THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

THE following candidates have been elected members of the Society:

Douglas Onslow Burgess, Analytical Chemist and Assayer to Messrs. Murex, Ltd., Essex.

Victor Carcamo Marquez, D.Sc. (Lima), Public Analyst for the City of Lima, Peru.

John Kay, Analytical and Works Chemist to the Scottish Co-operative Wholesale Society, Glasgow. (*Through the Scottish Section.*)

Charles Alexander MacDonald, B.Sc. (Lond.), F.I.C., Senior Chemist at Evans' Biological Institute, Runcorn, Cheshire.

Anavamuda Srinivasan, M.A. (Madras), Chemist at the Indian Government Store Department, London.

Arif Alamiddin, B.A. (Amer. Univ., Beirut), Government Central Laboratories, Jerusalem.

Peter Clarke, B.A. (Oxon.), Analyst and Works Manager.

Abdul-Razzak Dabbagh, B.A. (Amer. Univ., Beirut), Government Laboratory, Baghdad, Iraq.

Hans Leo Lehmann, Ph.D. (Heidelberg), Analytical Chemist in practice in London.

Richard William Morris, B.Sc. (Lond.), A.C.G.F.C., D.I.C., F.I.C., Chief Chemist to Messrs. Pearce, Duff & Co., Ltd.

Harold Sidney Young, B.Sc. (Lond.), A.I.C., Chief Chemist, Messrs. C. & E. Morton, Food Manufacturers.

Tawfig Iskander Zakharia, B.A. and B.Sc. (Amer. Univ., Beirut), Government Central Laboratories, Jerusalem.

Death

WITH deep regret we record the death of Sir William Pope. An obituary notice will be published later.

Obituary

HENRY TURNER LEA

HENRY TURNER LEA was born at Burton-on-Trent on September 10th, 1889. He was educated at Burton Grammar School, Wellington College, and Birmingham University, where he graduated in science and later obtained the M.Sc. degree. He became an Associate of the Institute of Chemistry in 1917, and was elected to the Fellowship in 1925.

On leaving the University in 1912 he served in the Government Laboratory until 1915, when he joined the Special Brigade of the Royal Engineers. While serving in the ranks he was gassed, and when he resumed duty he was promoted to the rank of Lieutenant and put in charge of the Gas School at Bethune.

In 1919 he took over the consulting practice of Dewhirst of Halifax and succeeded him as Public Analyst. Later he obtained other public appointments, becoming Public Analyst for Scarborough, Huddersfield and Burton-on-Trent.

He joined our Society in 1919 and served on the Council in 1926–7. He also took an active part in the formation of the Northern Section of the Society and, as its first Honorary Secretary, did much to promote its success.

The outstanding characteristic of Lea's personality was his abundant energy, for, in addition to enlarging and extending his practice, he was always ready to accept a responsible position in the many social organisations to which he belonged. He was, for instance, an enthusiastic member of the Halifax Thespians, and produced several successful plays.

He was for many years Honorary Secretary of Queen's Lawn Tennis Club, Halifax, and became an official referee of the Lawn Tennis Association. These and other social activities made for him many friends, by whom he will be greatly missed.

His direct and outspoken manner was appreciated by his clients, who admired his ability to cover his scientific knowledge with what the business man regards as common sense, and this contributed in no small measure to his professional success in the West Riding.

He enjoyed excellent health until a week before his death, which occurred on July 28th during what was thought to be a minor operation.

He married Miss Margaret A. Walsh of Halifax, and she and two children survive him.

At the funeral the Society was represented by the writer, and the Northern Section by Mr. C. H. Manley and Mr. J. Firth. H. M. MASON

Silicosis and the Analyst

By F. S. FOWWEATHER, M.Sc., F.I.C., M.D., M.R.C.P., D.P.H.

(*Read at the Meeting of the North of England Section, March* 25, 1939)

If a person comes in contact with a toxic substance as a consequence of his employment, he runs an "occupational" risk of contracting the disease to which this substance may give rise; should he become incapacitated by the disease he may be entitled to compensation, or his relatives may be entitled to compensation if the disease should contribute to his death.

In examining claims for compensation use is sometimes made of chemical evidence, and analysts are sometimes asked to determine the amount of silica in the lungs of possible victims of silicosis, in the belief that this would be of value in attempting to reach a correct diagnosis in such cases and to deal fairly with the question of compensation. It is of some importance to examine the relation between silicosis and the silica-content of the lungs of its victims in order to see how far this belief is justified, and that examination is the chief object of the present communication.

Silicosis usually runs a chronic course, and rarely makes its appearance until exposure to the dust has continued for a prolonged period. (In Rand gold-miners, for example, the average duration of work before the earliest detectable signs is 13 years.) The first symptom to make its appearance is dyspnoea. This is slight at first, and only becomes evident after prolonged or severe exertion. It is, however, progressive, and later comes to dominate the clinical picture; radiographs at this stage show some areas with discrete shadows. Gradually dyspnoea and cough increase, and physical signs become more definite; radiographs show increased shadows, with a tendency for some to coalesce and exhibit mottling.

Later still there is serious or total incapacity through intensification of symptoms, particularly dyspnoea. The radiograph then usually shows extensive, dense shadows, indicating massive consolidation.

Any other disease accompanying the silicosis may, of course, modify the symptoms, signs, radiographic appearances, and general course of the disease, and the most frequent accompaniment is pulmonary tuberculosis.

The changes in the lungs, which are the cause of the signs and symptoms just described, are the gradual development of areas of fibrous tissue, ultimately quite hard and dense, which take the place of the actively-functioning, more highly specialised, spongy lung tissue. In fatal cases of uncomplicated silicosis the lungs are generally large and of increased density, and generally show some pleural adhesions. On section they very frequently show numerous rounded nodules, which give a characteristic "shotty feel" to the lung tissue. The nodules are dense and tough and composed of fibrous tissue. They may be quite small (2–5 mm. in diameter) or many may coalesce to form larger, composite nodules. The nodules are most abundant in the upper and middle portions of the lung. Some cases show quite massive, fused areas of fibrosis, still retaining evidence, however, of the original nodular character, while others show a still more diffuse and uniform type of fibrosis.

In mild cases of silicosis (seen for example in workers exposed to silica dust who have died from some entirely unrelated disease) changes may be limited to fibrotic areas in the lymphatic glands near the hilum of the lungs, or there may be a few small scattered nodules in the lung substance, often immediately beneath the pleura; between this and the fully developed stage of the fatal case, all grades are possible.

In presence of tuberculosis the typical appearances found in silicosis are modified, sometimes to a very considerable degree, so that, in some cases, the recognition of silicosis, in presence of extensive tuberculosis, may be extremely difficult.

The principal occupations in which silicosis occurs are:

1. *Coal-mining.*—The incidence of the disease varies greatly in the different coal-fields, depending largely on the nature of the rock in which the coal seams lie. South Wales has the greatest incidence among the coal-fields of Great Britain. Silicosis in coal-miners must be distinguished from anthracosis, which is due simply to the accumulation of fine coal-dust in the lungs. This causes only relatively slight and non-progressive fibrosis and, if unaccompanied by silicosis, is a practically harmless condition; it does not appear to cause increased susceptibility to tuberculosis.

2. *Gold-mining.*—Though silicosis from this cause may be contracted in the mines of South Africa or Australia, it has some relevance to the incidence of silicosis in this country, on account of cases among miners who have gone to work in these gold-mines for a time, and then returned home suffering from the disease.

3. *Sand-blasting.*—Here the dust inhaled is almost pure silica, in a finely divided form. According to the Chief Inspector of Factories and Workshops,[1] "No other silicosis-producing industry shows such grave figures for the average working lifetime of fatal cases, or figures comparable to the sand-blasting trade, except the manufacture of scouring powders."

4. *Pottery manufacture.*—Here, of course, the risk occurs only in certain processes; the later processes of decoration and glazing, for example, are free from the risk.

5. *Sandstone industry.*—This includes the quarrying or mining of sandstones, and hence affects quarrymen, and also the preparing and dressing of such stones, which involves stonemasons.

6. *Grinding of metals.*—The risk to the grinder arises where grindstones composed of natural sandstones are used. In many instances the incidence has been reduced by the substitution of artificial abrasive wheels.

7. *Tin-mining.*—A number of cases have arisen in the Cornish industry.

8. *Iron-ore mining.*—Some cases have occurred in the haematite mines of West Cumberland and elsewhere.

9. *The refractories industries.*

10. *Manufacture of abrasive soaps.*—Here highly siliceous material is mixed with powdered soap, anhydrous sodium carbonate, and sometimes other substances. The silicosis risk was not at first appreciated, but the occurrence of a few rapid

and severe cases of the disease soon called attention to it. I have previously referred to a case in which the death of a worker in this industry occurred after only three years' exposure, followed by a three-year period of illness.[2]

The condition arising sometimes in workers with asbestos—called asbestosis—differs from silicosis in certain important respects. In all the industries giving rise to silicosis some part at least of the inhaled dust consists of free silica, whereas the dust giving rise to asbestosis consists of chemically combined silica—principally as magnesium silicate; moreover, the material is of finely fibrous structure, and much of the dust given off from asbestos in process of manufacture consists of fragments of fibres. The clinical condition does not differ greatly from silicosis; dyspnoea is the earliest symptom and the most striking, and gradually increases as the disease progresses. The cause is again a fibrosis of the lungs, but with definite differences from that in typical silicosis. Thus while the fibrosis of the latter is mainly nodular, that of asbestosis is diffuse. Pleural adhesions in asbestosis are usually extensive and dense, especially at the base.

