method of Wagner and Ross[6] depends for its success on the rigorous exclusion of moisture from the apparatus. The material under examination is ashed, with sufficient sodium carbonate to render it alkaline, and mixed with dry powdered quartz, and anhydrous copper sulphate. It is treated with anhydrous sulphuric acid. Volatile products are expelled by a current of dried gas (air, $CO_2$, $N_2$). They are purified by passing through towers containing respectively silver sulphate and chromic acid, both dissolved in anhydrous sulphuric acid, and then led into distilled water. Any hydrofluosilicic acid formed is determined by titration with decinormal soda, using phenolphthalein as indicator, and checked by precipitation with lead chloride as lead chlorofluoride. The method is fully described in " Official and Tentative Methods of Analysis."[7] The recovery is there given as approximately 90 per cent. The present author, when working with known amounts of fluorine, has not recovered more than 85 per cent.

When only small quantities of fluorine are expected, as in waters, the volatilization method of Boruff and Abbott[8] can be recommended. For waters, a known volume made alkaline with sodium carbonate is concentrated to 50 ccs. and transferred to a 250 cc. or 300 cc. distilling flask. Some glass beads or silica in some form is added (glass beads do excellently), then 20 ccs. concentrated sulphuric acid (or 60% perchloric acid) and water so that the boiling point is about 110°C. Distillation is carried out until the boiling point reaches 130° to 140°C., and the liquid is held at this temperature by adding water through a dropping funnel. 50—75 ccs. of distillate, or more are condensed and collected. (The passing of a current of air through the distilling flask assists in carrying off the distillate and lessens bumping.) The distillate is made alkaline with caustic soda and concentrated to small bulk.

The fluorine in the distillate is insufficient in quantity to be estimated by precipitation, and one of the other methods must be

used. The titanium-hydrogen peroxide decoloration method, modified by Wichmans and Dale[4] may be employed. Provided the solution is free from sulphate, the decoloration of ferric-thiocyanate solution may also be used.[5] Details are given by Foster.[9] Sulphate, however, is almost invariably present in the distillate, and the colour reaction with alizarin is probably the most reliable.

In faintly acid solution fluorine compounds give a yellow colour with alizarin. Thorium compounds give red-brown. Thorium fluoride is practically insoluble in 50% alcohol. The fluorine containing solution is evaporated to about, say, 15 ccs., an equal bulk of absolute alcohol added, 0.5 cc. of sodium alizarin sulphonate, 0.05%, and the solution made very faintly acid with decinormal hydrochloric acid. If fluorine is present, the solution is coloured yellow. Thorium chloride is run in until all fluorine is precipitated, when the solution assumes a brown tint. The thorium solution is standardised against a solution of known fluorine content.

The method is applicable to phosphate rock, which contains from 2 to 4 per cent. of fluorine, also to superphosphate, in which I have found about 1.3 per cent. I have used the method chiefly for the examination of potable waters. Mottled tooth enamel characterised by chalky white patches over the surface of the tooth, and frequent pitting and corrosion of enamel, is said to be caused by the use of drinking water containing three or more parts per million of fluorine.[8] The highest amount in any such water so far examined in the Wellington district is 0.6 p.p.m. present in artesian water from Paraparaumu. Most of the waters contained less than 0.2 p.p.m.

Information as to the effect of fluorine on vegetation and on animal life is rather scant, but the subject is receiving increasing attention.

With the methods now available for the determination of fluorine, and which include a spectrographic method to which no reference has been possible, investigations of its effect in agriculture, and in plant and animal life, should be very fruitful of result.

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# THIOCYANATE CO-ORDINATION COMPOUNDS.

R. J. McILROY, A. C. ESPINER AND A. D. MONRO.

When a solution of a metallic salt is mixed with a solution of potassium thiocyanate containing pyridine or other amines, a precipitate frequently appears, which on analysis proves to be a co-ordination compound of the type $\mathbf{R}(\text{amine})_x(\text{CNS})_n$. Many of these are to be found in the literature; some others are given in this paper. Their formation and stability offer several problems; the value of the co-ordination number is unexpectedly low; the solubility in various solvents differs considerably, whilst their solubility in water offers analytical uses which are well worth investigation.

(1) *Pyridine.*

$Ni(Py_4)(CNS)_2$—(Grossmann[1])—has been investigated by Spacu and Ripan[2] and recommended by them as a means of estimating nickel. The nickel is precipitated by pyridine and ammonium thiocyanate from neutral solution; the precipitate separated by filtration is washed and dissolved in dilute nitric acid. The thiocyanate group is then titrated with silver nitrate solution according to the method of Volhard. This method was tested by means of a solution of nickel sulphate (cobalt free), carefully standardised by the dimethyl glyoxime method; the results were at first low. This was traced to the hydrolysis of the co-ordination compound during the washing of the precipitate. It may be avoided by washing with 3-4% pyridine solution. If this is done either of two methods are possible:

(*a*) To 10 mls. of nickel solution containing approximately 0.06g. of nickel, add 30 mls. of potassium thiocyanate N/10 solution, and 1 ml. of pyridine. Filter cold and wash with water containing 3-4% pyridine until the ferric thiocyanate test is very weak. Dissolve the precipitate in 2N nitric acid and titrate with silver nitrate, using ferric alum as indicator.

(*b*) Using 30 mls. of standard N/10 thiocyanate, precipitate the nickel as before, filter, wash with dilute pyridine and titrate the filtrate by the Volhard method. (Found by dimethyl glyoxime, Ni equivalent to 0.0965N; by method (*a*), 0.0960N; by method (*b*), 0.0967N.) It appears that even with the pyridine wash slight hydrolysis occurs. Too high a percentage of pyridine may re-dissolve the precipitate.

Other compounds of interest include $Cu(Py)_2(CNS)_2$—Spacu[3]—which is soluble in chloroform and of a fine green colour;

$Co(Py_4)(CNS)_2$, which exists in red and blue forms; and $Zn(Py_4)(CNS)_2$, a white substance of low solubility. From the constitutional point of view, two possible formulae may be suggested:—

(*a*) $[MPy_4(CNS)_2]$. Such a compound would tend to be soluble in non-associated solvents.

(*b*) $[MPy_4]\ [CNS]_2$ insoluble in non-associated solvents.

It may be worthy of notice that the solubility of the copper pyridine compound in such solvents as chloroform is much greater than that of the tetra-pyridine class, suggesting that $[MPy_2(CNS)_2]$ of co-ordination number four is able to form where the corresponding six covalent form does not. The best solvent for the $Py_4$ class appears to be acetone, and a sample of the nickel compound recrystallised from acetone resembles copper sulphate in appearance. Morgan[4] has prepared the six covalent tris di pyridyl nickel thiocyanate; apparently the space saving by the union of two pyridine rings makes the higher co-ordination number possible.

(2) *Phenylene diamine.*

Co and Ni *p*-phenylene diamine thiocyanates can be produced by precipitation, the Co precipitate being brown and the nickel green. As the precipitates could not be recrystallised, the material obtained was not of high purity.

Found—Co 20.8, CNS 40.4.

$CoC_6H_4(NH_2)_2(CNS)_2$ requires Co 20.8, CNS 41.0.

Found—Ni 20.4, CNS 39.9.

$NiC_6H_4(NH_2)_2(CNS)_2$ requires Ni 20.7, CNS 41.0.

*m*-Phenylene diamine and *o*-phenylene diamine gave very small precipitates with cobalt salts, and it is believed that the precipitates which did appear were oxidation products.

*o*-Phenylene diamine gave a violet crystalline powder.

Found—CNS 29.7.

$Ni[C_6H_4(NH_2)_2](CNS)_2$ requires 29.8.

*m*-Phenylene diamine gave a gray-green powder.

Found—CNS 29.5.

$[Ni(C_6H_4)(NH_2)_2](CNS)_2$ requires 29.8.

All three phenylene diamines precipitated with *cupric* compounds, but the compounds formed differed widely in colour, solubility and composition. Thus the *ortho-compound* alone is sufficiently soluble in water to be crystallised from it, red-brown crystals being obtained. The *para*-compound was of a deep purple colour, and the *meta*-compound was violet-gray. Of the three, the *meta*-compound is by far the least soluble in water and alcohol, and its extremely low solubility suggests analytical uses. One of us has published a sepa-

ration of copper and cadmium based on the use of the *para*-compound[5]. The compounds are stable in the steam oven and analysis showed that the *para*-compound was of different type from the other two.

*m*-Phenylene diamine di-cuprous thiocyanate:—
Found—Cu 36.72, CNS 33.09, N 15.20.
*o*-Phenylene diamine di-cuprous thiocyanate—
Found—Cu 36.20, CNS 34.09.
$C_6H_4(NH_2)_2$, 2CuCNS requires Cu 36.16, CNS 33.08, N 15.93.

The values found for the *para*-compound were—
Cu 25.16, S 13.65, N 15.50.
$Cu(CNS)C_6H_4(NH_2)_2$ requires Cu 27.8, S 13.90, N 18.26.

Moreover the *para*-compound varies in composition according to the method of preparation, a phenomenon not found with the other two. Apparently some of the copper is in the cupric condition for when prepared in presence of sulphur dioxide the copper percentage may rise to 31.42. As regards structure, the evidence of chelation is not conclusive with regard to the *ortho*-compound. Although acting as a mordant dye, it chars without melting and shows low solubility in non-polar solvents. With the *meta*-compounds chelation is unlikely, whilst the *para*-compound may well have a chain structure analogous to those found by Tschugaeff[6] for nickel ammines.

(3) *o-, m-, and p-Toluidines.*

Nickel thiocyanate co-ordinates readily with *o*-, *m*-, *p*-toluidines, the resulting compounds being of uniform co-ordination number two, as the following analyses show:—

| | | |
|---|---|---|
| *ortho* | Found Ni | 14.70, 14.77, 14.89 |
| | CNS | 29.06, 29.24, 29.73 |
| *meta* | Found Ni | 14.74, 14.71, 14.85 |
| | CNS | 29.48, 29.36, 29.54 |
| *para* | Found Ni | 19.77, 14.84, 14.63 |
| | CNS | 29.68, 29.20, 29.40 |

Calculated for $(Tol)_2Ni(CNS)_2$ Ni 15.0, CNS 29.80.

Of these compounds the *ortho* and *para* were a pale green colour, the *meta* a dark green. The compounds attain constant weight in heating in a steam oven, or drying in a vacuum desiccator and the analyses quoted are done on the dry compounds. The solubilities are as follows (grams per litre of solution)—

| | *Water* | *Alcohol,* | *Acetone* | *Ether* | *Nitrobenzene* | *Benzene* |
|---|---|---|---|---|---|---|
| *o-* | 4.06 | 14.22 | 9.28 | 0.53 | 0.18 | insol. |
| *m-* | 2.25 | 4.61 | 2.41 | 0.26 | very slight | insol. |
| *p-* | 2.15 | 4.55 | 2.38 | 0.26 | insol. | insol. |

From these solubilities it appears that, as the solubility is greatest in associated solvents, the substances are electrovalent. Hence the formula must be $[Ni(Tol_2)](CNS)_2$ and not the covalent $[Ni(Tol_2)_1(CNS)_2]$. This is confirmed by the substances charring, not melting on heating, the *para*-compound (the least soluble of the three) charring at the highest temperature. Other substances which co-ordinate with nickel thiocyanate include:—

Aniline, forming the compound $Ni(aniline)_2(CNS)_2$, a dark green compound similar to the toluidine compounds.

(4) *Benzidine.*

The compound $(C_6H_4NH_2)_2Ni(CNS)_2$—found Ni 16.21, calc. 16.36—a compound of a yellow green colour is insoluble in water, acetone, and of low solubility in other common solvents. Spacu and Macarovici[7] have prepared an analogous cupric compound.

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Stable compounds were not found with dimethyl-aniline, piperidine, diphenylamine, quinoline, phenyl-hydrazine, guanidine, *p*-bromaniline, 2-4-dichloraniline, or *p*-amino-phenol. In some of these cases there was some evidence of a co-ordination precipitate forming, but the compound was too unstable to isolate, and the residue on drying was nickel thiocyanate.

The question of the stability of these compounds is a very interesting one, and one which it seems very difficult to give any reliable guide. It was at one time thought that the dissociation constant of the base might give a clue, but this appears difficult to apply. Volatility must be a factor, but the stability of pyridine derivatives shows it to be by no means the only one. The action of ammonia under suitable conditions causes total replacement of the co-ordinating group by ammonia in three instances tried by us. When pure dry ammonia gas was passed over nickel tetra-pyridine thiocyanate contained in a weighed boat, the pyridine was entirely replaced by ammonia. The boat lost in weight and after two hours at room temperature the weight corresponded to nickel hexammino thiocyanate, and the substance was a beautiful violet colour.

This substance is stable only in an atmosphere of ammonia, and must be weighed quickly, for on standing it gives off ammonia, turns blue and reverts to the tetra-ammino salt. With the toluidine compounds a more elaborate method was tried. The compound was contained in a weighed Gooch crucible, and a stream of ammonia gas passed through the crucible. After the reaction, the displaced toluidine was removed by washing with dry ether and the Gooch weighed again. Aftr two or three treatments constant weight was attained.

| | Weight Substance. | Constant Weight. | Percentage Ammonia. | Calc. for 6 $NH_3$. |
|---|---|---|---|---|
| ortho-tol ..... | 0.1218 | 0.0876 | 37.5 | 36.9 |
| meta-tol ..... | 0.2212 | 0.1536 | 35.3 | |
| para-tol ..... | 0.0680 | 0.0463 | 35.0 | |

Thus the reaction appears to be:—

$$6\ NH_3 + Ni(Tol)_2(CNS)_2 = Ni(NH_3)6(CNS)_2 + 2\ Tol.$$

In these cases the law of mass action must play a part, and the conclusion that ammonia is a stronger co-ordinating agent than the amine is not warranted. Excess of a toluidine, weak though it is, as a co-ordinator will displace di-methyl glyoxime from its nickel compound. It is hoped to attempt experiments in the future in which the effect of mass action is duly allowed for, for from such work some proper knowledge of the relative strengths of various co-ordinating agents can be obtained.