Thickening of the pleura is often a marked feature. The consistence of the whole lung is increased and large areas may show fibrous condensation of a decidedly tough nature.

Asbestosis is in general of more rapid onset than silicosis, the length of time which may elapse between exposure to the dust and a fatal termination being much less than in the average case of silicosis. The incidence of tuberculosis is high, though significantly less than in silicosis.

Having in mind some of the general facts relating to silicosis (and asbestosis), we can now pass on to a consideration of the diagnosis and the part played by chemical analysis. The diagnosis of silicosis and asbestosis during life is a matter for the physician, assisted by the radiologist; the analyst can rarely take any part. It is true that of the silica deposited in the lungs of sufferers, a portion is dissolved by the body fluids, passes to the blood stream and is excreted, but this is an extremely slow process, and its effect on the silica-content of blood and urine is small. A certain amount of silica is ingested with food and later excreted; in blood and urine changes in concentration resulting from ingested silica quite overshadow the changes caused by solution of inhaled silica. This is not simply a matter of probability; it has been the subject of investigation. King and Stantial[3] published a method for the determination of silica in blood and urine, and King and other collaborators have used this method in various experimental studies.

From these it appears that, under certain conditions which cause large increases in the concentration of urinary silica, no marked increase in the silica-content of the blood was observed. So far as urinary excretion of silica is concerned, King and McGeorge[4] say "Some evidence was obtained that the urinary silica was at a higher level among gold-miners than in a non-mining population, but the urinary silica values were found to be so dependent on the nature of the diet that no conclusions could be drawn in single cases."

Occasionally analysts have been asked to determine the silica-content of rock or other material worked by a patient, with a view to showing that he has been subjected to a harmful dust. This, of course, helps hardly at all in the matter of

diagnosis; it merely shows whether the occupation is, or is not, a possible cause of silicosis. Moreover, the silica-content alone is not the only factor; the size of the dust particle is of considerable importance, for it is generally agreed that the great majority of dust particles which find their way into the lung are less than 5μ in diameter, and very few exceed 10μ (with fibrous minerals, however, the *length* of fibres found in the lungs may greatly exceed 10μ).

In asbestosis there is one other finding that is of interest, *viz.* the presence of "asbestosis bodies" in the sputum. These are spindle-shaped structures with slender centres and bulbous extremities and vary in length up to 50 or 100μ, though some are much shorter. Many resemble close-set strings of beads, whilst others are apparently unsegmented. The colour varies from faint yellowish-green to deep brown. A fine, transparent asbestos fibre runs through the core of each body. "The bodies are readily demonstrated in the sputum of asbestos workers, at least after the first year or two of employment. In older workers they may be present in profusion, and are best demonstrated by the use of an antiformin concentration method. Their presence is not necessarily an indication that pulmonary fibrosis exists; they merely show that asbestos dust has been inhaled into the lungs and has remained there for some time. The presence of clumps of bodies in the sputum is a much more significant finding, pointing, as it does, to disintegration of lung tissue, whether of tuberculous or simple broncho-pneumonic nature" (Stewart[5]).

CHEMICAL AND PATHOLOGICAL DIAGNOSIS.—The diagnosis of silicosis after death is apparently of more importance to the analyst. Here let me point out that it does not follow that methods that have been useful in the scientific investigation of a condition, and in the elucidation of many important facts concerning it, will continue to be of similar usefulness after these facts have become clearly established; in other words, methods used in investigation may not be of equal value—may in fact be rarely needed—in matters concerned with routine diagnosis of individual cases. This should be quite obvious, yet I find that it is sometimes overlooked.

I believe that lung analyses, in cases of silicosis, have sometimes been asked for by someone who knows that such analyses have been used in the investigation of some of the problems of silicosis, and therefore thinks that they have an application in the consideration of each individual case. This is, in fact, only rarely true. It cannot be too strongly emphasised that the diagnosis of silicosis (and also of asbestosis) after death is essentially made on pathological, not chemical, grounds.

Silicosis is a disease, as we have seen, due to a pathological condition of the lungs. This, it is true, is caused by siliceous material, but unless it can be shown that the amount of silica to be found in the lungs, and the degree of pathological change maintain a reasonably constant relationship, chemical analysis of the lungs can never be a deciding factor in diagnosis. At best, all it can do is to provide certain additional evidence which, in cases where purely pathological evidence is doubtful, *may* possibly help to clarify the issue. We must therefore examine the evidence dealing with the relation between silica-content of lungs, and degree of silicotic fibrosis.

RELATION BETWEEN SILICA-CONTENT OF LUNGS AND FIBROSIS.—Certain general considerations suggest that the relationship is far from close, *viz.*

(1) Not all workers in the dangerous trades contract the disease, *i.e.* many who must have inhaled silica-containing dust, and who must therefore have an appreciable amount of silica in the lungs, do not get clinical silicosis.

(2) Some occupations are more dangerous than others, and this, not because the actual amount of silica inhaled is greater in the more dangerous trade, but presumably because of the nature of the inhaled material. Silicosis is believed to be due to a chemical and not to a physical action of silica; hence factors concerned with degree of chemical reactivity, *e.g.* particle size, may be, and almost certainly are, of much more importance than total quantity of silica.

(3) The great variability in reaction of the human body to toxic substances is well-known. A dose of a poison sufficient to cause death in one individual may cause little disturbance in another, and there is no reason to believe the reaction of the human body towards silica to be more constant than its reaction to most other harmful agents.

But we need not rely on general considerations only, since more precise facts are at our disposal. In considering these it is well to have in mind some figures relating to the silica in normal lungs. The cases I have personally been concerned with show values up to 0·20 per cent. (on the weight of dried lung) and most other investigators have obtained similar figures.

In a number of cases dealt with by Professor Stewart and myself, different portions of lungs from the same individual, showing different degrees of silicotic fibrosis, have been analysed separately. Even here, where the same dust has operated in the same individual, the correlation between amount of silica and degree of fibrosis is not a very close one. While, in general, the more fibrotic portion has been found to contain more silica than the less fibrotic portion, great differences between degrees of fibrosis have sometimes been found where differences in silica-content were relatively small, and *vice-versa.* A few examples will illustrate this:

(1) A portion of lungs showing massive, nodular silicosis contained 2·62 per cent. of silica, whilst the rest of the lungs, showing silicosis to a considerably less degree, contained 2·00 per cent.

(2) Portions of lungs which were densely silico-anthracotic contained 5·04 per cent. of silica, whilst portions with so little fibrosis as to justify the description of spongy, contained 2·22 per cent. In contrast with this—

(3) Portions of lung grossly silicotic contained 2·66 per cent. of silica, while spongy portions contained 0·33 per cent.

(4) In lungs with fairly widespread changes, the more silicotic portions contained 1·14 per cent. of silica, whilst the less silicotic (but not spongy) portions contained 0·28 per cent.

(5) In a case of very advanced silicosis the densely fibrotic portion contained 0·94 per cent. of silica, whilst portions that were less fibrotic, but contained scattered, dense nodules showed only 0·21 per cent.—practically a normal figure.

When we come to compare the lungs of different individuals, in different occupations, the lack of correlation between silica-content and degree of fibrosis

is often very striking. I do not propose to quote figures on this point, as I have already done so elsewhere[2] some time ago.

Since these figures were obtained many more analyses have been carried out, but these have not yet been fully examined. They include, however, sufficient figures for certain specific industries to allow of some comparisons between lungs of different individuals in the same occupation. It is probable that when they have been properly studied they will show a closer correspondence between silica-content and degree of fibrosis than where cases in different occupations are considered, but I have little doubt that here, too, this correspondence will prove to be only a very rough one.

It is true, of course, that the majority of silicotic lungs that have been examined show an increased silica-content. Hence, in a general way, it might be said that the finding of increased silica in lungs indicates the probability that silicosis may be present, and the degree of probability depends on the amount by which this increased silica exceeds the normal. But it is difficult to state any limiting figure beyond which it might be said that the probability becomes a certainty. Thus, in our own experience most lungs containing 1 per cent. or more of silica have been found to be silicotic, yet we have come across two or three cases with figures in the neighbourhood of 2 per cent. which showed little or no silicosis, and in one case in which the lungs contained over 6 per cent. of silica, there was only a moderate degree of fibrosis.

It must be remembered, too, that while many cases of silicosis are subjected to post-mortem examination, few cases of those in the same occupations who die of some cause having no obvious relation to silicosis receive such examination. So far as our own work is concerned, we have received material from cases of silicosis from various sources, while for material from cases without silicosis but with a silicosis risk we have been restricted to patients who have died in the Leeds General Infirmary, whose history has indicated an employment in a dangerous occupation. Our knowledge, therefore, of the amount of silica to be found in lungs of such cases is from a much smaller sample of the persons concerned, than of those suffering from silicosis, and is consequently much less complete. It is therefore possible that the number of cases of high lung silica, with little or no silicosis, is higher than the figures at present available indicate.

Again, the finding of a normal lung silica value does not with certainty establish the absence of silicosis, but only the probability of such absence. This is particularly true of asbestosis.

In considering the bearing of analytical results on any particular case, it is always desirable to take into account also as much evidence as can be obtained regarding the nature of the occupation, its duration, and the length of time which has elapsed between giving up the occupation and death.

Evidence of Silicosis.—In the majority of cases of possible silicosis which come up for consideration there is no difficulty in arriving at a true appreciation of the condition; there is clear pathological evidence of silicosis and a history of exposure to a harmful dust, usually over a considerable period of time. In cases where the degree of silicosis does not appear of itself to be the cause of death, and some other disease is also present, the question as to whether the silicosis is a

contributory cause of death is to be decided on a consideration of all the pathological evidence obtainable, together with, in some cases, the clinical evidence; chemical evidence is of little value.