*Summary.*

1. Co-ordination compounds of the metallic thiocyanates have been re-investigated, and some new compounds described.

2. Experiments on the replacement of the co-ordinating agents by ammonia have been carried out.

Victoria University College,
November, 1935.

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# THE NATURE, PROPERTIES, AND ESTIMATION OF IRON IN BLOOD.

EUNICE M. WALL and F. B. SHORLAND.

It has been shown recently that not all the iron in blood is firmly bound in haemoglobin. A certain small portion of the iron in vertebrate blood has been reported as distinct from haemoglobin. This iron fraction existing partly in the plasma and partly in the serum has been designated variously as "loosely bound iron,"[1] "easily split iron,"[2] "inorganic iron,"[3] "non-haemoglobinous iron."[4] Since the nature of this readily attacked iron does not appear to have been described, it is proposed in the present paper to include the unknown iron compound or compounds under the term *non-haemoglobin iron.*

The existence of non-haemoglobin iron in the blood is not in itself surprising if we consider the work of Robert Schneiders.[5] He has shown that the blood-iron of invertebrates is in a labile condition and can be directly indicated by chemical means. As he traced the evolution of animals, he found that with increasing phylogenetic development, the blood iron becomes more firmly bound, until in the case of the most highly developed forms, most of the iron is masked in the compound haemoglobin. The existence of a trace of non-haemoglobin iron in the more highly developed vertebrates might therefore be regarded as a vestigial characteristic. It is also interesting to note that the copper in the blood pigment haemocyanin found in such diverse forms as the earthworm and the crayfish is easily liberated by incubation with dilute hydrochloric acid.[6]

As early as 1898 Abderhalden[7] drew attention to the fact that the blood of certain animals contained more iron than could be accounted for by the haemoglobin content. The values for this excess varied from animal to animal but in general showed a remarkable agreement with the values for the non-haemoglobin iron recently given by Barkan.[2] The subject was again revived in 1925 when Lintzel[8] showed that digestion of the blood either with dilute hydrochloric acid or with a weakly alkaline buffer solution ($H=1.8 \times 10^{-8}$) resulted in the liberation of some 10% of the total iron in the blood. This iron splitting was found to be independent of the action of ferments such as pepsin and pancreatin. Quite independently Barkan[9] separated the non-haemoglobin iron from the haemoglobin iron by incubation with dilute hydrochloric acid followed by ultrafiltration. Later Starkenstein and Weden[10] extracted the non-haemoglobin iron by boiling with 5N hydrochloric acid. The iron thus liberated was

estimated on the protein free filtrate in the usual way. The essential agreement in the values obtained by such a diversity of methods affords striking evidence that vertebrate blood contains approximately 5-10% of the total iron in a different form of combination from that existing in the haemoglobin molecule.

The elucidation of the nature of the non-haemoglobin iron seems to have been left almost entirely to Barkan, and although the particular iron compounds involved are not known, a great deal of information has already been accumulated. The technique usually employed by Barkan consisted of incubating the sample diluted 5 times with distilled water with an equal volume of 0.8% hydrochloric acid at 37°C for a period of 24 hours. After ultrafiltration of the sample, the iron is determined colorimetrically on the filtrate with thiocyanate.

The reaction with the dilute hydrochloric acid is at first rapid and then gradually slows down, finally at the end of 24 hours reaching a constant value. It should be added that under these conditions no test for porphyrin is given, although freshly prepared haemoglobin crystals even after repeated crystallisation contained practically the same amount of non-haemoglobin iron as the blood solution. Curiously enough an older preparation of haemoglobin which had been kept several months under alcohol gave no non-haemoglobin iron.

The values for non-haemoglobin iron amounted to 1.7 mg. per 100 cc. for ox blood. Goose blood gave about the same value, while in the case of the horse and the dog slightly lower figures were obtained. The values for man and rabbit are perhaps a little lower, although Barkan has not yet observed a value for the non-haemoglobin iron below 0.8 mg. per 100 cc. In the case of anaemia the non-haemoglobin iron remains practically constant for varying haemoglobin content.

The question naturally arises as to whether this non-haemoglobin iron consists of a single compound or whether several compounds are involved. A partial answer has already been given by Barkan and Berger.[11] These investigators have shown that if blood is saturated with carbon monoxide, about 65-70% of the non-haemoglobin iron becomes unreactive to dilute hydrochloric acid. This characteristic inhibition with carbon monoxide therefore differentiates the non-haemoglobin iron into two fractions E and E′. E is that portion whose ionisation is checked by carbon monoxide and E′ that portion whose ionisation is unaffected by carbon monoxide. E′ is essentially ionised immediately on incubation with dilute hydrochloric acid, while E is for the most part ionised more slowly under these condi-

tions. Immediately split iron E′ is practically wholly ferric iron, but after one day's incubation as in the case of added ferric iron, is reduced largely to ferrous iron. Starkenstein and Weden[10] have shown that blood solution, i.e., plasma or serum, is devoid of reducing power. This reducing power must therefore reside in the corpuscles.

TABLE I. (Barkan[12]).
Fe. Mol $\times 10^{-6}$ in 1cc. Blood.

| Ox Blood. | Ferrous and Ferric. | Ferric. |
|---|---|---|
| Immediately ..... ..... ..... | 0.125 | 0.125 |
| 1 Day Incubation ..... ..... | 0.4 | 0.075 |

TABLE II (Barkan[12]).
24 hrs. Incubation with 0.4% HCl.
Fe. Mol. $\times 10^{-7}$ in 1cc. ultrafiltrate.

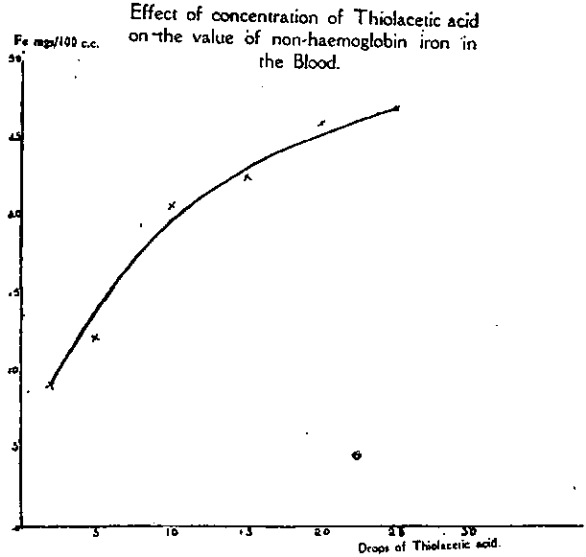
| | Ferrous and Ferric. | Ferric. | Ratio (Ferric / Ferrous). |
|---|---|---|---|
| Present ..... ..... | 0.4 | 0.075 | 0.23 |
| Added $FeCl_2$ ..... | 0.248 | | |
| Total ..... ..... | 0.648 | | |
| Found ..... ..... | 0.65 | 0.125 | 0.24 |

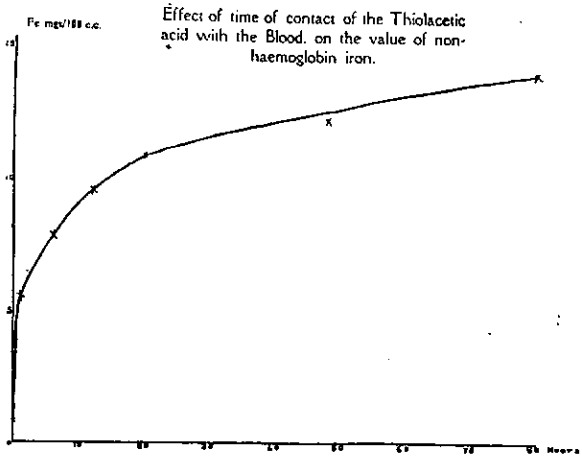
The ratio of ferrous to ferric iron in a given blood seems to be unaffected by the addition of ferrous salts to the blood.

It is by no means proved that the rapidly ionised E′ is inorganic iron, in fact the weight of evidence favours the idea that there is no inorganic iron in blood. Added ferrous and ferric salts behave in the same way as E′ as regards rapid ionisation but unlike E′ the salts remain only in the plasma. In this connection it is curious that added lead salts penetrate the blood cells (Behren and Pachur[13]). This distinction of E′ from inorganic might be considered trifling were it not for the fact that the non-haemoglobin iron is further distinguished from inorganic iron by its failure to be absorbed on freshly prepared aluminium hydroxide (Barkan[14]).

The iron content of the serum is normally 0.05 to 0.18 mg. per 100cc. This iron belongs to the type E′, the ionisation being unaffected by carbon monoxide. Although plasma iron is acid soluble it is not ultrafilterable prior to acidification and is therefore probably in the form of a suspension. According to Langer[15] the normal value of ferric iron was 0.11 mg. per 100 cc. In case of fevers this value was found to be much increased (up to 0.23%). Similarly a great increase was found in pernicious anaemia.

Quite recently and with little or no justification Tompsett[3] has used thiolacetic acid to estimate what he terms the inorganic iron of blood. Not only is the reagent he uses unsatisfactory for this particular purpose but the use of the term inorganic iron to describe the non-haemoglobin iron is scarcely accurate. It is true that the




non-haemoglobin iron after treatment with thiolacetic acid is transformed into inorganic iron but it is also equally true that the iron of haemoglobin is rendered ionic after treatment with concentrated sulphuric acid and potassium persulphate as in the case of the Wong method for the estimation of total iron.

Tompsett[3] found that if the blood were first treated with thiolacetic acid the added inorganic iron could be recovered in the

trichloracetic acid filtrate. Since, however, we have shown that thiolacetic acid slowly liberates from combination more than 20% of the total iron in blood it is clear that the method proposed by Tompsett cannot be valid. The results obtained by his method depend on the time the thiolacetic acid is in contact with the blood and also the concentration of the thiolacetic acid as shown by the accompanying graphs.

For the estimation of the "non-haemoglobin" iron the following method was finally adopted. Pipette 2cc. of whole blood and 2cc. of 4% sodium pyrophosphate into a test tube, stir well. After 15 minutes mix in 2cc. of 20% trichloracetic acid and filter through an iron free No. 40 Whatman paper. Take 2cc. of the filtrate and 1cc. of *a-a'*-dipyridyl solution. Add solid sodium hydrosulphite a few grains at a time until the maximum red colour is produced. Compare 1cc. of the solution with 1cc. of standard iron solution in a Duboscq colorimeter. The $\frac{12M}{10,000}$ *a-a'*-dipyridyl solution in 5N ammonium acetate ensures the required pH value.

TABLE III.

The Recovery of Inorganic Iron Added to Blood.

| Sample. | Mg. of Fe. per 100cc. in blood. | 1 mg. of Fe. per 100cc. added to blood. | Recovery of added inorganic iron mg. per 100cc. |
|---|---|---|---|
| A | 0.33 | 1.33 | 1.00 |
| B | 0.38 | 1.35 | 0.97 |
| C | 0.72 | 1.70 | 0.98 |
| D | 0.31 | 1.28 | 0.97 |
| | | 2 mg. Fe. added. | |
| A | 0.87 | 2.86 | 1.99 |
| B | 0.51 | 2.50 | 1.99 |
| C | 0.86 | 2.85 | 1.99 |

In order to discover whether added inorganic iron could be recovered quantitatively, the iron was first determined in the whole blood according to the method described above. Next 1cc. of blood was well mixed with a stock solution containing 1 or 2 mg. of Fe per 100 cc. and the iron determined as before. The Table III shows that the added iron may be quantitatively recovered.

Tompsett[16] has shown that the pyrophosphate radicle forms a complex with iron in the same way as the thiolacetic acid. It was thought necessary therefore to determine whether the pyrophosphate might not also slowly liberate the iron from haemoglobin.

TABLE IV.

The Influence of Time on the Liberation of Iron in Blood with Sodium Pyrophosphate.

| | Time. | Non-haemoglobin Iron Reported mg. per 100cc. |
|---|---|---|
| Sample A ..... | 10 minutes | 0.82 |
| " | 20 " | 0.83 |
| " | 5 " | 0.70 |
| Sample B ..... | 20 " | 0.70 |
| " | 50 " | 0.69 |

It is clear that time has no appreciable effect on the determination. As most of the blood samples analysed in this Laboratory could not be obtained in a perfectly fresh condition, it was necessary to measure the effect of ageing of blood on the non-haemoglobin iron. In Table V below, some figures are given for the non-haemoglobin iron in fresh blood and for the same blood after standing for three days.

TABLE V.

| Sample. | Fresh blood. mg. per 100cc. | Blood 3 days old. mg. per 100cc. |
|---|---|---|
| A ..... ..... ..... | 0.70 | 0.28 |
| | 0.72 | 0.32 |
| B ..... ..... ..... | 0.81 | 0.29 |
| | 0.82 | — |
| C ..... ..... ..... | 0.89 | 0.33 |
| D ..... ..... ..... | 0.86 | 0.32 |
| E ..... ..... ..... | 0.97 | 0.42 |

It is evident that the non-haemoglobin iron must be determined on the fresh blood. The value obtained by this method corresponds very closely with the value obtained with thiolacetic acid when the test is carried out in the shortest possible period of time.

Estimations of non-haemoglobin iron have also been made by the method of Starkenstein and Weden.[10] In this case the value obtained for the iron increases with the age of the blood.

In general the methods for the estimation of total iron were much more satisfactory than the methods for the estimation of non-haemoglobin iron. The following method from the point of view of convenience and simplicity seemed to offer advantages over pre-existing methods. Take 0.5cc. of whole blood in a pyrex test tube. Add 1.5cc. concentrated sulphuric acid and 0.5cc. of redistilled nitric acid. Heat cautiously adding nitric acid, a few drops at a time until the liquid is clear and free of nitrous fumes. The cooled solution is diluted with distilled water and made up to 25cc. in a standard flask. 1cc. of this solution is treated with 1cc. of

*a-a'*-dipyridyl reagent in the tube of a Lovibond tintometer. Sodium hydrosulphite is now added grain by grain with continuous shaking until the maximum colour is produced. The colour is then read off and the iron content evaluated from a graph.