The presence of tuberculosis sometimes raises difficulties. Fibrosis of the lung *per se* is not a reaction specific to silica; it is an accompaniment of most chronic diseases, and this is especially true of the more chronic forms of tuberculosis.

In many cases there is clear evidence of both silicosis and tuberculosis. Difficulties only arise where it may be impossible to decide whether silicosis is actually present or not. In such cases the history is of considerable importance, and where it clearly establishes exposure to a harmful dust (*i.e.* occupation in a dangerous trade), it will have very considerable influence on the final decision. Where the history is inconclusive, chemical analysis, if it establishes proof of exposure to a harmful dust, will become an important factor.

In the absence of tuberculosis, cases sometimes show some lung fibrosis, which though not characteristically of silicotic type, may be considered to be probably due to the action of silica; here, too, evidence regarding exposure is important. Chemical analysis may afford proof of exposure and also instigate a more careful investigation into the past history.

In doubtful cases, whether tuberculous or not, the possibility, on pathological grounds, that the condition may be silicotic, together with adequate proof of sufficient exposure to a harmful dust, will, as a rule, be accepted as sufficient grounds for establishing a claim for the condition to be considered as one of silicosis. For compensation purposes, at any rate, chemical analysis, apart from its bearing on the question of exposure, will very rarely be called for. From a more scientific point of view, the information obtainable from chemical analysis would probably justify consideration more frequently.

Chemical Evidence.—It will be realised from what has already been said, that the analyst can give very little help in the great majority of cases of silicosis; so far as the remainder are concerned, the object of his work will mainly be to supply evidence concerning exposure to a dangerous dust. One case in which analysis proved of considerable interest in this respect seems worth recording. During the examination of what were believed to be lungs from normal individuals, one case, that of a man described as a labourer, gave a figure for lung silica of 0·45 per cent. As this figure is more than double what had been found in other normal cases, it indicated, either that the normal range was greater than had previously been thought to be the case, or that the labourer had been exposed to a siliceous dust. A more careful examination of the history was therefore made, and it was proved that the man had been employed as a packer with the Leeds Fireclay Co. He was therefore not a "normal" from the point of view of exposure to dust, though his lungs showed no fibrosis.

Occasionally cases of silicosis arise in connection with occupations not normally considered to be dangerous from this point of view. One such case is reported by Edwards.[6] It concerns a grave-digger who died, after 17 years at this occupation, of what was believed at first to be tuberculosis; an expert, however, considered the case to be one of silico-tuberculosis. Unfortunately no analysis of the lungs

was made. It was found, however, that the graves dug by the man were in red sandstone, and pneumatic drills were often employed. The job was a very dusty one, particularly in dry weather. There was therefore clear evidence here of exposure to a dangerous dust. It is conceivable, however, that in some unusual cases, evidence of such exposure may depend on chemical analysis.

ANALYSIS OF LUNGS.—The method I have used for the analysis of lungs is on orthodox lines, and is not original. The specimen is cut up into pieces about half-an-inch in diameter, with scissors, and dried for three or four days in the steam-oven. It is then ground in an iron mortar to pass a 30-mesh sieve. Four g. are weighed into a platinum dish (5 × 2 cm.), or 3 g. if a high silica-content is expected, and the ash is determined, heating being at first carried out carefully over a small Bunsen flame until charring is complete, and then in a Davies crucible furnace heated with a Heinz burner.* After the weight of the ash has been determined, 12 to 15 times that weight of fusion mixture (equal parts of sodium and potassium carbonates) is added in the dish, and the mixture is fused in the furnace for 2½ hours.

After cooling, the fused substance is dissolved in 20 per cent. hydrochloric acid (*i.e.* 1 part of conc. hydrochloric acid to 4 parts of water), and the solution is evaporated to dryness in a porcelain dish on the water-bath. A further 20 ml. of 20 per cent. hydrochloric acid are added, and the mixture is again evaporated to dryness. The residue is then baked in an air-oven at 110° C. for from 30 mins. to an hour. The dish is cooled slightly, 1 ml. of conc. hydrochloric acid and 19 ml. of hot water are added, the dish is placed on a water-bath, and, after digesting for about 15 minutes, the contents are filtered through a No. 44 Whatman filter-paper. The filtrate and washings are evaporated to dryness, a further 20 ml. of 20 per cent. hydrochloric acid are added, and the liquid is again evaporated to dryness. The residue is baked, as before, at 110° C., treated with 1 ml. of hydrochloric acid and 19 ml. of hot water, allowed to simmer, and filtered through a second filter-paper. The two filter-papers are burnt together in a second platinum dish, and the residue is heated on the furnace for an hour, after which the residue of crude silica is weighed.

To this crude silica 1 ml. of water and 0·2 ml. of conc. sulphuric acid are added, and then 5 ml. of pure hydrofluoric acid, and the mixture is evaporated on the water-bath until only sulphuric acid is left. If necessary, a further 2 ml. of hydrofluoric acid are added and the mixture is again evaporated. Finally the remaining sulphuric acid is carefully driven off over a free flame, and the residue is then heated for half-an-hour in the furnace. The weight of the residue gives the amount of material not volatilised with hydrofluoric acid, and this is subtracted from the crude silica to give the weight of pure silica.

The platinum dish used for the incineration and fusion of the ash is attacked somewhat in the process, and after it has been used for a few times there is a tendency for scaling to occur. It is advisable, therefore, to scrape the inner surface after each fusion to remove such scale. I find that 60 to 70 incinerations and fusions can be carried out before it is necessary to renew the dish (at a cost of

* The Davies furnace, as supplied by Messrs. Gallenkamp & Co., is heated with a Teclu burner, but the Heinz burner (of foreign make) is more satisfactory.

about one pound). Dr. Faulds (personal communication) has used stainless steel dishes for this part of the process, and finds them satisfactory.

Colorimetric micro-methods for silica determination are also in use. King and Stantial,[3] for example, give methods for determining silica in blood, urine and tissues, the basis being the production of a yellow silico-molybdic acid complex, and the reduction of this to give a blue colour. For details of the method the original paper should be consulted.

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LEEDS
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The Determination of Manganese by means of 8-Hydroxyquinoline in Presence of Magnesium

BY G. STANLEY SMITH, B.Sc., A.I.C.

BERG[1] precipitated manganese as the hydroxyquinoline complex, $Mn(C_9H_6ON)_2$, $2H_2O$, from solutions faintly acid with acetic acid, or faintly ammoniacal, and obtained by either method a satisfactory separation from the alkaline earths, though not from magnesium.

Separation from magnesium, if possible, would be of importance, particularly since magnesium is the element most frequently determined by the hydroxyquinoline method.[2]

According to Gotô,[3] the reagent precipitates manganese, quantitatively in the *p*H range, 5·87 to 10·00, partially at *p*H 4·55 and 12·32, and not at all at *p*H 4·25. Hence, unless co-precipitation is unavoidable, a separation of manganese from magnesium, which is precipitated above *p*H 7, should, presumably, be possible.

The method for aluminium which I described recently[4] has now been applied to the determination of manganese. It appears from the results of the investigation detailed below, that, whilst moderately small amounts of magnesium (0·01 g.), cause no appreciable interference, amounts of the order 0·1 to 0·5 g. cannot be separated with certainty unless the manganese precipitation is repeated.

Except for other details shown later, the method followed that for aluminium. The manganese solution, prepared by reducing a permanganate solution with hydrogen peroxide in presence of dilute sulphuric acid and boiling off the excess of peroxide, was treated with 8-hydroxyquinoline solution (3 per cent. in 0·2 *N* hydrochloric acid), and dilute ammonia solution was added, drop by drop, to the nearly boiling solution until a cloudiness remained. A known volume of *N* hydrochloric

acid was added, and then 10 ml. of the acidity-regulating solution (28 g. of potassium bromate, 120 g. of potassium bromide and 250 g. of sodium thiosulphate per litre), the solution (100 to 110 ml.) was boiled for exactly one minute and filtered, and the precipitate was washed with hot water and dissolved in hydrochloric acid (30 ml. of concentrated acid with 90 ml. of water). The solution was cooled,

TABLE I

Manganese mg.	Magnesium g.	Hydroxyquinoline 3 per cent. ml.	Hydroxylamine hydrochloride g.	Hydrochloric acid, *N* ml.	Bromine, 0·1 *N* reqd. ml.	Bromine, 0·1 *N* calc. ml.
27·5	—	10	0·025	2	41·05	40·05
22·0	—	10	0·025	2	32·35	32·04
					32·35	32·04
16·5	—	10	0·025	2	24·5	24·03
27·5	—	6	0·025	2	40·4	40·05
16·5	—	4	0·025	2	23·7	24·03
11·0	0·5	6	0·025	3	17·7	16·02
11·0	0·1	6	0·05	2	17·7	16·02
16·5	—	6	0·1	3	24·05	24·03
27·5	—	6	0·1	3	37·75	40·05
27·5	0·2	6	0·2	2	35·8	40·05
27·5	—	7·5	0·2	1	39·4	40·05
27·5	—	7·5	0·1	1	39·95	40·05
27·5	0·4	7·5	0·1	1	40·65	40·05
22·0	—	10	0·1	1	32·55	32·04
5·5	—	6	0·1	2	8·15	8·01
5·5	0·2	6	0·1	2	13·2	8·01
16·5	0·2	6	0·1	2	25·25	24·03
5·5	—	6	0·1	4	8·0	8·01
					7·85	8·01
5·5	—	6	0·1	5	6·25	8·01
27·5	—	10	0·02	3	40·7	40·05
27·5	0·1	10	0·02	3	39·3	40·05
					40·75	40·05
27·5	0·1	6	0·02	3	32·8	40·05
27·5	0·1	10	0·02	2·5	41·0	40·05
					42·0	40·05
27·5	—	10	0·02	1	40·6	40·05
27·5	0·2	10	0·02	2	40·9	40·05
5·5	0·1	10	0·01	3	9·15	8·01
16·5	0·1	10	0·01	3	25·0	24·03
5·5	0·1	10	0·01	4	8·8	8·01
16·5	0·1	10	0·01	4	25·0	24·03
5·5	0·1	10	0·01	5	7·6	8·01
16·5	0·1	10	0·01	5	23·7	24·03
16·5	0·1	10	0·01	5	24·25	24·03
16·5	0·1	10	0·01	4·5	24·3	24·03
16·5	—	10	0·01	6	20·85	24·03

0·1 *N* bromine solution (2·805 g. of potassium bromate, 12 g. of potassium bromide and 25 ml. of 0·5 per cent. indigo carmine solution per litre) were added in small excess, and the excess was determined by back-titration with 0·1 *N* thiosulphate solution, after addition of potassium iodide and finally starch.

One ml. of 0·1 *N* bromine ≡ 0·6866 mg. of manganese.

The figures shown below for ml. of 0·1 *N* bromine solution required represent the volume actually used, less the volume of thiosulphate solution required in the back-titration. Magnesium, when included in the solution with the manganese, was added as the chloride.

The following modifications of the method were tried:

(1) The manganese solution, containing 10 ml. of hydroxyquinoline reagent, nearly boiling, was treated with weak ammonia until one drop produced a cloudiness, and then boiled for one minute with the "buffer" solution.

Mn, 22·0 mg.; Mg, nil; 0·1 *N* bromine, 32·6, 32·65, 32·5 (calc., 32·04).

Mn, 22·0 mg.; Mg, 0·01 g.; 0·1 *N* bromine, 36·6, 35·1 (calc. 32·04).

These precipitates were of a brown colour, possibly owing to the presence of manganese in a higher state of oxidation. Berg used sulphur dioxide or hydroxylamine to reduce manganese to the bivalent state before precipitation.

(2) A few drops of sulphur dioxide solution were added before the ammonia; 3 ml. of *N* hydrochloric acid were added on the appearance of cloudiness produced by ammonia.

Mn, 16·5 mg.; Mg, nil; 0·1 *N* bromine, 24·6 (calc., 24·03); brown ppt.

Mn, 16·5 mg.; Mg, 0·5 g.; 0·1 *N* bromine, 25·05; yellow ppt.

(3) In the experiments (Table I), p. 788, hydroxylamine hydrochloride was added to the manganese solution with the hydroxyquinoline. Ammonia solution (approximately 2 *N*) was dropped into the nearly boiling solution until a cloudiness appeared, *N* hydrochloric acid was added in the amounts shown on p. 788, and then, after a short period of boiling, 10 ml. of the "buffer."

TABLE II

Manganese mg.	Magnesium g.	Hydroxyquinoline, 3 per cent. ml.	Hydrochloric acid, *N* ml.	Bromine, 0·1 *N* reqd. ml.	Bromine, 0·1 *N* calc. ml.
16·5	—	6	3	24·3	24·03
16·5	0·1	6	3	25·15	24·03
16·5	—	10	3	24·0	24·03
				24·2	24·03
				24·1	24·03
16·5	0·1	10	3	25·2	24·03
16·5	0·01	10	3	24·2	24·03
22·0	0·002	10	3	32·15	32·04
22·0	0·01	10	3	32·2	32·04
22·0	—	10	5	32·0	32·04
22·0	0·1	10	5	33·4	32·04

The precipitates obtained in presence of hydroxylamine were yellow when magnesium was absent. The colours tended to be greenish-yellow, sometimes a decided green, when magnesium was present, and the filtrates were also more or less green.

(4) In the above experiments (Table II) the solution before the precipitation contained ammonium chloride equivalent to 10 ml. of conc. hydrochloric acid. No sulphur dioxide or hydroxylamine was added, but the acid solution was

boiled for several minutes immediately before the introduction of the "buffer" solution.

All the precipitates were pale yellow, but they tended to clog the filter, making filtration somewhat slower than in absence of ammonium chloride.

(5) Hydrogen peroxide was added immediately before the "buffer" solution. Ten ml. of 3 per cent. hydroxyquinoline solution were present in each experiment (Table III).

TABLE III

Manganese mg.	Magnesium g.	Hydrogen peroxide) (20 vol.) ml.	Hydrochloric acid, *N* ml.	Bromine, 0·1 *N* reqd. ml.	Bromine, 0·1 *N* calc. ml.
5·5	—	1	3	8·1	8·01
5·5	0·2	1	3	14·3	8·01
22·0	0·4	1	4	34·2	32·04
22·0	—	2	3	32·35	32·04
5·5	—	2	5	8·15	8·01
5·5	0·5	2	5	11·7	8·01
16·5	2·0	2	4	25·1	24·03
16·5	0·5	2	5	30·4	24·03

All these precipitates were yellow, and could be filtered off rapidly.

(6) Ammonium chloride present equivalent to 10 ml. of conc. hydrochloric acid. Hydrogen peroxide (1 ml. of 20 vol.) was added, and the solution was boiled for about one minute before the "buffer" solution was added. Ten ml. of hydroxyquinoline solution were present in each experiment (Table IV).

TABLE IV

Manganese mg.	Magnesium g.	Hydrochloric acid, *N* ml.	Bromine, 0·1 *N* reqd. ml.	Bromine, 0·1 *N* calc. ml.
16·5	—	4	24·1	24·03
16·5	—	5	24·0	24·03
16·5	0·01	4	24·05	24·03
16·5	0·025	5	24·35	24·03
27·5	0·05	5	40·3	40·05
27·5	0·5	5	42·7	40·05

These precipitates were yellow and readily filterable. It is important not to boil the manganese solution containing both hydroxyquinoline and hydrogen peroxide for several minutes, as a deep brown solution results, from which the "buffer" solution throws down a sticky brown precipitate, whether ammonium chloride is present or not.

The method recommended for the precipitation is No. 6 above, followed by a re-precipitation under the same conditions if the magnesium exceeds 0·10 g. The manganese solution (about 100 ml.), nearly boiling, and containing about 6 g. of ammonium chloride or 10 ml. of conc. hydrochloric acid and 10 ml. of the hydroxyquinoline reagent, is neutralised with ammonia solution (finally with 2 *N* ammonia) until a permanent precipitate appears. Hydrochloric acid (4 or 5 ml. of an *N* solution) and a few drops of hydrogen peroxide are then added, the

solution is boiled, 10 ml. of the "buffer" solution are added, boiling is continued for exactly one minute, and the solution is filtered.

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* NOTE.—In studies of hydroxyquinoline precipitations Gotô's results are of interest. A summary is given below.

*p*H RANGES FOR HYDROXYQUINOLINE PRECIPITATIONS, ACCORDING TO H. GOTÔ

(*Sci. Rep. Tôhoku*, 1937, **26**, 391; *ibid.*, 1938, **26**, 418 [Mo and V])

Metal	No ppt. (acid)	Min. *p*H for complete pptn.	Max. *p*H for complete pptn.	No ppt. (alkaline)
Al	2·8	4·2	9·8	12·3
Zn	2·8	4·4	Very great	—
Cd	4·0	5·4	do.	—
Ni	2·8	4·6	10·0	(>13·2)
Mn	4·3	5·9	10·0	(>12·3)
Co	2·8	4·2	11·6	—
Ti	3·5	4·8	8·6	12·0
U	3·1	4·1	8·8	12·1
Th	3·7	4·4	8·8	12·5
Pb	4·8	8·4	12·3	—
Ca	6·1	9·2	Very great	—
Mg	6·7	8·2	do.	—
Fe (ferric)	2·4	2·8	11·2	—
Cu	2·2	2·7	Very great	—
Bi	3·5	4·8	10·5	12·9
Mo	0·7	3·3	7·6	13·1
V	1·1	2·7	6·1	7·3

G. S. S.

The Determination of Ethyl Alcohol in presence of Methyl Alcohol, *iso*Propyl Alcohol and Acetone

BY E. J. BOORMAN, B.Sc., PH.D., D.I.C.

METHYL alcohol, *iso*propyl alcohol and acetone are frequently present with ethyl alcohol in modern solvents and lacquers. Since they are not completely removed when the Thorpe and Holmes[1] method for the determination of ethyl alcohol is applied, their presence reduces the specific gravity of the distillates, and consequently increases the apparent proportion of ethyl alcohol present. There is no convenient, rapid, accurate method for the determination of the ethyl alcohol under these conditions. The following work describes such a method.