*Summary.*

Various methods for the estimation of iron in blood have been considered. Those for the non-haemoglobin iron are not altogether satisfactory. They suggest that there may be two types of non-haemoglobin iron. Also the variation in the values of non-haemoglobin iron seems to have no correlation with the variation in the values for the total iron of blood.

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# A SUMMARY OF CERTAIN MICROCHEMICAL METHODS

T. A. THOMSON.

One of the most noteworthy advances in recent chemical practice is the widespread adoption of microchemical technique.

This paper is intended to indicate in a general manner the theoretical foundations of certain microchemical manipulations.

*A.—Complex Formation.*

Stimulated by the work of Werner an intense study of many complex substances has been made. From the microchemical point of view the formation of inner complexes by the combination of metals and oximes is exceptionally important. The well known tests for nickel with dimethyl glyoxime or *a*-Benzil dioxime have been known

for about 30 years, but their broader significance was overlooked, until Pfeiffer and others[1] brought forward the conception of specific organic groupings. A large number of compounds containing the group—

were investigated, and it was found that these formed insoluble compounds with Nickel salts in ammoniacal solution. The scope was enlarged and two specific groupings for Copper and one each for Bismuth, Silver, Thallium, Ferrous Iron, Zirconium, were known by 1931.

Examples of the reagents used are:—

Dimethyl glyoxime, *a*-Benzil dioxime } for Nickel.
*p*-dimethylaminobenzylidinerhodanine for Silver.
*a*-*a*'-Dipyridyl for Iron.
*a*-Benzoin oxime, Salicylaldoxime } for Copper.

Many of these reagents are of great value in gravimetric work as:

(1) The final product contains a small percentage of active compound (generally 5-15%). This leads to perhaps a tenfold increase in accuracy as 10 mg. of Copper give approximately 12.5 mg. Copper oxide, while 10 mg. Copper would give perhaps 100 mg. of Copper oxime complex. (If an ordinary analytical balance is used the increase in accuracy is readily appreciated).

(2) The high specific action of the reagents tends to eliminate all group separations and so effects a distinct gain in time and accuracy, e.g., *a*-Benzoin oxime[2]; Salicylaldoxime[3].

*B.—Formation of Deeply Coloured Substances.*

(1) *Colorimetric Possibilities.*

(*a*) The violet colour of an alcoholic solution of 1.2.5.8-tetahydroxyanthraquinone is changed to cornflour blue by the presence of magnesium and alkali. This reaction may be made to detect .001 $\gamma$ Magnesium where $\gamma = 1/10^6$ gm. Colorimetric estimations are said to be accurate to 1.2%.

(*b*) The violet colour of Ferric salts with sulphosalicylic acid is changed to intense orange by ammonia.

This reaction is specially suited for colorimetric determination of ferric or ferrous iron as the following figures show:—

| Iron Present mg. | Iron Found mg. |
|---|---|
| .0300 Fe | .0301 |
| .0500 Fe | .0503 |
| .0800 Fe | .0805 |
| .0030 Fe | .0031 |
| .0340 Fe | .0341 |
| .0900 Fe | .0901 |

The accuracy is high for this kind of work[4].

(2) *By the Absorption of Dyes on Precipitates.*

(*a*) Test for magnesium in tap water.

To one c.c. tap water add 1 drop of .01% *p*-nitrobenzene-azo-*a*-naphthol and 2 drops .25N NaOH. Change from violet to blue indicates more than .19γ (Weisselberg[5]).

(*b*) Test for Aluminium in presence of other ions. Place one drop of test solution on dry ferrocyanide paper. This removes Iron, Chromium, etc. To centre of spot add one drop of water to drive the aluminium solution out from any precipitated ferrocyanides. To the edge of this zone add one drop of .1% alcoholic solution of alizarin, and expose to ammonia to form the lake. The purple ammonium alizarate is destroyed by adding 90% acetic acid, when a persisting red colour indicates more than .15γ Aluminium.[6]

*C.—Catalytic and Induced Reactions.*

It is well known that many catalytic and induced reactions are of extraordinary sensitivity.

A test for Bismuth (Feigl[7]) employs an interesting mechanism. Lead salts are reduced by alkali stannite very slowly at room temperature—

$$Pb(OH)_2 + Na_2SnO_2 = Pb + Na_2SnO_3 + H_2O.$$

A trace of Bismuth accelerates this reaction. To the test add 1 drop sat. solution of lead chloride and 2 drops of Alkali stannite (equal volumes of 25% Sodium hydroxide and 5% Stannous chloride solution). Immediate appearance of brown or black metallic lead indicates more than 1.0γ Bismuth.

A very complete paper on quantitative and qualitative reactions involving catalysis appears in Lucas and Grassner.[8]

*D.—Oxidation.*

Benzidine on autoxidation yields an intense blue oxidation product.[9]

This has been used as a generic test for oxidising substances, one example of which may easily be followed:—

Place one drop of the neutral test solution on a filter paper and add a drop of .05 N. alkali. Then add one drop of .05% solution of Benzidine in 10% acetic acid. Appearance of blue colour indicates not less than .15γ Manganese.[10]

By the employment of 100 cc of test solution manganese in tap water has been demonstrated, at a dilution of 1/125,000,000

*E.—Reduction.*

One of the products of the action of dilute nitric acid on Brucine is Kakotheline. In acid solution Stannous chloride can reduce Kakotheline to a violet compound of unknown composition. Most reducing salts including ferrous salts, cannot do this. Limit of identification= 2γ Tin.[11]

*F.—Indirect Methods.*

The well graded character of Chlorine, Bromine, and Iodine presents difficulties in their separation. However, the following reaction of chlorides is peculiar:—

$$H_2Cr_2O_7 + 4\ HCl = 2\ CrO_2Cl_2 + 3\ H_2O.$$

The chromium oxychloride is generated in a small crucible and is absorbed in a drop of water on the under side of a microscope slide which covers the crucible.

After a short time the water is tested for chromium, by the delicate so called Cazeneuve reagent (Diphenylcarbazide). The limit of identification is 1.5γ chloride (Kapulitzas, see Feigl[12]).

*G.*

In metallurgy it is frequently necessary to examine the homegeneity of an alloy. A very useful method is the following:—

On a smooth surface of the test material is placed the required test paper which is then moistened with electrolyte. Over this is placed a suitable metal plate which is attached to the negative pole of a cell. The circuit is completed by connecting the test material to the anode and after the current has been passed for some time characteristic patterns will indicate the location of the metal under investigation.

For such purposes suitable papers are given:—

| Metal. | Test Paper. |
|---|---|
| Iron | Ferrocyanide |
| Nickel | Dimethylglyoxime |
| Cobalt | Pot. nitrite and Pot. thiocyanate |
| Copper | Ferrocyanide |
| Lead | Pot. chromate |
| Cadmium | Hydrogen sulphide[13] |

*H.—Applications as Indicators.*

*Titration of Sulphates.*—Sodium rhodizonate gives with Barium a red precipitate[14] and thus can be used as a sensitive internal indicator in the titration of sulphate with standard solutions of barium salts.

*I.*

Lack of space precludes any but the most scanty reference to " spot " testing for organic groups, but it is desirable to include Feigl's Sodium azide—Iodine reaction.

The reaction

$$2\ NaN_3 + I_2 = 2\ NaI + 3\ N_2$$

takes place infinitely slowly but it is catalysed by the following groups:—

$$= C = S$$

and $= C-SH$

The following are a few of the substances which may be recognised, together with the limits of identification:—

| | |
|---|---|
| Thiourea | .005γ |
| Thioacetic acid | .0003γ |
| Rubeanic acid | .03γ |
| Rhodanine | .003γ |
| Potassium ethyl xanthate | .04γ |

(Feigl has indeed worked out a very complete scheme for a great number of other organic groupings—alcohols, amines, etc.)

*Methods of Qualitative Manipulation.*

(1) Employment of filter paper.

The capillary properties of the paper can produce filtration in the plane of the paper, e.g., the above-mentioned test for Aluminium.

Moreover, the holding back of an immediately precipitated compound in the centre of the "spot" frequently allows subsequent precipitation of other compounds under different conditions to be observed.

Impregnate a paper with dithio-oxamide (so called Rubeanic acid) and dry. On it place one drop of acetic acid solution which may contain Copper, Cobalt and Nickel. In the centre appears a green spot due to copper, surrounded by two distinct zones—a purple ring due to Nickel and a brown one due to Cobalt. Hence we may detect Copper, Cobalt and Nickel simultaneously.[15]

(2) The impregnation of gelatine with reagents decreases the speed of diffusion and causes a sort of " frozen " reaction which is very characteristic.[16]

(3) In many reactions a considerable depth (1—2 cms) of test solution is required to render visible any colour produced. By using a vertical capillary 3 cm long and .5 mm internal diameter, viewed

longitudinally by a low power microscope, a marked increase in sensitivity is obtained.[17]

The author of this paper has used this principle to extend the limit of the very sensitive *p*-nitrobenzene-azo-*a*-Naphthol test for Magnesium (.19γ) to .005 to .01γ at similar dilutions.

I regret that I have made little or no reference to the microscopical work of Emich and Behrens, the gravimetric work of Emich, or the fields of organic and biochemistry which have all been enthusiastically explored in the last thirty years.

In conclusion I should like to express my gratitude to Doz. Dr. Fritz Feigl, of Vienna, and Prof. Dr. Friedrich Emich, of Graz—the two masters of modern microchemistry. I beg to acknowledge their kind advice and assistance in the preparation of this paper.

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## AUTO-OXIDATION AND ANTIOXIDANTS.

J. M. BUTLER.

The study of catalysis has proved to be one of the most interesting and fruitful fields of chemical investigation. In view of the importance of the discoveries in biochemistry and agricultural chemistry of substances which are remarkably active and effective even in small concentrations the attention of the chemist must naturally be drawn to work in other fields where similarly interesting and valuable results are being obtained. The subject of autoxidation and antioxidants is one which is rapidly gaining prominence, and the object of this paper is to give a brief resumé of some of the more important aspects.

During the Great War, acrolein ($CH_2$=CH. CHO) was required in large quantities in France for the manufacture of poison and irritant gases (allyl isocyanide, etc.). This substance, which appears at first sight to be easily prepared, actually proved to be most difficult to obtain in large quantities, and prior to 1915 the largest single quantity successfully prepared was some 2½ kgs. used in Fischer's famous synthesis of sugars. In the presence of the merest trace of oxygen the limpid liquid acrolein polymerises in a short time to the dark brown resin disacryl, a useless stable product.

Two well known French professors, Moureau and Dufraisse, set to work on the problem and discovered quite a number of substances which even in a 0.1% concentration were able to retard the polymerisation, and by using hydroquinone 0.1% they were able to proceed with manufacture of acrolein even up to 1½ tons per day.

From 1920 onwards they continued their researches and showed that auto-oxidation is a common phenonemon and that its acceleration or retardation is a matter of considerable importance. During their earlier work they studied benzaldehyde and styrene as well as acrolein, and postulated the following:—

(1) The most effective antioxidants are substances which are themselves easily oxidised. (Phenol, pyrogallol, etc.)

(2) The effect of the catalysts on the rate of oxidation depends on the conditions. ($MeNH_2HI$ acts as an antioxidant towards benzaldehyde but as a pro-oxidant towards styrene.)

(3) The more easily oxidisable a substance the greater its effectiveness as an antioxidant.

They accumulated a great deal of valuable data using a very simple type of oxygen absorption apparatus, and, broadly speaking, their work has paved the way for later experimenters. In a review of their work[1] they have made further generalisations, most of which are generally accepted, and are worth noting.

1. Power of preventing oxidation must belong to oxidisable substances and exclusively to such.

2. Activity localised in oxidisable portion of the molecule.

3. There should be a definite relationship between the catalytic activity and the ease of oxidation.

4. Under suitable conditions every oxidisable substance should be able to act as an antioxidant.

*Theories of Auto-oxidation.*

Auto-oxidation reactions may be recognised by the following facts:—

(1) They are autocatalytic, hence the increasing speed of oxygen absorption after an initial period of seemingly little action (induction period).
(2) They are susceptible to positive and negative catalysts.
(3) They often induce the oxidation of other substances unaffected by free oxygen.
(4) They often induce the polymerisation of auto-oxidants.
(5) They are sometimes accompanied by chemi-luminescence.

Various theories to account for the action of antioxidants in the negative catalysis of auto-oxidation have been advanced. Moureau and Dufraisse[2] assume the oxidation of the antioxidant and its return to its original state, but this is severely criticised from extensive experimental evidence owing to the fact that the oxidation of the anti-oxidant actually takes place, though slowly perhaps, during the induction period.

Backstrom[3] states that during the period in which it protects a substance, the antioxidant is slowly oxidised, and that this oxidation is an induced reaction.

The most widely accepted theory is the Chain Theory of Christiansen. In a bimolecular reaction unless it is immeasurably fast only a fraction of the pairs of molecules which collide are able to react. Those reacting are ones whose energy exceeds a certain value. Just after reaction the molecules of the reaction products possess energy greatly in excess of the mean energy at the temperature considered. Now these very " hot " molecules have sufficient energy to activate at their first encounter and so on. In negative catalysis " foreign " molecules are able to take up this excess energy from the " hot " molecules, thus slowing up the reaction. Milas[4] has stated the theory in a slightly modified form. In auto-oxidation reaction there is the preliminary addition of $O_2$ atoms containing molecular valence electrons with subsequent formation of highly metastable peroxides having a high energy content. These peroxides may transfer their excess energy to other molecules and thereby initiate new reaction chains by reverting to ordinary peroxides or by intermolecular rearrangements with subsequent splitting off of $H_2O_2$ or of organic peroxides.

*Application of Antioxidants (Inhibitors) and Tests.*

*Rubber.*—(1) Auto-oxidation takes place during the milling of rubber and the character of the change depends largely on the history of the sample, as there are naturally occurring antioxidants in latex which are reinforced by the absorption of pyrocatechol and wood tar derivatives during the smoking or curing process.