The preparation of a distillate containing only water and the four compounds mentioned above is normally readily achieved by the method of Thorpe and

Holmes,[1] or by suitable modifications thereof. The presence of methyl alcohol in this distillate may be shown by Simmonds' modification[2] of Denigès' test[3] which, under these conditions, is specific for methyl alcohol; that of acetone by Adams and Nicholls's test,[4] or the iodoform reaction; that of *iso*propyl alcohol by Bodendorf's test.[5] This latter, however, is not specific; a more reliable test is that of Adams and Nicholls[4] (*loc. cit.*) after removal of acetone by methods already known (Hoskins,[7] Hoff and Macoun,[8] Macoun[9]). Ethyl alcohol may be detected by the "aldehyde resin" test of Thresh.[10]

It has been shown by Denigès,[6] and later by Hoskins,[7] that acetone forms an insoluble compound with mercuric sulphate; this reaction may be used to remove small quantities of acetone from aqueous solution. The present method depends on the formation of an analogous compound with mercuric dichromate, which produces a deep orange or red precipitate when an aqueous solution of stoichiometrically equivalent amounts of mercuric sulphate and potassium dichromate is heated to 70–80° C., with acetone. In presence of a large excess of reagent the precipitation of the acetone is quantitative. As sulphuric acid is used to prepare the mercuric sulphate solution, the liquid has strong oxidising properties, and under the conditions of the experiment, *iso*propyl alcohol is oxidised to acetone which, before further oxidation can occur, reacts to form the insoluble mercury dichromate compound. Methyl alcohol is oxidised to carbon dioxide and water, and ethyl alcohol quantitatively to acetic acid. The acetic acid may be distilled in steam and titrated with standard alkali. The compound of acetone appears to be quite unaffected under these conditions, which are such that free acetone would be rapidly oxidised. The nature of the compound has not yet been elucidated, but work on the subject is proceeding.

Methyl ethyl ketone has been found to yield an analogous compound.

Warning

These mercury chromium compounds, when moist, are stable, but when dry are sensitive to heat or shock and explode violently when struck. They are readily destroyed by conc. hydrochloric acid. It is necessary to emphasise strongly their dangerous character. For this reason, the method described should be used only when others are inconvenient, and then only by skilled workers.

The acetic acid produced by the oxidation of 0·5 ml. of proof spirit is equivalent to 49·5 ml. of $N/10$ alkali. It has been found that 100 ml. of the reagent are capable of retaining acetone equivalent (in sp.gr.) to about 0·7 ml. of proof spirit and of completely oxidising considerably more than this quantity of methyl alcohol. Thus the experiments have been conducted with 100 ml. of reagent and a solution containing a total of not more than 0·55 ml. of apparent proof spirit, for convenience of the volume of steam distillate required and its titre with $N/10$ alkali.

Method.—The reagent is prepared by dissolving 100 g. of mercuric oxide in 250 ml. of conc. sulphuric acid diluted with approximately 3 volumes of water and making up to 2 litres with water, in which is dissolved 135·7 g. of potassium dichromate. The distillate resulting from the process of purification already indicated, if of high strength, is diluted to admit of accurate measurement of a

suitable volume containing not more than 0·5 ml. of apparent proof spirit, and to this quantity are added 100 ml. of reagent. The whole is allowed to stand at room temperature in a well-stoppered flask for 30 minutes, with occasional agitation. This ensures complete oxidation of the ethyl alcohol. Heating the solution without this preliminary period of cold reaction leads to loss of acetaldehyde. The solution is then boiled under reflux for 15 to 20 minutes. In presence of acetone or *iso*propyl alcohol a heavy precipitate is thrown down at approximately

TABLE I

Ethyl alcohol, as proof spirit ml.	Other ingredient, equivalent as proof spirit ml.	Total apparent proof spirit ml.	Ethyl alcohol found, as proof spirit ml.
0·5185	—	0·5185	0·5175
0·4148	—	0·4148	0·4146
0·3111	—	0·3111	0·3105
0·2074	—	0·2074	0·2072
0·1037	—	0·1037	0·1040
0·0519	—	0·0519	0·0525
	Acetone		
0·4148	0·1037	0·5185	0·4138
0·2074	0·3111	0·5185	0·2070
0·1037	0·4148	0·5185	0·1035
	Methyl alcohol		
0·4148	0·1137	0·5285	0·4145
0·2074	0·3411	0·5485	0·2077
0·1037	0·4548	0·5585	0·1040
	*iso*Propyl alcohol		
0·4148	0·0989	0·5137	0·4140
0·2074	0·2967	0·5041	0·2078
0·1037	0·3956	0·4993	0·1035

80° C., and in presence of methyl alcohol carbon dioxide is evolved. This boiling is necessary to drive off any carbon dioxide formed and to ensure completion of oxidation. The flask is then partly cooled, the condenser is rinsed down with water, and the liquid is distilled in steam. The volume may be conveniently reduced to about 75 ml. during the distillation. It has been found that by using slightly alkaline distilled water in the steam generator, the deleterious effect of entrained acid gases on the titration is practically eliminated. Five hundred ml. of distillate are normally sufficient, and are titrated against $N/10$ alkali, phenolphthalein being used. A further 50 ml. is then collected, and should the titre of this exceed 0·1 ml. of $N/10$ alkali, a further 150 ml. are collected and titrated. From the total titre the amount of ethyl alcohol present may be calculated, 1 ml. of $N/10$ alkali being equivalent to 0·0101 ml. of proof spirit.

RESULTS.—Series of experiments have been made with the single substances as controls; also with mixtures of ethyl alcohol with each of the other compounds singly, and with mixtures of all four. With methyl and *iso*propyl alcohols and acetone alone in quantities up to 0·7 ml. of apparent proof spirit, figures obtained

for the distillates (50 ml.) were all less than that equivalent to 0·0005 ml. of proof spirit, whilst with distillates of 500 ml. all were less than that equivalent to 0·0025 ml. of proof spirit.

Table I gives figures for ethyl alcohol alone, and with single added impurities. Table II gives results for four component blends. The fourth place of decimals is given as calculated, although, from the figures quoted, the accuracy of the method is apparently of the order of $\pm 1 \times 10^{-3}$ ml. of proof spirit.

TABLE II

EXPRESSED AS (APPARENT) PROOF SPIRIT

Ethyl alcohol ml.	Methyl alcohol ml.	*iso*Propyl alcohol ml.	Acetone ml.	Total ml.	Ethyl alcohol found ml.
0·0519	0·0828	0·1824	0·2374	0·5545	0·0525
0·1037	0·1592	0·1978	0·0622	0·5229	0·1040
0·2074	0·1024	0·1780	0·0414	0·5292	0·2070
0·4150	0·0456	0·0593	0·0207	0·5406	0·4149
0·0519	0·1656	0·2736	0·0791	0·5702	0·0518
0·1037	0·2276	0·0593	0·1244	0·5150	0·1040
0·2075	0·2048	0·0396	0·0933	0·5452	0·2075
0·4150	0·0684	0·0198	0·0414	0·5446	0·4145
0·0519	0·2484	0·0912	0·1582	0·5497	0·0522
0·1038	0·0684	0·1385	0·2073	0·5180	0·1045
0·2075	0·0456	0·0890	0·1866	0·5287	0·2080
0·4150	0·0228	0·0396	0·0622	0·5396	0·4145

SUMMARY.—Methyl and *iso*propyl alcohols and acetone are removed in one operation from their mixtures with ethyl alcohol. The ethyl alcohol is oxidised quantitatively to acetic acid and estimated as such after distillation in steam from the reaction mixture.

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Extract of Malt with Cod-Liver Oil: Determination of Oil and Vitamin A

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(*Read at the Meeting, May* 3, 1939)

The determination of the oil-content of Extract of Malt with Cod-liver Oil, and of the vitamins in the oil, is a matter of considerable importance to buyers who wish to check the quality of this article supplied to them. It appeared to those responsible for approving supplies to the London County Council (as a large user) that the matter required investigation in order to see whether the full quantity and quality of oil admixed in the manufacture could be recovered by any simple process, and hence the rejection be justified of any consignment which, on analysis, was found to be deficient in either respect.

Some methods for determination of oil in this preparation could be traced in the literature, but little work on the vitamin A content of the recovered product has been published.

In preliminary experiments attempts were made to determine the vitamin A content of the extracted oils without making any attempt to obtain quantitative yields of the oil. This procedure subsequently seemed inadvisable, since direct spectrographic determination of $E^{1\%}_{1cm.}$ $328m\mu$ on the extracted portion gave very high figures, indicating extraction of light-absorbing substances out of proportion to the true $E^{1\%}_{1cm.}$ $328m\mu$ value of the oil. This is clearly demonstrated by the following results:

Table I

		$E^{1\%}_{1\,cm.}$ $328m\mu$
(*a*)	Direct extraction of oil with cold ether after "massing" with anhydrous sodium sulphate ..	0·83
	With very small proportionate recovery.. ..	Not less than 1·0
(*b*)	Direct extraction with light petroleum containing ether, after solution in water	0·87
	With very small proportionate recovery.. ..	General absorption
(*c*)	Cod-liver oil used	0·60

It was soon evident that, with the small quantities of oil being handled, relatively large losses of vitamin A could occur during standing and heating, and it was decided that, to avoid unnecessary risk, an extraction in duplicate was desirable, the oil extracted for vitamin A assay being calculated from the gravimetric result. This would minimise possible loss of vitamin A and, incidentally, some oil would be obtained that could be used for determination of the normal constants. The avoidance of the drying and weighing of the oil was considered a particularly necessary innovation for obtaining accurate quantitative vitamin A results; it involved the use of a method which could be relied upon to give reproducible and correct results.

Hence the investigation resolved itself into two problems: (i) the quantitative extraction of oil from the emulsion, (ii) the suitability of the extracted oil for

determining vitamin A. Although these problems were investigated together, it will be convenient to consider each separately.

(1) THE QUANTITATIVE EXTRACTION OF OIL FROM EXTRACT OF MALT WITH COD-LIVER OIL.—Several methods for the direct determination of oil in this preparation are known; they mostly appear to be evolved from general methods of fat determination and, with one exception, none published has been based on an investigation to show how closely the recovery of oil compared with the actual quantity present. From time to time I had tried many of these methods and modifications. Those more likely to be successful for full recovery of oil are briefly reviewed below and criticised in view of the requirement that the extracted oil shall contain its original vitamin A content.