(2) During vulcanisation certain organic accelerators are used, such as diphenyl guanidine, tetramethyl-thiuram, mercapto-benzothiazole, etc. These substances act as antioxidants to the vulcanised product.

(3) Direct inclusion of antioxidants.

Rubbers compounded with antioxidants show much greater stability on shelf ageing tests than exactly similar rubbers without them: the superiority is also shown from results in oxygen pressure bombs and under service conditions.

*Paints.*—The drying of paints and drying oils constitutes one of the most generally well known cases of auto-oxidation, and as the products of oxidation are accelerators the oxidation is autocatalytic. There is a distinct field for research to find substances which while at first inactive are so acted on by ultra-violet light that they liberate antioxidants in the drying film and thus prevent the film from becoming too brittle or lifeless.

*Coal Tar.*—The drying and hardening of coal tar is due to the combined effect of the loss of the more volatile constituents by evaporation and of the auto-oxidation of the oxidisable heavier content. The addition of suitable antioxidants can aid to a considerable extent in the prevention of brittleness and lack of ductility in the pitchy residue.

*Gum in Cracked Motor Spirits, Benzol, etc.*

Gum in motor spirits may be defined as the resinous polymerisation product formed from unstable unsaturated hydrocarbons on oxidation. The presence of gum in anything but very small amounts is generally agreed to be harmful, and a great deal of excellent research has recently been carried out with the object of minimising its formation by the use of anti-oxidants.

Ramsay[5] by using a stainless steel bomb in which the motor spirit is kept in contact with oxygen and measuring the induction period as the time taken for a definite pressure drop due to the absorption of oxygen to occur, has shown that the $O_2$ pressure plays a relatively small part.

Actually $I_{\text{atm. air}} = I_{\text{oxygen 100 lbs. in}^2} \times 1.41$, where I = induction period.

The temperature, of course, has a marked effect, and Ramsay gives the relationship

$\log I = a - bT$ where T = abs. temp. a and b are constants.

Rogers, Bussies and Ward[6] used another type of apparatus for measuring the oxygen absorption in which the drop in pressure is recorded and plotted against the time.

It is now accepted that the induction period and the period of storage stability can be roughly correlated; actual storage conditions vary so much that no quantitative relation is attempted.

The rate of formation of gum or of "potential gum" during quiet storage in large tanks depends on the rate of solution of oxygen, but the protection afforded by maintaining a low oxygen supply is not entirely a practical insurance against gum trouble (cf. acrolein). Tests with acrolein have proved that it is oxygen combined with acrolein and not free oxygen that is the active agent in promoting polymerisation, since the change occurs even when acrolein is freed from air or oxygen by evacuation and also since a non-volatile catalyst containing oxygen is found in the residue on distillation.

Antioxidants have proved their efficiency in obtaining gum stability in cracked motor spirits, and their value to the petroleum refining industry promises to be considerable. Briefly, the advantages accruing from their use are as follows:—

(1) They reduce and in many instances eliminate entirely acid treatments.
(2) Redistillation is often avoided.
(3) Equipment and maintenance charges are lowered due to the elimination of acid corrosion.
(4) They prevent gum formation.
(5) They prevent material loss of initial anti-knock value.

*Chemical Composition and Antioxidant Efficiency.*

Lowry[7] has shown that a relationship exists between the ease of oxidisability of the antioxidant as measured by its oxidation-reduction potential and its efficiency as measured by the increase in the induction period. Aromatic compounds are generally much superior in antioxidant efficiency than are the corresponding aliphatic types. Polyphenols and amino phenols are the most effective.

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# HUMIDITY-CONTROL; OZONISATION; DE-AERATION OF FRUIT JUICES—SOME LABORATORY IMPROVISATIONS.

J. B. HYATT.

While it is true that properly designed commercial apparatus may now be obtained for almost any laboratory purpose, there are many reasons why such equipment is not always available to the worker when required. The need may arise in a hurry; the magnitude of the operation may not justify a large outlay, or the requirement may be of a transitory nature. It is with experience of meeting such contingencies that the writer proposes to describe a few easily assembled pieces of equipment which have been found, in many cases, to operate quite as successfully as the commercial article.

## 1.—THE PRODUCTION AND CONTROL OF HUMIDITY IN SMALL-SCALE AIR-CONDITIONING.

In connection with experiments in the ripening of fruit, it was recently necessary to provide a humidifier with variable automatic control. This was first applied to a small cabinet, and took the form of an evaporator associated with relay and hair-control. Following is a description of the three units.

(*a*) *Humidifier*:

A square piece of flannel (about 9″ × 9″) is pierced at its centre by a hole of sufficient diameter to admit the metal base of a 60 watt carbon filament lamp. The assembly is then suspended from a lampholder and flex in such a way that the surplus flannel, draping the lamp, is well immersed in a bowl of water. The lamp itself may be partly immersed without fear of breakage, but sufficient area of flannel should be left exposed to afford an adequate evaporative surface. The level of water should not be allowed to fall unduly low, though a quite wide margin is permissible.

(*b*) *Controller*:

A human hair, of maximum length, is suspended as a plumb-line, the plummet being provided with a platinum contact and connected to one terminal of the control circuit by means of a very flexible lead. (Head-telephone flex, stripped of all insulation, is usually sufficiently flexible.) The other contact, also of platinum, is set in the surface of a levelling-screw, which bears on its casting the second terminal of the control circuit.

Selection of humidity-level is effected by adjusting the levelling-screw. Control within 2% relative humidity is easily possible under constant temperature conditions. When the temperature is altered, however, it becomes necessary to re-adjust the humidity control. Before putting into service, this instrument should be allowed to remain undisturbed for a week in order that the hair may accommodate itself to the weight of the plummet. (Fig. 1.)

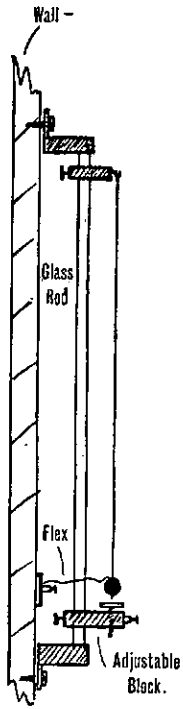


FIG. 1

(c) *Relay*:

When the heating element is not above a wattage of about 100. an ordinary low-tension relay may be used, with a suitable condenser connected across the output contacts. In emergency, even the coils and armature of an electric bell may be pressed into service. In the case of the more powerful humidifying unit to be described later, it is necessary to employ a properly designed relay capable of handling 2 KW. The writer used an instrument of the rocking mercury-tube type.

*Modification of the Above Plant for Conditioning a Small Room*:

It became necessary, later, to condition a small room measuring 10′ × 10′ × 10′, and provided with forced ventilation. The hair control was retained in its original form, but much more powerful

lamps were used for the evaporators, associated with the commercial relay referred to above. The evaporating unit (provided in triplicate) consists of an old-type carbon filament radiator globe covered with loose cotton wicking (replacing the flannel jacket used in the small-scale plant), and, mounted horizontally over a sink, with the ends of the wicks depending into the water. In order to counteract a tendency to float, the ends of the wicking should be weighted, and at least six inches of wick material should be immersed.

The method of preparation adopted by the writer was to cut a large number of fifteen-inch lengths of the wicking, and lay them, closely-packed, over the circumference of the radiator-globe. The weighting may be conveniently effected by compressing the dependent ends of the wicks between two horizontal glass rods, secured together with elastic bands. The whole is then mounted horizontally in a lampholder so orientated as to extend the complete unit over the sink. A support is necessary for the free end of the globe, and the whole system should be earthed. Before putting into operation, the whole of the evaporative surface should be thoroughly wetted, after which saturation is readily maintained by capillarity. In a case like this, where evaporation is rapid, a constant water-feed should be provided to the sink. The circuit is the same as for the small-scale plant, except that, as a rule, no battery will be required. Most commercial relay-panels provide the necessary low-tension voltage from the mains supply.

## 2.—AN OZONISING CHAMBER FOR SMALL-SCALE EXPERIMENTS.

It was recently desired to provide equipment for exposing small quantities of fruit to ozone at low concentrations. A large glass desiccator was selected to contain the fruit, and an ozonising unit, constructed as follows, was inserted through the orifice which would normally carry the desiccator stop-cock. Provision was made for slow ventilation.

*Details of Construction* (Fig. 2):

An open glass tube (A) of length depending on the depth of the desiccator, and of internal diameter about ½", carries, concentrically and internally, a longer tube (B) of about ¼" *external* diameter. The mounting is merely a cork bored to take the narrower tube, and fitting the wider. The tube (B) is sealed at the bottom, reaches to within about 1" of the open end of (A), and protrudes at the top for about 3". A larger cork, selected to fit the orifice in the desiccator-lid, is bored to take the projecting portion of (B),

and is forced over the latter. This cork also carries two additional small holes for receiving the air inlet and exhaust. The outer

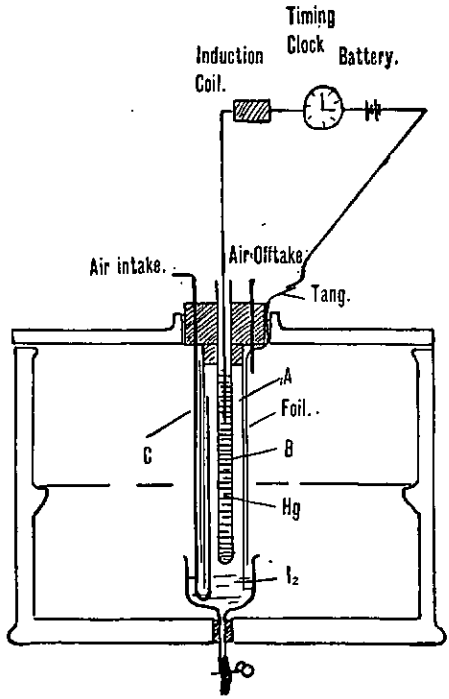


FIG. 2

tube (A) is now covered smoothly with tin-foil, leaving a tongue of foil which protrudes over the edge of the large cork. The foil should not extend to the bottom of (A), but about one inch of clear glass should be left. The foil is bound into place with a layer of asbestos paper, which is secured, in its turn, with asbestos cord. These latter coverings are, for the sake of simplicity, omitted from the sketch.

Next, a long U-tube (C) is made from fine thin-walled tubing of about 1/16″ internal diameter. One limb should be about 4″ longer than the other, and the U-bend should be as sharp as possible. The long limb is inserted through the air-intake hole in the large cork, and the shorter limb is intruded up the $\frac{1}{8}$″ annular space between the two major tubes. It should extend nearly to the small cork, and, for convenience, has been drawn as a solid line in the sketch. The central tube (B) is now filled with mercury to a depth equivalent to the effective length of the outer tube (A), and a bare copper wire is pushed down into the mercury. A short right-angle bend, piercing the air-exhaust hole in the large cork, completes the assembly. The protruding copper wire, and the foil tongue, constitute connections to an induction-coil.

The complete unit is held in position in the desiccator by means of the large cork. Connection is made to the induction coil through a timing-clock equipped with pegs providing electrical contacts. By spacing the pegs in a suitable manner, the rate of ozonisation, and therefore the ozone concentration within the desiccator, may be controlled. A slow stream of air is drawn through the apparatus by means of an aspirator.

*Evaluation of Ozone Concentration:*

In the case under consideration, the concentration was checked from time to time, and any irregularities compensated by adjustment either of voltage, or of peg-spacings, or both. The method of evaluation was as follows.

A central hole was drilled in the base of the desiccator for the purpose of receiving a Gooch adaptor, provided with pinch-cock as illustrated. A measured excess of alkaline potassium iodide was pumped into the cup thus formed, and the pinch-cock closed. The apparatus was then left for half-an-hour, during which time the ozonised air was, of course, bubbled through the iodide solution. The latter was then drawn off by means of the pinch-cock, and titrated against standard thiosulphate. Knowing the speed of ventilation, the concentration within the desiccator was readily calculated.

## 3.—APPARATUS FOR THE DE-AERATION OF FRUIT-JUICES.

The writer has had occasion, from time to time, to make certain juice-preservation trials which have involved the de-aeration and bottling of the juice with a minimum exposure to room-air. The following assembly (fig. 3) has been utilised with success. The diagram is self-explanatory.

A trapped filter-pump (not shown) is connected to (A) and the three-way cock (H) is set to communicate with the filter-flask (B). The vacuum should be built up, reading on guage (C), to its maximum value; the stopcock (D) on the separating-funnel (E) being, of course, closed. The fruit is halved and burred, and the juice is introduced at atmospheric pressure to (E) through the loosely-fitting Buchner funnel (F). The juice from each half is *immediately* drawn into (B) by operating (D). This should, however, be done with a little caution, so that the continuous draught from the pump may prevent the charge from being prematurely drawn into the preserving-bottle (G) (also under vacuum). No air, of course, must be admitted *via* (D) at this stage. The whole process is repeated until excess juice is present in (B).

The assembly is left under vacuum until all frothing has subsided. Stopcock (D) is opened a mere shade so as to allow the juice to trickle slowly into (G). The complete closing of (D) will effect a *gradual* stoppage of the stream, and this lag must be allowed for when (G) is nearly full.

When the stream has been stopped in this manner, the three-

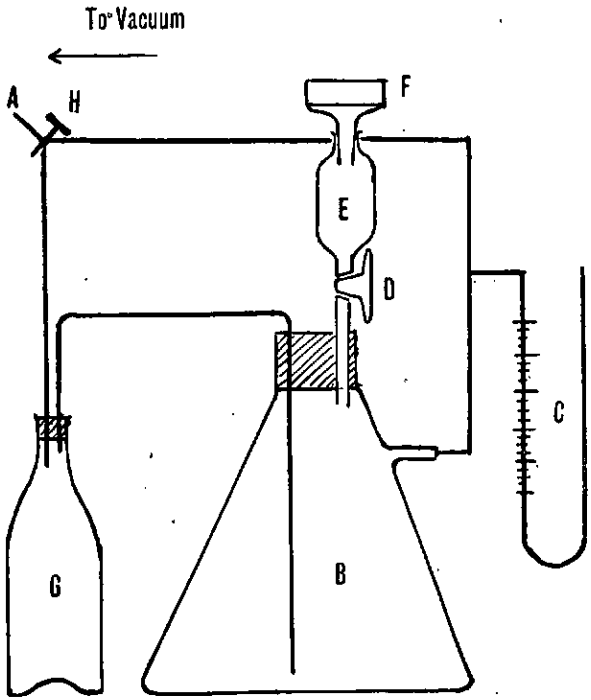


FIG. 3

way stopcock (H) is placed in an intermediate position (all channels closed), and the vacuum is released at the pump. The whole system, however, is still under vacuum, and this is released, *via* (G), by carefully turning stopcock (H) to communicate with (G). The release must be very gradual. The bottle (G) is then removed, the neck slightly heated, and capped. Sterilization of the apparatus may be effected by boiling water in (B), and drawing steam through all tubes by manipulating the stopcocks appropriately.