(*a*) *The Werner–Schmidt method.*—When this process is used for Extract of Malt with Cod-liver Oil, considerable heating is necessary to break down the emulsion, and the extracted oil is oxidised and quite unsuitable for the determination of the vitamin A content. High results for the oil-content are common.

(*b*) *Extraction with ether or light petroleum in presence of alcohol after some acid hydrolysis.*—Intractable emulsions in the solvent layers are very frequent and low results are common; long periods of standing may be necessary for separations. A modification of this method, involving the use of strong alcoholic solution and extraction with light petroleum, is given by Waggoner and Glover.[1] Large volumes of solvent are required.

(*c*) *Adams' method (modified) for fat in milk.*—A greatly diluted suspension of the extract is filtered through paper pulp, which is dried and extracted with ether. The method is tedious, and in the drying process the extracted oil is highly oxidised and all vitamin A is destroyed.

(*d*) The preparation is "massed" with anhydrous sodium sulphate until a dry powder is obtained; this is extracted in a Soxhlet apparatus with solvent. Long-continued Soxhlet extraction is necessary to ensure quantitative extraction of the oil. Accurate results appear to be fortuitous.

(*e*) Saponification of the preparation with alcoholic potash, removal of alcohol, acidification and extraction of the fatty acids and unsaponifiable matter. The oil percentage is then obtained by calculation. Considerable exposure of the oil to heat and oxygen is necessary in this method.

The above methods were discarded without trial in this investigation as being almost certain to give either unreliable oil recovery or, where full recovery was expected, low vitamin A figures.

Two methods of assay, *viz.* the Rose–Gottlieb method and the Gunn and Venables[2] method, seemed to offer the best chance of effecting a sharp separation of the oil without unnecessary heating or exposure, and it was decided to concentrate attention on these methods and any modifications of them.

(*f*) *The Rose–Gottlieb method.*—Disperse about 5 g. of the preparation in 5 ml. of water and transfer the mixture to a stoppered 100-ml. tube by means of a further 5 ml. of water. Add 1 ml. of ammonia solution (sp.gr. 0·880) and 5 ml. of alcohol followed by 25 ml. of ether, using part to rinse in any oil possibly remaining in the original weighing vessel. Stopper and shake vigorously for two or three minutes. Add 25 ml. of light petroleum (40°–60° C.) and shake again.

Allow the mixture to stand at least half-an-hour to separate, and syphon off the solvent layer into a tared flask. Repeat twice the shaking and extraction with the ether and light petroleum, using 15- to 20-ml. portions of each for these extractions. Evaporate, re-evaporate after addition of a few ml. of alcohol or acetone, dry and weigh the oil. Different quantities of extract of malt with cod-liver oil give comparable results. When 5-g. quantities are used there is a greater tendency to emulsification, and small quantities, *e.g.* 1 g., are inclined to give somewhat high figures, since slight solubility of malt extractives increases the apparent yield of oil unduly. The following modifications of this method were tried.

(i) *The Society of Public Analysts method*[3] for condensed milk. Results were in agreement.

(ii) The formation of emulsions between the solvent and aqueous layers may often be avoided by heating the aqueous-alcoholic dilution of the sample in a water-bath just to the b.p. of the alcohol, with subsequent cooling before adding ammonia and solvent.

For extract of malt with cod-liver oil such a modification was sometimes found to be helpful and sometimes of no value, or even detrimental—quite at random.

(iii) Stokes' milk tubes (19 × 2·5 cm.), specially made to fit a Gerber centrifuge and holding about 65 ml. of liquid, were successfully adapted for this determination, the quantities of ether and light petroleum each being reduced to 20 ml. for the first extraction, with corresponding reduction in volumes for the second and third extractions. The tubes were centrifuged for two minutes at 1000 r.p.m., and gave sharp separations, so that the time was considerably reduced—a useful point in assaying vitamin A.

Scriba[4] suggested the use of a separator for the Rose–Gottlieb method, but the difficulty of running off the aqueous layer completely makes the manipulation difficult, and the method was discarded.

(*g*) *Gunn and Venables*[2] *method.*—In this method the dextrin present is precipitated with alcohol and carries the oil down with it, leaving a clear supernatant aqueous-alcoholic layer. Kaolin is added to obtain a powdery precipitate which, after filtration, can be washed free from oil with ether.

Weigh 5 to 10 g. of extract in a beaker and mix thoroughly with distilled water, using 3 ml. for every g. taken. Add alcohol, in the ratio of 8 parts of absolute alcohol to 5 parts of the above dilution, and 0·4 g. of purified kaolin. Stir thoroughly and allow the precipitate to settle. Filter the clear supernatant liquid through filter-paper of ordinary grade, and add to the precipitate about 50 ml. of 70 per cent. alcohol, stir again, and allow the precipitate to settle. Filter and collect the residue in the filter, washing out the beaker with 70 per cent. alcohol. When the precipitate has been drained, wash the residue with ether from a wash-bottle and collect the ether in a separating funnel. Any precipitate adhering to the paper should be separated with a rounded glass rod. Continue washing with ether until a drop of the washings shows no film of oil on evaporation; about 150 ml. are necessary. Wash the ether in the separating funnel with three portions of 30 ml. each of water. Evaporate, add a few ml. of absolute alcohol, re-evaporate, cool and weigh the residue.

In practice it has been found advisable to use an 11-cm. filter-paper and to

wash the residue with a little strong alcohol before the ether. Extraction of the oil is usually almost complete after about 100 ml. of ether have been used, but in this method of washing complete extraction is difficult.

A modification of this process is extraction of the oil by placing the wet filter-paper and contents in a Soxhlet thimble and extracting as usual with ether for two or three hours, and then transferring the extract to a separator and washing with water as directed above. Considerably less ether is used and complete extraction is more certain. In all experiments during this work, both for oil determination and vitamin A content, the filter-papers used for extraction with cold ether were submitted afterwards to this Soxhlet extraction. Figures are given later.

Applications of modifications to reduce the filtration period were not successful. Rapid filter-papers allowed finely-divided solid matter to pass through, and suction-filters and Gooch pads became clogged.

It is necessary to evaporate and dry all extracted oils in an atmosphere of nitrogen, not only for vitamin A determination, but also for oil assay. It is to be expected that a highly unsaturated oil, such as cod-liver oil, would easily gain in weight if heated in air, and the following results confirm the necessity for caution in drying oil that has been extracted from a mixture with extract of malt.

A solvent was prepared by shaking equal parts of ether and light petroleum with one-fifth its volume of water plus one-tenth volume of alcohol and 1/50th volume of ammonia solution (sp.gr. 0·880) and separating the solvent layer. Oil was dissolved in it so that it contained 0·2513 g. in each 25-ml. portion, *i.e.* approximately the amount weighed in the Rose–Gottlieb method.

(*a*) Twenty-five ml. were evaporated in a wide-necked extraction flask, the residue was re-evaporated with a few ml. of acetone and the final residue was heated for twenty minutes at 100° C. Weight of oil, 0·2551 g.

(*b*) Oil from (*a*) was heated for a further twenty minutes at 100° C. Weight of oil, 0·2568 g.

(*c*) Twenty-five ml. were evaporated and dried as in (*a*), but with the use of a Brewis flask, *i.e.* with a large surface exposed. Weight of oil, 0·2881 g.

(*d*) Twenty-five ml. were evaporated and dried with acetone in an atmosphere of nitrogen, the flask being partly immersed in hot water. Weight of oil, 0·2508 g.

Further experiments on similar lines with quantities of oil approximating to the amount weighed in the Gunn and Venables method gave comparable results.

(*e*) 0·9039 g., dried for twenty minutes at 100° C., weighed 0·9090 g.

(*f*) Oil from (*e*) heated for a further twenty minutes at 100° C. weighed 0·9118 g.

(*g*) 0·8212 g., dried, as in (*d*), in nitrogen, weighed 0·8214 g.

To test the accuracy of the two methods advocated, fresh cod-liver oil was stirred with approximately ten times its weight of malt extract in a small beaker until emulsified, and the whole was then assayed, with the results shown in Table II.

Extract of malt will give 1 or 2 mg. of residue in these determinations.

It is realised that the experiments described above are not strictly comparable with estimations on commercial preparations, since the degree of emulsification was probably less and other substances are often introduced by manufacturers into

the preparation; different brands of extract of malt with cod-liver oil may vary considerably in their power of emulsifying extracting solvents.

The official Extract of Malt with Cod-liver Oil containing 10 per cent. of oil is formulated on a weight in weight basis, and is stated to contain approximately 15 per cent. v/v of oil. Large batches are most conveniently manufactured by volume measure, and this is the common practice. For investigation of the oil-content it was thought preferable to examine samples from material prepared by weight. A representative working batch of about three tons was manufactured

TABLE II

Method	Malt used g.	Oil weighed g.	Oil recovered g.
Modified Gunn and Venables	6·599	0·664	0·665
Rose–Gottlieb (centrifuged)	4·540	0·523	0·515
,, ,, ,,	2·349	0·313	0·315
,, ,, ,,	0·934	0·098	0·099

for us entirely by weight and contained 10·64 per cent. of oil w/w; by calculation of the sp.gr. of the malt extract from its refractive index—a result which must be accepted with some reserve—the percentage of oil in the finished product was 15·53 per cent. v/v. At intervals throughout the running of the batch six samples of the mixture were drawn into containers. Samples of the original oil and the malt extract used were also obtained. The samples were kept under what was considered average storage conditions, in the dark brown screw-capped bottles generally used for this preparation, on a laboratory bench in a well-lighted room but not in direct sunlight. Sample No. 1 was examined immediately on delivery, and samples 2 to 6 were opened successively at monthly intervals. The following results were obtained:—

TABLE III

PERCENTAGE OF OIL FOUND

Method	No. 1	No. 2 1 month	No. 3 2 months	No. 4 3 months	No. 5 4 months	No. 6 5 months
Gunn and Venables	10·53 (0·37)	10·59 (0·15)	10·31 (0·08) 10·36 (0·13) 10·33 (0·11)	10·23 (0·41)	10·07 (0·14)	9·96 (0·12)
Gunn and Venables, modified ..	10·73	10·45	10·24 10·28	10·28	10·07	9·85
Gunn and Venables, ether not washed	10·78	10·67	10·44	—	—	10·03
Average ..	10·71	10·58	10·33	10·26	10·07	9·95
Rose–Gottlieb, heated, not centrifuged ..	10·77	10·56 10·53	10·24 10·39	10·21	10·17	10·47
Rose–Gottlieb, centrifuged ..	—	10·51	10·57 10·62 10·51	—	—	—
Rose–Gottlieb, not heated, centrifuged	10·77	10·47	10·30	10·27	10·15	10·41 10·34
Average ..	10·77	10·51	10·44	10·24	10·16	10·41
Extract of malt (by Gunn and Venables method)						0·04
,, ,, (by Rose–Gottlieb method)						0·05

It is to be noted that extract of malt yields a small quantity of ether-soluble material. The figures in brackets in Table III are additional oil found by Soxhlet extraction and included in the totals.

The results were not considered satisfactory, since non-uniformity throughout the mass would not account for such large differences; manufacturers consider a very small figure as likely for maximum deviation in oil-content of different parts of the batch. Further, an unusual discrepancy was observed between the results obtained by different methods in sample No. 6; this was evident also, but to a much less extent, in No. 5.

The possibility that the ether and light petroleum in the Rose–Gottlieb method needed washing with water before evaporation was investigated. Washing is not necessary, but unexpected results were obtained.

TABLE IV

ROSE–GOTTLIEB METHOD

Sample	Ethers washed Oil Per Cent.	Ethers not washed Oil Per Cent.	Original content (Table III) Oil Per Cent.
No. 2 ..	10·71	10·75	10·51
No. 4 ..	10·71	10·81	10·24
No. 6 ..	10·92	10·80	10·41

It will be seen that a considerable increase in apparent oil-content, evidently due to increase in the weight of oil by oxidation, had occurred; the time of determination was one year after the investigation was begun. Conversely, the Gunn and Venables method gave a considerable decrease in apparent oil-content with age; this will be discussed later, but the reason for the discrepancies in the later specimens in Table III becomes more apparent.

After a further six months (18 months from the beginning of the investigation) the samples were re-tested (Table V).

TABLE V

ROSE–GOTTLIEB METHOD

Samples tested 18 months after the beginning of the investigation

Sample	Amount taken approx. 1 g. Oil Per Cent.	Amount taken approx. 2·5 g. Oil Per Cent.	Original content (Table III) Oil Per Cent.
No. 1 ..	10·88	10·90	10·77
No. 2 ..	10·76	10·90	10·51
No. 3 ..	10·85	10·88	10·44
No. 4 ..	11·29	11·16*	10·24
No. 5 ..	10·81	10·92	10·16
No. 6 ..	11·00	11·03	10·41

* The extracted oil, 0·286 g., with 3 g. of extract of malt gave by the Gunn and Venables method 0·231 g. of oil = 9·01 per cent. calculated on the original weight taken for the Rose–Gottlieb method.

The results are a little higher than in Table IV and rather discordant. The alkaline residues, after acidification, gave small, variable yields of fatty acids; partition of strongly hydrolysed soap might explain such variance.

The effect of the age of the samples on the results obtained by the Gunn and Venables method is more remarkable (Table VI).

TABLE VI

GUNN AND VENABLES METHOD

Samples re-tested several months after the beginning of the investigation

Sample		Oil Per Cent.
No. 1	After 18 months	8·72
		8·83
No. 2	,, 18 ,, ...	8·95
		8·98
No. 3	,, 18 ,, ...	8·82
No. 4	,, 18 ,, ...	9·21
No. 5	,, 18 ,, ...	8·91
No. 6	,, 6 ,, ...	9·95*
	,, 12 ,, ...	9·15
	,, 18 ,, ...	9·01

* *i.e.* 1 month after opening.

The filtrates from the determination of oil in sample No. 4, after adjustment to 30 per cent. alcoholic strength, yielded a further 2·21 per cent. of semi-liquid oil on extraction with ether, and sample No. 5 similarly gave 2·29 per cent.; the acid value of this extract was 173·7 and the iodine value 130·9.

Hence, as the age of the oil increases, results are lowered in the Gunn and Venables method owing to the increased solubility of a portion of the oil in the alcohol. This possibility was forecast by Evers[5] during a discussion on the method when it was presented at the British Pharmaceutical Conference in 1936.

Specimens of commercial preparations known to have been manufactured from different makes of malt extract were purchased, and the oil was determined by the modified Gunn and Venables and Rose–Gottlieb methods, with the results shown in Table VII.

Here, also, with known fresh samples the results obtained by the methods agreed well.

Jones and McLachlan[6] found a variation of 2·5 to 19·8 per cent. of oil in commercial samples tested by them.

II. DETERMINATION OF VITAMIN A IN EXTRACT OF MALT WITH COD-LIVER OIL.—This investigation was undertaken not only to determine the extent of recovery of vitamin A from the preparation, but also to see whether any idea of the deterioration of the vitamin-content on storage could be gauged.

Jones and Evers[7] examined the oils obtained from commercial preparations of extract of malt with cod-liver oil for vitamin A by the Carr–Price colour test, and by this method observed considerable variation in quality. No literature on the examination of this preparation for recovery of vitamin has been noted.

For quantitative determination of its vitamin A content the oil should be extracted completely. It has been shown that on fresh preparations complete extraction is probably achieved by the Gunn and Venables and Rose–Gottlieb methods; the problem remaining is to find the most suitable modification of these methods that will give the nearest figure to the true vitamin A content.

TABLE VII

	Rose–Gottlieb method Oil Per Cent.	Gunn and Venables method (modified) Oil Per Cent.
A	17·31	17·20
B	10·35	10·01
C	10·50	7·12
After 3 months ..	—	6·43
„ 5 „ ..	—	5·98
D (Halibut oil) ..	5·48	5·33
E*	10·88	10·90
On 5 g.	10·79	—
F*	11·06	11·04
On 5 g.	11·05	—

* Examined within 1 week of manufacture.

The small quantities of oil extracted (0·5 to 0·8 g.) require protection against oxidation. When the oil was extracted by either of the proposed methods without precautions against oxidation the vitamin A content found was low. It was considered advisable to avoid the greatest chance of deterioration, *i.e.* in the drying and weighing of the oil, by making the extraction in duplicate, on the assumption that the percentage extracted and weighed would, by simple calculation, give the equivalent of oil in the vitamin determination. Results showed this method to be quite satisfactory.

The following precautions were considered necessary to obtain full recovery in the assay for vitamin A:

(*a*) Delay was avoided in dissolving, precipitating and filtering in the Gunn and Venables method; when ethereal solutions had to stand between extractions in the Rose–Gottlieb method (*i.e.* when not centrifuged) they were kept under nitrogen.

(*b*) All ethereal solutions of oil were evaporated and cooled under nitrogen.

(*c*) The residual oil was not dried but immediately saponified with alcoholic potash for a maximum of five minutes.

(*d*) The unsaponifiable matter was extracted by the method given in the B.P. Addendum 1936, p. 89.

(*e*) The solution of unsaponifiable matter was evaporated under nitrogen, a few ml. of acetone of analytical reagent quality were added, the liquid was re-evaporated and the unsaponifiable matter was cooled in nitrogen.

(*f*) Spectroscopically pure cyclohexane was introduced into the flask, and the unsaponifiable matter was dissolved before stopping the flow of inert gas. The solution was then diluted to a suitable volume.

(*g*) No delay was allowed before the spectrographic determination; all determinations were completed the same day that they were begun. Absorption spectra were measured by means of a Bellingham and Stanley Medium Quartz Spectrograph with a B-S rotating sector photometer, tungsten-steel electrodes and a high-voltage spark being used.

(*h*) Importance was attached to the purity of the extracting solvents. The ether and light petroleum (b.p. 40°–60° C.) used were of analytical reagent quality.

Direct extraction of the unsaponifiable matter with cyclohexane gave consistent but low results; measurement of absorption by direct transference of the ethereal solution of the unsaponifiable matter to the cell of the spectrophotometer gave very discordant figures.

TABLE VIII

$E^{1\%}_{1cm.}$ 328$m\mu$ VALUE OF EXTRACTED OIL

Method		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Gunn and Venables							
(*a*) Modified ..	No precautions ..	0·48	—	—	—	—	—
	Weighed: N_2 used	0·51	—	—	—	—	—
	All precautions ..	0·49	0·52	0·43	0·55	—	—
		0·52	—	0·56	—	—	—
(*b*) Cold extraction	,, ,, ..	0·56	0·49	0·58	0·49	0·59	0·57
		0·52	0·57	—	0·58	—	—
Rose–Gottlieb							
(*a*) Preliminary heating:	No precautions ..	0·51	—	—	—	—	—
	All ,, ..	0·56	0·54	0·58	0·60	—	—
		0·52	—	—	—	—	—
Centrifuged ..	,, ,, ..	0·59	0·57	0·55	0·67	—	—
		0·55	—	—	—	—	—
(*b*) No preliminary heating:	,, ,, ..	0·59	0·60	0·58	0·68	—	—
Centrifuged	,, ,, ..	0·59	0·62	0·59	0·67	0·58	0·52
		—	—	0·63	—	—	—
	Cod-liver oil						
	All precautions ..	0·60	0·62	0·63	0·65	0·54	0·51
		0·60	—	—	0·64	0·53	—
		0·60	—	—	—	—	—

After the determinations by the original Gunn and Venables method, the residual solid matter was extracted further with ether in a Soxhlet apparatus for two to three hours, and the weight of oil obtained was subtracted from that calculated to be present, before calculating the $E^{1\%}_{1cm.}$ 328$m\mu$ value.