*Acknowledgments.*—The writer wishes to thank Mr. W. Donovan, Director, Dominion Laboratory, for permission to publish this article, and acknowledges his guidance and advice. He also wishes to acknowledge the help of Mr. H. H. Edwards, Auckland Farmers' Freezing Co., who suggested the principle of the hair-control.

# PIGMENTS: OLD AND NEW.

L. R. L. DUNN.

In presenting the above paper, the author stated that his intention was to attempt a general survey of pigments, to trace their evolution from past to present, to deal briefly with a few of the special fields in which pigments were used, and finally to indicate present day trends.

In the evaluation of paint pigments the fundamental properties to be considered are " oil absorption," " opacity," and " covering power." The ideal pigment should be durable, insoluble, of low oil absorption, of high opacity, of good covering power, and inert. Unfortunately, the ideal pigment does not exist, and in formulating paints it is generally necessary to use a mixture of pigments so chosen that the disadvantages of the one may be offset by the advantages of the other. When dealing with white pigments, it will be shown how such fundamental properties of pigments are utilised in practice in formulating house paints.

The use of pigments can be traced back to remote antiquity. At Altamira, in Spain, coloured wall paintings, probably 20,000 years old, have been found, the pigments used being confined to the natural earth colours, such as the red and yellow ochres, charcoal and chalk. Again, in the early civilisations of Assyria, Egypt, and Greece the use of natural mineral colours for decorative work became common, and at least one instance of the manufacture of an artificial inorganic pigment came to light, the famous " Egyptian Blue," since shown to consist of a copper " frit " or glass. The next great advance took place in Roman times with the production of White Lead, a pigment that has stood the test of time ever since. But, with one or two exceptions, there were available at the beginning of the Christian era only a very limited number of pigments, mostly naturally occurring products. Except for advances in methods of production of natural ultramarine (obtained from impure lapis lazuli) in early mediaeval times, little progress was made till the beginning of the 18th Century. Progress was then rapid. In 1700, the production of Prussian Blue was announced, while in 1778 Scheele discovered the pigment which bears his name and consists of copper arsenite. In 1802, came Colbalt Blue, and then, following on the discovery in 1818 of chrome iron ore, came the production of chrome yellow. Lead chromates of many shades, varying from deep orange-red to pale lemon, are now available. How great that advance really was will be realised when it is con-

sidered that by using various combinations of lead chromes with Prussian Blue, a range of colours extending over two-thirds of the visible spectrum can be obtained. In 1829, came cadmium yellow and zinc oxide, and in 1830, the synthetic production by Gmelin of ultramarine, probably one of the outstanding achievements in the field of modern inorganic chemistry. Other great advances were chromium oxide green (1870), cadmium scarlet (1920), and titanium oxide (1920).

The position to-day is that there is at the disposal of artists or commercial painters, a range and variety of pigments never dreamed of, say, two centuries ago. The criticism is often heard that modern pigments lack the permanance of those used in past times: it must be remembered, however, that formerly only a limited number of pigments, mostly natural earth colours, and therefore comparatively stable, were available. Then again the artist of, say, the Dutch School was a craftsman with specialised knowledge of the materials with which he worked, whereas the modern artist had the choice of numerous pigments, many of which are incompatible or fugitive to light, so that it is not surprising that failures sometimes occur. There is no mystery whatever about the pigments used by the ancients; all of them are reproducible to-day, and most of them had become obsolete only because equally reliable synthetic substitutes are now available. One instance of this is the replacement of lapis lazuli by ultramarine.

The blue pigments, as a class, are of particular interest from the historical point of view. The successful replacement by the Italians in the Middle Ages of the very rare " lapis lazuli " of the Egyptians and Romans by natural ultramarine involved concentration of the low-grade mineral by a method that was probably the first application of the modern " flotation process." With the rapid development of the Arts at the end of the Middle Ages, the demand for the pigment could not be met. This led the French Government in 1824 to offer a prize for a cheap and reliable substitute. The prize was awarded to Guimet in 1828, and by 1830, synthetic ultramarine was being manufactured in Germany and is to-day one of the cheapest blue pigments available. Previous to this discovery, a pigment known as " smalt," really a dispersion of cobalt oxide in a fusible glass, was in common use as a blue pigment, but owing probably to its alkaline reaction, was never entirely satisfactory. A more successful attempt to find a substitute for natural ultramarine was made by Thénard in 1802. By fusing together a mixture of cobalt phosphate and aluminium hydroxide, an excellent blue pigment known as " Cobalt Blue "

or " Thénard's Blue " was obtained. Cobalt Blue is a pigment of great stability, and is still widely used, but is too expensive to compete, as a rule, with the cheaper and for most purposes reliable synthetic ultramarine. About the year 1704 the preparation of Prussian Blue was first carried out. Owing to the extraordinary colouring power possessed by this pigment, it is extensively used at the present time, chiefly in mixtures, for the production of the various Brunswick Greens. Unfortunately, it is readily decomposed by alkali and in situations where it is subject to alkaline attack, as in distempers, it has to be replaced by a blue such as ultramarine. The announcement has recently been made by Imperial Chemical Industries, Ltd., of the discovery of a new insoluble blue pigment to which the name Monastral Fast Blue BS has been given. Provided the claims being made as regards brilliance, fastness to light, and resistance to both acids and alkalies, are substantiated in practice, the new pigment is sure to become of considerable industrial importance.

The space available here does not permit of a similar discussion of, say, the green or the yellow pigments, but no review on pigments would be satisfactory which did not deal with the various whites. The manufacture of commercial paints, for the protection and decoration of wood and other structures, is a huge industry. The durability of such paints is to a large extent dependent upon the nature of the white pigments used in their formulation, decorative effects being obtained by the addition of the various tinting pigments, such as the ochres, the umbres, or the siennas.

The first synthetic pigment to be dealt with is White Lead. Its use was well known to the Romans, who prepared it from metallic lead and vinegar. Probably the first works for its production on a large scale were situated in Holland, and the " Old Dutch Process " or " Stack " White Lead Process, is still used in all parts of the world with little variation. A modern variation of the process, first introduced in Germany, is the "Chamber Process," and the greater part of the White Lead on the market to-day is made in that way. The " Chamber Process " gives a product whiter in colour than that of the " Dutch Process," but of less opacity. Many other variations of the process have since been introduced including the " precipitation " and the " electrolytic." The products obtained by the three main methods vary to some extent. Thus, the " Stack," lead has a lower oil absorption than the others and is easily wetted by oil, so that it is the most suitable variety for making white lead pastes. On the other hand, it has not the whiteness of the others and generally has to be toned up

by the addition of a trace of Prussian Blue. White lead is still accepted as one of the most durable of pigments available for the weather-proofing of structures, its main disadvantages being its poisonous nature and its liability to attack by sulphur-containing gases.

Numerous attempts have been made to find a substitute for White Lead, particularly a non-poisonous one. Basic Lead Sulphate has most of the valuable properties of White Lead, but is not non-poisonous, as originally claimed. The first real competitor was Zinc Oxide. Though first introduced in France in 1781, it was only with the discovery of the use of manganese dioxide as a dryer in 1845 that its use became widespread. With it a glossy type of finish, impossible with White Lead, can be obtained, hence its use in many of the best enamels. One important disadvantage of Zinc Oxide was found to be its inferior " opacity " or " hiding power." Zinc Sulphide having a considerably higher refractive index than the oxide, soon suggested itself as a substitute, but owing to technical difficulties never became important. It was only when the idea was conceived of combining it with Barium Sulphate to form lithopone that the sulphide came into its own. The development of composite pigments, such as the lithopones, is one of the greatest advances taking place to-day. The high opacity, excellent whiteness, soft texture, and non-poisonous properties of lithopone, are the factors responsible for the enormous yearly consumption of the pigment. Its relative instability to light, as well as a pronounced tendency to flake off and chalk in outside exposures are inherent defects. Also when used to paint steel structures, it tends to promote corrosion, owing to decomposition of zinc sulphide and formation of acids. The next major development as regards white pigments was the introduction of the " titanium whites," and again the composite pigment principle was adhered to. The titanium pigments, especially those of high dioxide content, are characterised by low specific gravity and high refractive index, and therefore possess high covering power and high opacity. In addition they are chemically inert, heat resistant, and of exceptional whiteness, so that at first sight it would appear that the ideal pigment has at last been attained.

So much of the literature on the subject of pigments is of the trade variety, that it is difficult to arrive at definite conclusions as regards the comparative merits of the various white pigments available. Thus, the lithopone makers claim to have recently produced an improved product, stable to light, miscible with lead compounds without discoloration taking place. In the meantime, the best policy

is to recognise the inherent advantages of each, and so to combine them that the resultant product approaches the ideal. White lead has excellent weather-proofing properties, with a slight tendency to chalk. Its reputation for durability is due chiefly to the fact that the combination of the pigment with the oil, gives rise to an elastic film of great weather resistance and quick-drying properties. The white-lead substitutes, though of undoubted value, do not possess this desirable reactive property and require the assistance of various dryers, always an undesirable constituent in paint if used in excess. Zinc oxide gives a hard, brittle, glossy finish, but when used in combination with white lead, gives excellent results. Similarly with the titanium whites and lithopones. Alone, neither gives satisfaction for outdoor exposures and in each case it is good practice to incorporate some zinc oxide. As an instance of the application of these principles in the field of paint design the case of a sample of outside paint recently examined, which contained white lead, zinc oxide, titanium white, antimony oxide, and tinting pigment, might be mentioned.

In formulating an indoor house paint, the conditions are entirely different. Lead is usually excluded on account of its poisonous nature, while the lithopone-zinc oxide, and titanium-zinc oxide mixtures are quite satisfactory. It has been estimated that in America, the ratio of interior to outside paints is as high as 100 to 1, which gives some idea of the enormous field that is open to the various white lead substitutes described.

A few instances of the application of the "composite pigment," in the field of coloured pigments, may be of interest. Mention has already been made of cadmium sulphide. In the refining of zinc, large stocks of cadmium, for which little use could be found, had accumulated. Cadmium yellow had been known for some time, but was expensive. It has a brilliant yellow colour, and unlike lead chromate is fast to alkalies and sulphur gases, so that it is adapted as a pigment for distempers or for painting concrete. The production of the "cadmopones" or cadmium sulphide-barium sulphate mixtures, resulted in a considerable cheapening of the pigment. A quite recent innovation was the replacement of the sulphur by selenium. Cadmium selenide is yellow, but on calcination becomes a brilliant red, known as "cadmium scarlet." Formerly, the only inorganic red that was really bright was cinnabar, a pigment well known to the Egyptians and in constant use ever since, but too costly for general use. Most of the brilliant red paints seen at present (for instance on letter-boxes) are brightened up by means of organic lakes such as para-red, but now that cadmium scarlet is

available, it will probably find many uses and incidentally provide an outlet for accumulated stocks of selenium. By co-precipitation of zinc sulphide, cadmium sulphide, and cadmium selenide, alone or mixed, with barium sulphate, a series of cadmium lithopones can be obtained, ranging in colour from a lemon yellow to a brilliant scarlet according to the S/Se ratio. Such pigments are now established on the market, and the brilliant reds and oranges seen in cast-iron enamels or motor-car finishes are probably often derived in such a way.

A green pigment that has lately become prominent is chromium-oxide or "Permanent Green," well known as a constituent of the best roof paints. According to a recent patent, a mixture of barium chromate and sulphuric acid is caused to react, and, on calcination, gives rise to a pale-green product, corresponding in composition to a chromium lithopone and having the composition $Cr_2O_3$-$BaSO_4$. In fact, the tendency in pigment manufacture appears at present to be generally along such lines.

Mention has already been made of some of the natural earth colours used by the ancients, such as native cinnabar, orpiment, and the copper blues and greens, but by far the most important were those whose colour was due to iron, or a combination of iron with manganese. Pigments of this class are still of outstanding importance, and are available in a large variety of shades, ranging from a pale yellow to a deep red or brown. Their value has not only in their decorative properties, but in their permanence, cheapness, and general applicability for protective and decorative work, and also their compatability with almost all other pigments. The industry for the preparation of the natural earth colours is a wide-spread one, being particularly well developed in France, Spain and England. The method of manufacture is a simple process, involving grinding of the crude natural iron oxide to the requisite degree of fineness combined sometimes with levigation to get rid of undesirable impurities. The products obtained have such a multiplicity of names, that it is difficult to arrive at any very satisfactory classification, and such names as Venetian Red, Indian Red, or Persian Red, though at one time an indication of the source of origin, may now be applied to an entirely different product, often synthetic. Such names as Yellow Ochre, Naples Yellow, Raw and Burnt Siennas, Raw and Burnt Umbers, Indian Red, Turkey Red, Venetian Red and Tuscan Red are household words in the paint trade to-day, but owing to space limitations cannot be further described. An interesting continuous process for the manufacture of artificial yellow ochre and raw sienna has recently been described in the patent literature, and

is cited as an indication of the modern trend to substitute the synthetic for the naturally occurring product. A solution of ferrous sulphate containing pieces of scrap iron is brought to the boil in a wooden-vat, air being constantly blown into the solution. The action results in the formation of a ferric iron salt, while ferric hydrate is precipitated out. The ferric salt then reacts with the scrap iron forming more ferrous sulphate, making the process continuous. The only materials that require renewal are iron, steam, and air, different shades being produced by modifying concentration and other details. The Ferrite Yellows, as they are called, are claimed to have far greater colour strength than ordinary ochres, and to be preferable for the tinting of enamels and distempers for cream and buff shades.

Another very interesting modern development is the use of the silicon-ester type of paint. Upon hydrolysis paints of this nature give rise to a film consisting entirely of silica, a complete break-away from the old-established oil-bound paints. Its chief use is for the painting of surfaces containing free lime, such as concrete, asbestos sheet, and gypsum plaster, and for the decoration of surfaces exposed to high temperatures, the finish obtained being a "matt" one, of pleasing appearance. In order to obtain colour effects, various tinting pigments can be incorporated, such as ilmenite black, chromium oxide green, ultramarine blue, cadmium yellow, and cobalt blue, these being first wetted with an inert solvent such as cyclo-hexanol, but basic pigments such as white lead and zinc oxide must be avoided. Their value lies in the fact that they can be applied to concrete as soon as the shuttering is removed, without previous treatment of the surface with zinc sulphate, and that they give rise to an imitation stone effect. Unfortunately, the porous nature of the film and its incompatibility with basic pigments renders it unsuitable for the preservation of iron and steel.

The choice of pigments for the painting and decoration of structural steel and concrete is an essentially modern problem to which full justice cannot be given without some consideration being paid to the theoretical principles involved, but the subject will probably be dealt with in a second paper at some future date.

The pigments so far mentioned have been inorganic in nature, but developments during recent years in the manufacture of the synthetic organic lakes derived from coal-tar dyes have increased enormously, and the erroneous idea held by many that all such colours are fugitive to light will probably soon be dispelled. The first synthetic lakes produced by precipitating the dye on to a base of alumina, were known as transparent colours, but in order to

develop body for the paint industry, addition of such bases as barytes, zinc oxide, or orange lead is being now made, giving rise to "lake-pigment" colours, of much better body and covering power. The usual precipitating agents are barium chloride for acid dyes, and tannic acid for basic dyes, but recent research appears to have been along the lines of the production of lime-fast and light-fast lakes, by the use of new precipitating agents, such as salts of manganese, chromium, and strontium, a remarkable modern development being the new "Fanal" colours, first produced in Germany but now also in England under the name of "Brillfast" colours. These new colours, which consist of pure compounds of the phospho-molybdo-tungstic acid complex with the dyestuff, are said to be remarkably fast to light, the colours so far obtained being yellows, blues, violets, and reds. It is more than probable that in the future the mineral pigment colours will be more and more replaced, for decorative work, by organic substitutes of such a type.

## ANNUAL JOINT CONFERENCE, 1935.

The annual joint Conference of the New Zealand Institute of Chemistry and the Institute of Chemistry of Great Britain and Ireland (New Zealand Section) was held at Hamilton on January 24 and 25, 1935. Some twenty-five delegates attended. In addition to the business sessions and the reading of several papers, the programme included the following visits: Hamilton Gas Works, the N.Z. Co-operative Dairy Company's butter and box factories, the Hamilton Waterworks, and the Glaxo factory and Dr. Annett's experimental farm—both at Matangi.

The papers read are briefly reported below.

The Presidential Address of Professor H. G. Denham covered the activities of the N.Z. Department of Scientific and Industrial Research for the past five years; for details, readers are referred to the Annual Reports of the Department.

# "THE FROZEN MEAT INDUSTRY."

G. A. LAWRENCE

*(Presidential Address to the N.Z. Section, Institute of Chemistry of Great Britain and Ireland.)*

It was a noteworthy coincidence in the progress of the world's history that at a period when Great Britain was fast losing ground in her ability to grow enough to feed her ever increasing industrial masses, two of her youngest colonies were seeking outlets for their excess produce. This demand on the one hand and the desire to dispose of surplus stock on the other provided the necessary incentive to hasten the development of artificial methods of producing cold to preserve perishable goods over long periods.

The preservation of flesh foods by means of low temperature was by no means a new idea. It was, no doubt, known and practised by the peoples of the polar and temperate zones for centuries. We know that the cooling of water, and even the production of ice by means of the porous pot method, was in use in Egypt in the days of the Pharoahs, and this simple apparatus is still in use in that country in its original form.

Several early historical records of the use of snow and water for cooling purposes were cited, and it was stated that in 1816 some Esquimaux sent cases of frozen game to England. In 1875 Eastman sent the first frozen beef to Great Britain from the United States. Ice and salt were the means of refrigeration and the meat was packed in cases. Two years later the first shipment of chilled beef was sent from the Argentine, but in this case the reduced temperature had been brought about by artificial means invented by the Frenchman, Charles Tellier.

No real advancement took place, however, until the underlying principles were more fully understood. The discovery by Joseph Priestley in 1773 of the gases carbon dioxide and ammonia was of great moment, because these two gases were ultimately to become the most important refrigerants. In 1829, Michael Faraday liquified carbon dioxide and ammonia by pressure, but it was not until 1868 that Thomas Andrews discovered the critical temperature of gases.

Jacob Perkin's patent in 1834 of an ether compression machine marks one of the most important steps, because it included the four main features in the present day compression machines, namely, compressor, condenser, expansion valve and evaporator. Harrison in Australia improved upon Perkin's machine and he installed the world's first refrigerator plant in a brewery. The absorption system of refrigeration originated by the brothers Carré was taken up by Mort and Nicholle in Australia, who spent much time and money in their endeavour to apply refrigeration to ships. Mort had many disappointments, but he must be credited with establishing the first freezing works in the world in Sydney in 1861. It was in February, 1882, that the sailing ship *Dunedin* left New Zealand with what later proved to be the first successful shipment of frozen meat from this country.

The meat freezing industry is a curious mixture of the old and the new, and the centralisation of an old industry through the discovery of mechanical refrigeration created many new problems, but as the sequel has shown, it has been brought to a state of efficiency which would have been

impossible under the old scattered system. Considering that the industry is based on a scientific principle, science paid a surprisingly small part in the first 20 years.

The chemist was first employed by the great American Meat Packing industry in the early 'nineties of last century, and about 10 years elapsed before such a step was taken in New Zealand. The industry in the two countries has many points in common, but that in the United States has the advantage of being much nearer the world's markets.

The first necessity in the scientific control of any industry is that the managers and foremen should know and appreciate the significance of analyses and other data pertaining to the products being handled. In the early stages, kettle and steam rendering were the processes used for the recovery of fat, and the residual tankage and the blood were pressed and dried. The drying was carried out by the old-fashioned fire dryer process, and unless the temperature was very carefully controlled the product was either left too wet and fermentation took place, or the product was overheated with resultant decomposition of the protein. The introduction of the steam dryer process in later years resulted in greater ease of control and much improvement in the products.

The early chemist knew little or nothing of the theory of autolysis, but he did know that rapid deterioration took place in the animal products if they were allowed to accumulate without cooling. The necessity of treating the offal as soon as possible after killing, and the profound influence this factor had on the quality of the fat, dried blood and tankage was a point which had to be stressed by the chemist not only to the foreman responsible for the processing but also in many cases to the management because of the frequent tendency for the killing capacity of the works to outstrip the capacity of the by-products department.

The need for an outlet for the by-products was a burning question. The common practice in the early days of the industry was to bury the viscera and pelts from the slaughtered animals. To the people engaged in the industry this was obviously a wasteful practice, more especially in view of the increasing development of the fertiliser industry in the older countries and more particularly in connection with the packing industry in the United States.

The use of animal matter for manure has probably been known for thousands of years, but the great problem was that of convincing the farmers in New Zealand of the necessity for using fertilisers. At a period 35 years ago, there was already land in New Zealand which had practically become barren because nothing had been done to replace the fertility of the soil removed by successive generations of stock. It is not surprising that this was overlooked because at that time large areas of virgin land were still being denuded of bush and laid down in grass and the luxuriant pastures obtained lulled the farmer into a sense of false security.

But the fertiliser industry was gradually established and an outlet made for the by-products of the rapidly growing freezing industry, and one may say that the development of the fertiliser industry in this country is in no small measure due to the efforts of the early chemist in the freezing industry. The results attained during the past 30 years have amply justified the pioneering work they did.

The benefits derived from the more intensive feeding of stock, and the development of the pig and poultry raising industries, within recent years,

has resulted in an increasing demand for by-products for feeding purposes. Improved methods of processing the raw material has made it possible to produce better quality meat meals with less odour than formerly. This has probably been an important factor in the increased demand; moreover, the ever-increasing demand in Britain and the United States for New Zealand meat meal and dried blood for feeding purposes shows not only that the feeding value of these products is fully appreciated in these countries, but is also a tribute to their quality.

New Zealand is at the dawn of a new era in the feeding of animals, and it can be confidently expected that a still greater proportion of the freezing works' by-products will go into feeding meals, which is its proper place in the economic structure of the industry. The old slogan of the American Meat Packer, "From the farm back to the farm," will then attain its fuller meaning.

The introduction of the dry rendering and the solvent extraction processes of dealing with freezing works' products during recent years has resulted in a considerable saving and improvement in the quality of the materials being processed.

A number of changes have been brought about in the process for the recovery, and also in the refining of fats. The quality 30 years ago had not advanced much beyond that ruling in the old boiling down days. By keeping a check on the quality and pointing out the reasons for the defects, the chemist has been able to raise the standard considerably.

A lot of work has been done in recent years on the theory of the cause of rancidity, and as a result of this work it may be possible to do a great deal more in the future towards inhibiting the development of rancidity in fats. It is fortunate, however, that the main cause for the deterioration of fats has been known for many years, and this knowledge has made it possible to produce some excellent fats in our freezing works in the past.

The remoteness of New Zealand from the world markets has not enabled the industry to embark on the elaborate methods of refining and bleaching low grade fats to the same extent as it is practised in the United States, but the actual quality of fats, produced at the present day from the various raw materials, leaves little to be desired.

The production of premier jus or oleo has of late years received a considerable check owing to the large scale hardening of whale oil, but this specialised branch of the industry has been well to the fore for years and reports from overseas consumers show that the New Zealand made article has a very high standing in the open market.

The primary consideration with the buyer of stock for freezing purposes is the condition and quality of the meat the animal will yield, blemishes on the hides or skins due to branding, contact with wire and the all too frequent blemishes in sheep skins due to careless shearing must be taken as they come. It is pleasing to note that of late years more attention is being given to this question and it is to be hoped that more care will be taken to eliminate as far as possible the causes of these blemishes.

The freezing companies only concern themselves with the preserving of the hides and the removal of the wool from the sheep skins, the drying of the wool and the preserving of the pelts. In the early days of the industry the quality of the salt used in the fellmongery left a great deal to be desired. By focussing attention to these defects the chemist has

gradually induced manufacturers of salt to pay more attention to the elimination of these impurities and the salt coming forward at the present day is of good quality.

By the end of last century the old sweating process for the removal of wool from sheep skins had been entirely replaced by the quicker and more easily controlled sulphide depilatory. It is an unfortunate thing, and one that is still extant, that many faults which may occur in the processing of pelts for export cannot be detected until the goods are tanned, and some of the faults are only detected when the pelts are dyed.

The intestines used to be freed from the partially digested food and passed with the other inedible material for the recovery of fat and fertiliser. The increasing demand or sausage casings, particularly in the United States, made it worth while to treat the intestines especially for this purpose.

For a number of years glands for the preparation of pharmaceutical products have been exported from New Zealand, but up to the present this business has not reached very large dimensions.

The great stride made in our knowledge of the therapeutic value of the extracts from glands, and the research work that is being carried on in this branch of medicine may result in a considerable demand for those products in the future.

The chemist was often called upon to explain many defects which occurred from time to time in the meat. Perhaps the most prevalent of these defects was the growth of mould on the carcases. The cause was nearly always traceable to the temperature not being kept low enough, either through the over-taxation or complete failure of the plant; or to defects in the circulation system. The rapid advances in recent years by instituting a more thorough control throughout the period of transport and a better understanding of the cause of mould growth, has rendered the percentage of mould-infected frozen meat a negligible quantity.

The relative digestibility and nutritive properties of frozen meat as compared with fresh meat has always been a contentious matter, and it is of interest to quote results from the work carried out in 1896 and 1897 by the late Dr. Samuel Rideal:—

Mutton (English).—Weight when delivered by butcher, 8lb. 6ozs.; weight when taken from oven, 5lb. 15ozs.

Mutton (New Zealand).—Weight when delivered by butcher, 7lb. 14ozs.; weight when taken from oven, 5lb. 13ozs.

However, in view of the conflicting reports which have recently been published, it seems desirable that some competent authority should appoint a committee or board of experts to carry out the necessary experimental work and make a comprehensive report on the subject in order that something definite and authoritative will be available.

In New Zealand with the waning prices of primary products in the overseas markets, with increased foreign competition, it is essential that we should use every endeavour to utilise our scientific resources to improve the quality of our products, increase production, seek new avenues for the utilisation of waste materials and investigate new products. These are preeminently scientific problems and any curtailment of investigational work in this sphere would be a calamity.

## THE OXIDATION OF BUTTERFAT.

W. WILLIAMS.

The speaker pointed out that the chief cause of rancidity in the past had been the production of free butyric acid by the action of enzymes. This difficulty was now overcome by efficient pasteurisation of the cream which rendered fat-splitting enzymes inert. Checks on the total bacterial, yeast and mould content of butter were not only a check on the efficiency of pasteurisation but also on factory plant contamination. The production of fishy flavours in dairy produce and its association with rancidity and oxidation flavours had involved a study of the phospholipid lecithin. Under acid conditions this compound was hydrolysed to produce trimethylamine. Careful attention to the neutralisation of the cream and the avoidance of light and metallic wrapping diminished this effect.

As oleic acid was the chief unsaturated acid in butter, this had been used for the investigation of the oxidation changes which give rise to the tallowy flavours. Schibsted's method for determining aldehydes is of great use for this purpose, and results indicated that by this method incipient oxidation changes might be detected and checked. Amongst many factors which had been investigated as accelerators in producing oxidation of butter-fat were heat, light, acidity, enzymes and certain metals—particularly copper. In this connection both the effect of added anti-oxidants and the copper and iron content of butter-wrappings were briefly discussed and the analytical methods outlined. Cream in dairy-factory plant is frequently badly contaminated with copper, whilst cream which had been exposed to sunlight for only 15-20 minutes was readily selected by experts as containing oxidation flavours.

## THE ROLE OF COPPER IN MAMMALIAN TISSUES.

J. C. ANDREWS.

It is now well known that copper plays an important part in the life of mammals although the amounts present are very minute. Various workers overseas, and Cunningham in New Zealand, have shown that it is an essential constituent of the blood, and lack of it prevents the iron from functioning normally in regenerating haemoglobin; this is doubtless one of the causes of anaemia, various problems of which were discussed.

Examination of the available analytical methods showed that the use of sodium diethyldithiocarbamate was entirely reliable,

whereas the older methods (including ferrocyanide, ammonium thiocyanate and pyridine, etc.) must be regarded as unsatisfactory. It is necessary to digest the material by wet oxidation, since in dry ashing there is a considerable loss of copper.

Some interesting figures were given concerning the copper content of sheep and cattle livers as determined at various stages of life, and these were compared with the values for iron and manganese. During the pre-natal period, copper increases to a maximum at birth and then diminishes until weaning; it subsequently increases again to reach an almost constant level until old age when it again decreases. The results for iron are quite similar, but the actual quantities present are larger. The theory was advanced that possibly there was first synthesised a copper complex in the blood, the copper being later replaced by iron entering into combination.

Further investigation should be made to show to what extent anaemia might exist even in the presence of normal amounts of copper and iron. In concluding, the possible relationship of copper and other " trace " elements to " bush-sickness " and other similar diseases of stock were discussed.

## SOME APPLICATIONS OF THE PHOTO-ELECTRIC CELL.

H. H. EDWARDS.

The Photo-Electric Cell has within the past few years, placed yet another instrument in the hands of the chemist. Its principle of operation, that of changing its resistance under the stimulus of light, opens up great possibilities and lends itself to limitless applications. The ordinary Photo-cell operates with an external circuit voltage, that is, a voltage is supplied to the cell which, under the influence of light, lowers its resistance and allows more current to flow. This current is then amplified by vacuum tubes and is used to operate a suitable relay which, in turn, operates the device it is wished to control.

There is, however, a new Photo-cell now on the market which needs no external source of voltage, developing its own voltage when acted upon by light. This type of cell being cheap and simple to adapt, is of the greater interest to chemists, and is a useful adjunct to any research or chemical laboratory. It will supply .014 amperes in direct sunlight and will operate the cheapest galvanometer, using ordinary artificial lighting conditions. This type of cell is useful for Photo-Electric titrations in that it offers a means of ascertaining colorimetric end-points which are free from subjective error. Titrations can be made by day or night or by a colour-

blind observer; furthermore, it lends itself to automatic control. A "dead stop" end-point can be obtained to better than 0.05 cc. of 0.1 N alkali.

This appartus can be easily set up from items found in most laboratories and is readily assembled. The principle of operation employs the Poggendorf principle of opposing the E.M.F. of a potentiometer to that of the Photo-cell and balancing by means of a galvanometer as a null-point instrument. Bromo-thymol blue is used as the indicator, and as the light which shines through the solution is unaltered until near the end-point, the galvanometer remains steady. On addition of the last few drops of solution, the colour of the indicator begins to change and at the end-point the needle of the galvanometer deflects strongly. Another application is in colorimetric measurements. In this case two Photo-cells are electrically opposed and the current developed by them is balanced by means of a variable resistance. A galvanometer is again used as an indicator. The intensity of the light transmitted through the solution under test is measured in terms of the resistance needed to balance the two cells.

Photo-cells eliminate the human factor where results depend on our eyesight. For instance, in measuring humidities at the works of the Auckland Farmers' Freezing Company Limited at Auckland, the author used the dew point method. A highly polished silver thimble was cooled by means of ether, and on the temperature reaching the dew-point, the excess moisture was deposited in the form of a mist or dew on the surface of the silver thimble. The temperature was then noted and the relative humidity calculated from the temperature of the dew-point. The trouble with this instrument previously was that no two observers could agree as to what constituted a mist, or when it appeared, or when it disappeared. Another apparatus was constructed and a light was directed against the surface of the silver thimble and was reflected by it to a Photo-cell which in turn was connected to a micrometer. The reading was noted, and when the first sign of mist appeared on the thimble, the reflecting power of the silver being lowered, the fact was immediately registered as a strong movement of the galvanometer needle.

In addition to the foregoing applications, there are numerous others, but in the limited time a brief mention of some of the more important ones will suffice. Some of these applications depend on the interruption of a beam of light shining on the cell for their operation. Mention can be made of counting mechanisms where objects to be counted break the beam of light in their passage and

thus operated the counter. Turbidity indicators, smoke meters, guards against the operator getting the hand caught in pressing machines; grading machines for grading fruit or eggs, etc., into various sizes; regulation of the light intensity in drawing offices by causing the sunlight to actuate louvres attached to the windows or skylights. One firm in America has occasion during part of a process to pass articles through a bath of inflammable solvent; the fire risk is very great and as a safeguard a ray of light shines across the top of the tank containing the solvent and impinges on a Photo-cell on the opposite wall. Any trace of flame or smoke would, by interference with the beam of light, precipitate many tons of water from a reservoir built directly over the bath.

However, the uses of this Photo-cell are practically limitless and there is hardly an industry which could not utilise one or more of these useful little sentinels. The price of a self-exciting cell is about 30/- in New Zealand.

## THE IMPORTANCE OF HYDROGEN ION CONCENTRATION IN LEATHER MANUFACTURE.

P. WHITE.

Although the manufacture of leather is nearly as old as the human race, it was not until the end of the 19th century that Professor Procter, of Leeds, began a scientific investigation into the problems involved. Even to-day comparatively little is known, so that the tanner's own science is often far more reliable than chemistry in the industry. The chemist who attempts pioneering work in a tannery finds that whatever change he institutes in a given operation frequently results in a lowering of the quality of the finished leather.

Procter's original work was connected with the swelling of gelatine, but skin reacts in a similar manner. The amount of swelling is great in both acid and alkaline media. The first suggested method of control was to determine the amount of free acid in the tan liquors; this gave the so-called "lime-water figure." Introduction of pH control was more satisfactory, since it is not the amount of acid or alkali in solution which affects the swelling of collangen, but the effective acidity.

Three important factors are effected by pH in the process of tanning: (a) *Swelling of Skin*—If the fibres of skin are tanned in a shrunken condition, thin empty and harsh leather is produced, and its strength is diminished; (b) *Rate of fixation of vegetable tan*—Low pH increases the rate of fixation, but the interstices rapidly block

up; it is better to begin with a high pH and then, when penetration has been obtained, to reduce it in order to fix the tannin; (c) *Colour*—Vegetable tanning solutions act as indicators, so that acid conditions produce a lighter, and alkaline conditions a darker colour.

As a high yield of leather is naturally desirable, the amount of tannin absorbed should be high, but there is a danger that the grain side may be over-tanned. It was pointed out that quinhydrone electrodes do not work well in bleach liquors—it is advisable to use the Morton electrode.

In *chrome tanning*, control of pH is again important. Solutions of chromic sulphate change their pH on standing or on boiling. A rise in pH increases the size of the chromium molecule; consequently for rapid penetration the pH should be low and fixation brought about by the addition of alkali.

In *dyeing*, the correct colour, richness of shade, regularity and penetration are affected by variations in hydrogen-ion concentration. Economy results from its control.

It is well known that *fat-liquoring* introduces oils which are necessary to render the leather soft and pliable. The fat-liquors are usually oil emulsions, the emulsifying agent being most frequently a sulphonated oil. The pH of the fat liquor influences its effect upon the leather and in some cases it is not desirable for the oil to penetrate far into the leather, a fairly low pH being then required.

Hydrogen-ion control does not eliminate the ancient art of tanning, which is based upon centuries of experience, but it is one of the greatest aids that have so far been placed in the hands of the tanner.

## CELLULOSE PULP FROM NEW ZEALAND FLAX.

L. S. SPACKMAN.

Several years ago interest was intensified in the utilisation of New Zealand Flax (*Phormium tenax*) as a possible source of cellulose for the manufacture of high-grade pulps. The reason is twofold: first, the cellulose content of Phormium is high, being inferior only to cotton linters, and it does not contain resinous matter which would introduce difficulties in the manufacture of the pulp; and second, the chemical and physical nature of the flax cellulose lends itself admirably to the manufacture of high-grade pulp. Above all in importance is the length of the ultimate fibres, those in flax being the longest in any known substance—longer even than those of cotton. It is not exactly known why the fibre-length should have such

a bearing upon the ultimate pulp, but it is a well-known fact that the greater the fibre length the better is the grade of pulp produced.

The speaker gave a review of the industries using quantities of cellulose and a brief survey of the related substances occurring in the plant.

The economics of the production of pulp from *Phormium tenax* have been gone into exhaustively and there seems every reason to believe that it should be possible to produce a pulp in New Zealand to sell in England at a price which will admit of an adequate profit.

## THE AGRICULTURAL SCIENTIST GONE WRONG.

H. E. ANNETT.

" The longer we live the less we know " is especially true of Agriculture. The lecturer had had a long experience in Agricultural Research and Agricultural Education, but his seven years of farming experience in New Zealand had taught him to look with a different eye upon the work of the Research worker, as it had shown him how invaluable knowledge of local conditions really was. New Zealand was fortunate in some of the excellent work being done by the Plant Research Station, Cawthron Institute, Lincoln and Massey Colleges, and the Dairy Research Institute, and a great deal of knowledge had been acquired, but the methods of bringing this knowledge to the farmer in a form he could use needed strengthening.

The farm could be considered as a laboratory, but the experiments carried out were not so simple as chemical ones. In the latter all the factors, except the one under trial, could be kept constant, but in Agriculture the factors were often unknown and seldom capable of control. While a certain practice might be successful on one farm, it might not be on the next, so that to make sweeping and confident recommendations to farmers was very unwise.

Numerous pieces of research work could be carried out on the farm. The lecturer had already become interested in white clover, and its effect on taint and test. The necessity for experiments in the feeding of milking cows with individual grasses and clovers was stressed; also the feeding of plants kept in the dark as against plants kept in light. It may be that the high enzyme content of plants at night has an effect on the fat content of milk and hence might explain the reason for the fact that morning's milk is poorer in fat than evening milk. It had been found in India that certain weeds had a marked effect on milk production. It was known that

Yohimbine hydrochloride greatly stimulated milk production, and it was possible that certain plant constitutents acted in the same way. Another problem for research was the significance of the cyanogenetic glucoside found in white clover, which at times reached a concentration high enough to be toxic. Again, what was the cause of fluorescence in ultra-violet light of the rootlets of germinating seedlings of the true perennial type of rye grass?

There was a wide field for research into nutrition problems. In order to be in a position to calculate how far recognised food standards were correct in practice, it was essential that records be kept as is done on the lecturer's own farm for all animals carried on each paddock, and of the production of milk, meat and wool. Provided that the composition of the grass as regards food constituents and minerals was known, as well as the amount and composition of the manure secreted, food requirements could be calculated. Seven years of experience in the feeding of animals with a high protein diet on the lecturer's own farm had failed to show any harmful effect. Highly nitrogenous diets might be objected to on the ground of expense, but had no other disadvantages. The use of meat meal in the feeding of pigs had proved most successful, even when no other food except milk by-products and grass were fed.

The speaker then outlined the controversy between Liebig, on the one hand, and Lawes and Gilbert on the other, as to what were the actual effective agents in the mineral nutrition of plants. Liebig argued that the ash constituents (K, P, Ca and Mg salts) alone were necessary, and that there was no need to supply N, as the plant would get all it needed of this from the ammonia of the air. Lawes and Gilbert acknowledged that the ash constituents were required, but insisted that it was also necessary to supply nitrogenous compounds; this they succeeded in verifying by a series of classical experiments on the farm. As time went on great emphasis was paid to the importance of the three elements, phosphorus, potash and nitrogen, and manurial practice had been practically confined to supplying those elements.

Some parts of the world, such as South Africa and New Zealand, were particularly deficient in phosphorus. In New Zealand, the use of superphosphate had largely increased production and the number of stock carried on a given area. The great danger to New Zealand lay in the fact that phosphates are our mainstay, and more stock per acre are being carried than in any country in the world by one-sided phosphate manuring. Such one-sided manuring could not go on for ever. New Zealand was a country

with light soils and a high rainfall, and in consequence the lime content of her soils was generally low—the profuse growth of the bracken fern being itself an indication of lack of lime. There was a dangerous tendency in New Zealand to decry the use of lime. Frequently this opinion had been formed as a result of one or two years' trial with lime whereas it was the experience in most countries that the effect of lime took several years to become obvious. On low quality pasture a cow might get actual foodstuffs to produce, say, three gallons of milk a day, yet the pasture she consumed provided enough lime in the summer for only two gallons of milk and in the winter for one gallon. Nature seemed to have laid down that the lime content of milk remained more or less constant, and in order to provide the lime shortage, the cow had to draw on the lime content of her skeleton. This meant a weakening of the animal's constitution and the onset of disease.

The position in regard to potash was becoming of more and more importance where heavy stocking of farms was practised. Far too little potash was being used and since a shortage of potash was frequently accompanied by disease in plants, it was possible that the health of animals might suffer from the consumption of unhealthy food. The importance of potash manurial trials being extended over a number of years could not be too highly stressed. Both potash and lime have largely increased the stock carried on certain paddocks of the author's farm but not before the fourth year of treatment.

An ample supply of nitrogen in a readily available form was of first importance to plant life. Though the soil might contain ample stocks of nitrogen, it was only in the presence of sufficient moisture and at a sufficiently high temperature that the soil organisms became active for the production of the nitrates required by the plants. A heavy fall of rain, after a dry summer period, brought about a great increase in soil nitrate. During the winter the limiting factor in the action of the soil organisms was the low temperature. By the use of sulphate of ammonia dressings the lecturer had been able to bring about a profuse growth of ryegrass at quite low temperatures, thus enabling all-the-year-round-milking to be practised.

Increasing attention must be paid also to some of the rarer elements, such as magnesium. The latter, being a constituent of chlorophyll, was obviously all important for plant life. Until recent years it was assumed that soils provided ample magnesium. Experiments in New Zealand with potatoes had, however, shown no increased yield with the use of potash, whereas, overseas, potash

usually can be relied upon to give increased yields. The explanation might be a shortage of magnesium, since similar non-response to potash had been observed in certain parts of the U.S.A. However, when magnesium sulphate was applied with the potash, response was marked. The extra production was not obtained with magnesium sulphate alone, but only with the magnesium and potash combined, showing that the limiting factor was a magnesium shortage. Magnesium shortage was important as it might be responsible for a cattle disease known as grass staggers.

Instances of other deficiency diseases, such as possible shortage of iron in bush sickness, copper and iron in anaemia, boron deficiency in apples, were described. Manganese was occasionally needed, instances being "Gray speck" in oats in Australia, and pineapple disease in Florida. Zinc controlled rosette disease in citrus fruits and pecan nuts, and a deficiency of zinc resulted in bronzing of tung oil trees. The response to zinc in such cases was said to be amazing.

The lecture concluded with reference to some of the practical manurial problems being investigated on his own farm.

## LABORATORY ORGANISATION.

P. R. PARR

Various internal details in the organisation and control of works laboratories were dealt with. The speaker commented upon certain successful procedures operating in the laboratories of his company, with special reference to costing, sampling, record-systems, etc., and staff relationships.

## PROPERTIES OF DIESEL FUEL.

M. L. H. STEWART

The main chemical and physical characteristics of a diesel fuel were discussed, and certain phases of research in the author's and other laboratories were noted.

(The paper will be published in extended form in the next issue of this *Journal*).

# THE BRANCHES

## AUCKLAND.

*Papers read—*

"The Manufacture of Sugar."—*A. W. Blomfield.*

"Chemistry of the Resinols."—*Dr. L. H. Briggs.*

"Biological Significance of Minute Amounts of Copper."
—*Dr. J. C. Andrews and R. T. Danvers.*

"Some Applications of the Phase Rule."—*Dr. Robinson.*

One of the above papers has been reported, in abstracted form, under the proceedings of the Annual Conference.

## WELLINGTON.

*Papers read—*

"Paint Pigments."—*L. R. L. Dunn.*

"Chemistry in Daily Life."—*R. E. R. Grimmett.*

"The Estimation of Iodine in Iodised Salt."
—*R. L. Andrew and J. L. Mandeno.*

"The Nature and Estimation of Iron in Blood."—
—*Eunice M. Wall and F. B. Shorland.*

"The Animal Nutrition Laboratory, Adelaide."—*S. W. Josland.*

"Auto-oxidation and Antioxidants."—*J. M. Butler.*

"The Determination of Fluorine."—*W. Donovan.*

Some of these have been published in the main body of the Journal.

## CANTERBURY.

*Papers read—*

"The Training of Chemical Engineers," "Corrosion and Its Causes," "Science and Industry."—*H. G. Denham.*

"Some Well-known Chemists," "The Frustration of Science."
—*H. N. Parton.*

"Reflections of an Industrial Chemist."—*L. P. Symes.*

"Some Observations on Corrosion."—*D. E. Parton.*

"Corrosion-resisting Metals and Alloys."—*C. M. Gray.*

### REFLECTIONS OF AN INDUSTRIAL CHEMIST.

L. P. SYMES.

(Chairman's Address)

Until recently knowledge of the chemistry and physics of animal and vegetable tissues has made slow progress. In the last few years the concerted attack of team workers has made remarkable advances, so that now the picture of what happens during the freezing or thawing of tissues is becoming clear. Purely

scientific problems have been investigated as they arose in connection with the practical aspects of meat, fish or fruit freezing. The major problems of the commercial freezing of meat are associated with desiccation, denaturing of the cell contents, oxidation (particularly of fats), and the control of moulds or bacteria. Various forms of damage resulting from these causes were described.

In New Zealand comparatively little interest is taken in the quick freezing processes owing to the development of gas storage based on the fungicidal and bactericidal effect of carbon dioxide at temperatures slightly above the freezing-point.

The handling of the various parts of the intestines for the manufacture of sausage-casings, racquet-strings and the like was described, with some of the causes of defects, particularly the susceptibility to damage by iron. Apparently little scientific information about the fermentation of gut in these processes has been published.

Salt and lime are supplies whose values are difficult to state in figures, and lime is very difficult to sample truly. Figures showing comparative purity in salts and limes may be very misleading, the distribution of the impurities being usually much more important than their quantity.

## CORROSION AND ITS CAUSES.

H. G. DENHAM.

The enormous damage to metals through never-ceasing corrosive agencies and the outlay civilisation is called upon to face and combat that attack are known to all. The problem is a complex one, and it is small wonder that numerous theories have been propounded, each supported experimentally, and each designed to explain away the underlying causes of this many-sided problem.

Calvert's original acid theory, so strenuously advocated by Moody and Friend, seeks to associate corrosive phenomena with the ever-present carbon dioxide, which provides the hydrogen ions necessary to stimulate the attack, the acid being regenerated by the hydrolysis of the resultant carbonate. Naturally any acid generated in the presence of a reactive metal would be capable of setting up this cycle of operations, e.g., a steel rich in sulphur is generally a potent source of danger, as the reactive sulphur readily produces sulphuric acid, the presence of which can be demonstrated in the rust.

The electrolytic theory so strenuously put forward by the American school postulates the pressure of a variable potential difference over the surface of the metal arising from a lack of

true homogeneity in the metal. In the presence of a film of salt-containing moisture small local currents are set up on the surface of the metal, and pitting or localised attack is facilitated, the anodic areas being rapidly eaten away. Obviously any extraneous current such as may owe its existence to faulty underground electric cables, to a badly designed tramway system, will act in the same way, though generally more rapidly. More recently Evans has attempted to attribute the setting up of these electrolytic currents rather to differential aerations. The oxygen is here regarded as a depolariser of the film of hydrogen set free on the cathodic areas, which would otherwise slow up the action of the local current. In fact it can be shown that two pieces of zinc immersed at varying heights in a solution of salt or even in pure water will give a definite kick when connected through a galvanometer, the current flowing in such a way as to indicate that the more highly oxygenated pole is cathodic. But anyone who has seen the extensive corrosion occurring in localised patches on a ship's plate subject to no differential aeration must at once rule out the Evans theory as being no more than an auxiliary factor in promoting electrolytic corrosion.

The colloid theory of Friend presumes that the first product of corrosion is colloidal ferrous hydroxide which then oxidises to the ferric state. Interaction between the ferric hydroxide and the iron again leads to an increase in the concentration of the colloidal ferrous compound, and the process continues until ultimately some of the colloidal ferric hydroxide coagulates as rust. The theory affords a satisfactory explanation of the fact that the corrosive action of an acid medium on a metal is proportional to the velocity with which the acid passes over the metal, whilst in the case of a salt solution a definite maximum rate is soon attained, the corrosive action at high speeds falling to that comparable with the effect of mere erosion.

In the opinion of the writer no single theory can explain the many facets exhibited by corrosion, but the "acid" theory and the "electrolytic" theory, based as it is on the existence of segregation or lack of true homogeneity in the metal, suffice to explain the underlying cause of the break-down of a metal structure through corrosion.

## SOME OBSERVATIONS ON CORROSION.

D. E. PARTON

One of the main questions which has to be answered when a case of corrosion is being investigated, is whether the phenomenon

is due to the proximity of electrical systems or not. The identification of electrolytic corrosion is not an easy matter without a knowledge of all the surrounding circumstances, and even typical samples of the affected metal are not always sufficient for the purpose.

While leakage of current is usually regarded as being responsible for most cases of corrosion, it has been shown that underground structures are corroded by chemical action due to the soil conditions. Electric traction systems are given more blame than is warranted because stray currents are easily traced to them, and it is known that reasonable precautions have not always been taken.

The corrosion of cast iron, wrought iron, and steel was discussed. On account of the higher content of impurities in cast iron, the initial rate of corrosion is greatest in this material. If a wrought iron tube is without surface defects—a condition very rare in practice—it will not rust as readily as a cast-iron tube.

## CORROSION-RESISTING METALS AND ALLOYS.

C. M. GRAY.

It was pointed out that like other chemical reactions, corrosion reactions are governed by two factors: (a) intrinsic possibility of reaction, and (b) rate of reaction. If reaction between the metal and its environment is possible, we can only resist corrosion by influencing the reaction rate, by introducing a slow stage into the reaction. The physical process of diffusion affords such a slow stage, and the formation of an oxide film only one molecule thick has been shown to reduce the rate of oxidation of a metal by half, by retarding the diffusion of oxygen to the metal surface. Almost all metals are covered with a thin oxide film at ordinary temperatures, and the resistance of metals such as aluminium to corrosion is due to the stability of the film and its tendency to be self-repairing if damaged.

The film naturally produced on iron and steel is not of a kind which stops corrosion, as it does not repair itself, is pervious to oxygen and is not strong. By the addition of alloying elements to iron, the nature of the film may be altered to increase its protective power. Thus 0.25% of copper so improves steel that an increase in its life from two to four times results. The addition of sufficient chromium will alter the film in such a way as to stop oxidation altogether. In alloys containing more than 9% of chromium, each iron atom is adjacent to at least one chromium atom, and the film of oxides is adherent and impervious to oxygen.

The principal advances in the production of stainless alloys have been made in the familiar "stainless steels," which are essentially alloys of iron with about 18% of chromium and 8% of nickel. These are austenitic alloys, the carbon being in solid solution, and contrasted with those not containing nickel in not having to be hardened and polished to be resistant to corrosion. Two main difficulties have presented themselves. When these steels are welded, a zone on each side of the weld is found to be less resistant to corrosion than the remainder of the sample. In common with other austenitic steels, these alloys are difficult to machine. The addition of selenium promises to be of value in this connection.

The stainless steels show how research in the field of the less common metals has often been profitable. Future developments may be expected to be along the lines of the formation of protective films, perhaps by anodic oxidation as in the Bengough-Stewart process for aluminium.

## THE FRUSTRATION OF SCIENCE.

H. N. PARTON.

The development of scientific knowledge is an integral part of the development of the culture to which we are heirs, as science sprang from a revolt against the Roman tradition of authority. Scientific thought is free in the sense that it is disciplined, not by authority, but by the nature of the things which are thought about. It was the freeing of thought which gave rise to the vast material and economic progress of the world, and the Industrial Revolution was the fruit of the mathematical achievements of Galileo and Newton.

Along with the economic developments, there emerged a social structure organically related to the means of production, and the system we call capitalism is seen to have been suited to an age of scarcity, when in order to devote part of the resources of the community to the making of "capital" goods, abstemption from consumption was necessary, a function which was carried out by individual saving motivated by the desire for profits. Capitalism thus solved the problem of production, but has failed to solve that of consumption. Evidence was quoted to show how goods are being destroyed and the potential productivity of scientifically controlled industry is not being used. The main conclusion was that it lies within the capacity of physical science to solve the material problems of human existence, but that there is no reason to think that because it is possible, it will necessarily happen.

An analysis was made of the reasons for rejecting the belief in the inevitability of progress. It was suggested that man's intelligence is equal to the task of deriving a juster and more efficient and elastic social order, and that the main inhibitor is fear, which is an emotional principle. There seems little reason to believe that the spread of intellectual education will lead inevitably to social justice, though it can achieve much. What has been called the failure of democracy is really the discovery that political democracy is incompatible with economic autocracy. Only a true democracy, economic as well as political, will be able to use scientific knowledge for the benefit of the community. For this reason scientific workers must be concerned in the struggle for freedom, for the frustration of science, especially in the deliberate limiting of production in the interests of profit, is in the long run, the frustration of human freedom.

## OTAGO.

*Papers read—*

"The Chemistry and Manufacture of Malt Extract."—*W. B. Seymour.*
"Modern Micro-chemistry."—*T. A. Thomson.*
"Engine Performance of Petrol."—*J. H. Goodey.*
"Chemical Problems of Refrigeration."—*G. A. Holmes.*
"Hydrogen-ion Concentration."—*F. R. Meldrum.*

One of these papers has been received for publication in the main body of the Journal.

### ENGINE PERFORMANCE OF PETROL.

J. H. GOODEY.

It was explained that the performance of a motor spirit depends on (a) volatility, (b) energy, (c) knock characteristic, (d) stability.

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The horsepower of an engine, if knocking does not occur, was shown to be practically independent of the fuel. The cause of fuel knock was explained and illustrated by pressure diagrams and photographs. The knock characteristic of various fuels and hydro-carbons was given, and current theories and researches reviewed.

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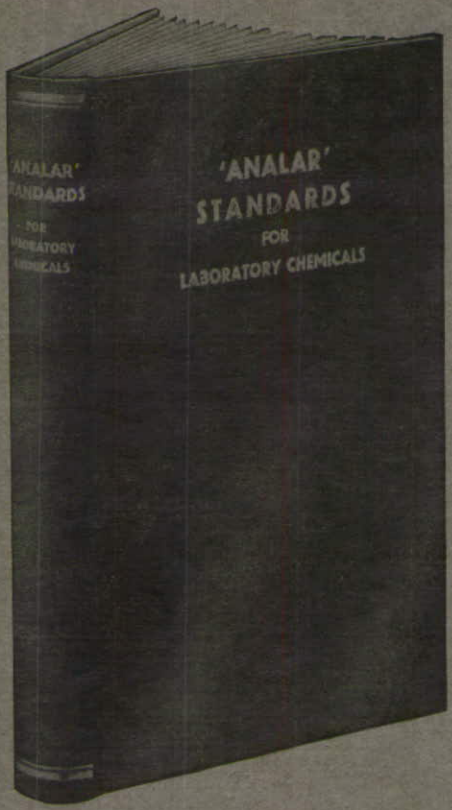


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