From the figures given it will be seen that the Gunn and Venables method yielded slightly low divergent results. This was probably due to exposure of the oil in a finely divided state on kaolin during filtration and, in the modified method, to oxidation during three hours' warm extraction. Slight adsorption of vitamin A by the kaolin is possible. Using the Carr–Price colour test, Gunn and Venables found no diminution in vitamin A content in the extracted oils they examined.

The effect of apparently small details is shown in the results for the Rose–Gottlieb method. Consistently lower figures were given when the dilution of extract of malt with cod-liver oil was heated before extraction; this was only for a few minutes, but loss undoubtedly occurs. Centrifuging is of great value in preventing losses on standing between extractions.

Full recovery of vitamin A can be obtained by the Rose–Gottlieb method.

It will be noted that the $E^{1\%}_{1cm.}$ 328$m\mu$ value of the original oil and of the oil contained in the malt extract rises to a maximum on keeping. This is in accordance with the observations of previous workers (Griffiths, Hilditch and Rae,[8] Garratt[9]). The investigation was started in November, and it may be noticed that the rapid fall in the $E^{1\%}_{1cm.}$ 328$m\mu$ value coincided with longer daylight and rise in average temperatures. It should also be borne in mind that the bottle of cod-liver oil used as a standard for comparison was opened repeatedly during the investigation.

After use the samples were closed and kept under similar conditions and re-tested after further periods in order to observe any deterioration. The following results were obtained:

TABLE IX

Sample	Time after original opening	$E^{1\%}_{1cm.}$ 328$m\mu$	Time after original opening	$E^{1\%}_{1cm.}$ 328$m\mu$
No. 1 ..	4 months	0·52	7 months	0·47
			12 ,,	0·49
No. 2 ..	3 ,,	0·55	6 ,,	0·46
No. 3 ..	2 ,,	0·54	5 ,,	0·48
No. 4 ..	1 month	0·53	4 ,,	0·45
No. 5 ..	..	—	3 ,,	0·42
No. 6 ..	..	—	2 ,,	0·44
Cod-liver oil		0·43		0·44

The shape of the absorption curve of the cod-liver oil, after twelve months' standing, was normal, with a slight shift further into the ultra-violet; the absorption curve for the oil extracted after twelve months from the malt extract with cod-liver oil showed practically no inflexion and a decided shift into the ultra-violet. It has been found (Robinson,[10] Smith[11]) that oxidation products of vitamin A may show considerable absorption at 328$m\mu$ and, as the band showed poor persistence, the figure for $E^{1\%}_{1cm.}$ 328$m\mu$ of the vitamin A in Sample No. 1 thus obtained by spectrophotometric assay after 12 months is probably in excess of the corresponding true vitamin A content.

These experiments indicate that under normal storage conditions little loss of vitamin A occurs in extract of malt with cod-liver oil within six months of manufacture, and the deterioration was even less than that of the original oil under the same conditions (although, as stated above, the latter was opened more frequently). After 12 months, deterioration had progressed, and the samples which had been opened frequently then had an unpleasant taste and odour and had darkened considerably.

SUMMARY.—Various methods for the determination of oil in Extract of Malt with Cod-liver Oil have been considered with a view to accurate determination both of the oil and the vitamin A content. The Rose–Gottlieb and Gunn and Venables methods were considered most suitable to satisfy both requirements and have been critically compared. For fresh preparations both methods gave results that agreed well and afforded an accurate measure of the oil-content, but with increase in age of the preparation the Gunn and Venables method gave low results.

The vitamin A content of the extracted oil has been determined spectrophotometrically; it has been shown that full recovery could be obtained when the Rose–Gottlieb method of extraction of the oil was used, provided that precautions were taken against oxidation. Slightly lower figures were found by the Gunn and Venables method.

In view of the findings summarised above, the method recommended for the determination of oil in Extract of Malt with Cod-liver Oil and of vitamin A in the extracted oil, is the Rose–Gottlieb method, modified by use of a centrifuge and with precautions taken against oxidation.

Duplicate extraction is advocated—one for assay of oil-content, the other for vitamin A determination. Little loss of vitamin A occurs in Extract of Malt with Cod-liver Oil for some months under normal conditions of storage.

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DISCUSSION

Mr. N. EVERS congratulated Dr. Garratt on this thorough piece of work. He, himself, had had some experience of trying to determine the oil in malt extract and oil and, until recently, had not been successful. He had used the Rose–Gottlieb method before the Gunn and Venables method was published and had found it quite satisfactory. He had been able to test Dr. Garratt's modification of the Gunn and Venables method and, on the whole, he did not quite agree with Dr. Garratt that the Gunn and Venables method gave lower results than the Rose–Gottlieb method—he had found that it gave slightly higher results. It also had the advantage of enabling one to use a larger quantity of the sample. He was surprised that this oxidation of the oils, and also the development of acidity, occurred in these emulsions. One would expect that the oil would be

protected against oxidation in a fine emulsion of this kind. He asked if Dr. Garratt had tried to determine the vitamin A not recovered in the oil extracts.

Mr. PINDER mentioned that Dr. Garratt had suggested that one of the possibilities might be due to the length of time the precipitate had to drain on the filter-paper. He, himself, had tried to adapt the Gunn and Venables method to the determination of fat in milk. He had found that the inner tube of a Bolton and Williams extractor could be fitted by means of a bung to a Buchner filter-flask, and, if the cotton wool at the bottom of the extractor tube was carefully packed and a moderate vacuum was used, the precipitate could be filtered off and washed in a very short time. The bung was then removed and the tube placed in the extractor and extracted in the usual way. Some such technique might possibly be developed to enable the oil to be rapidly extracted from an admixture with extract of malt.

Mr. NICHOLLS observed that he had tried this method of getting a measure of the vitamin A by extracting a portion of the oil and had obtained high results. It was fairly obvious that one did not get the same distribution of the total oil and vitamin A between the upper and the lower layers.

Mr. S. G. STEVENS suggested that possibly the slightly increased weight might be due to the flavouring that was sometimes added. He would also like to know what standard Dr. Garratt proposed for a B.P. extract.

Dr. GARRATT, replying, remarked that he was quite prepared to hear criticisms to the effect that with the Gunn and Venables method better vitamin recovery might be obtained by some workers than by others; it was a question of the personal interpretation of the technique of the method and that the small details involved might have a pronounced effect on the estimation of vitamin A. He thought that Mr. Evers would agree that the discrepancy was very small and would not lead to the rejection of a sample. He had not attempted the recovery of vitamin A from the fatty extracts. The question of flavouring had not come into the investigation, as he knew from the manufacturers what flavouring had been used; the proportion was small, and the non-volatile matter in it was within the experimental error of the determination. If flavouring were added in any quantity, the analyst must do his best to separate it. He had tried Mr. Pinder's suggested method of extraction of malt and oil and found that it clogged the filters. He understood that standards for malt and cod-liver oil were being prepared.

Tests available for the Identification of small quantities of the War Gases

By H. E. COX, D.Sc., Ph.D., F.I.C.

It appears that the Public Analyst may at any time be called upon to test suspected foodstuffs for contamination with the war gases. Such work will have to be done promptly, so it is desirable to be prepared for it by having the necessary materials and tests ready to hand. In a recent paper in *Chemistry and Industry*,[12] A. P. B. Page has described the principles which operate in relation to the absorption, contamination and de-contamination of foodstuffs by poisonous gases and vapours, but he does not give details of any practical tests. The Home Office A.R.P. Department have issued a Memorandum No. C.9 "On the detection and identification of War Gases."* This consists primarily of notes for the use of gas Identification Officers who may not normally have opportunity for carrying out chemical work on the identification of war gases. It includes, however, a résumé of the methods available for the chemical identification of the more important gases and of laboratory technique employed in the handling of contaminated materials, but it does not give analytical details applicable to small quantities. The Memorandum expresses the opinion that, in general, air-flow analysis will be the simplest and most satisfactory method for the examination of contaminated materials. It would not usually be difficult to devise a simple bubbler through which to aspirate air slowly after passing it round or through the suspect material, which may with advantage be warmed to volatilise more readily any liquid "gases." So far as possible, rubber joints should be excluded, and the use of small sintered-glass diffusers will enable the gas to be passed into, and absorbed by, a minimum volume of the reagents employed for the tests. The number of gases which undergo hydrolysis in water or dilute alkali indicates that in many cases it will be possible to make direct tests for the products of hydrolysis in the aqueous portion of materials which contain much water. Contamination with arsenical dusts as a group will be readily detected by a determination of arsenic by the well-known methods of wet oxidation, which may be applied to the foodstuff itself.

For the examination of some materials, not foods, J. Studinger[5] suggests extraction with a dry organic solvent. This may sometimes be a convenient procedure, as it has the advantage that all the war gases are soluble in organic solvents. When a solvent is employed, anhydrous ether or benzene is to be preferred, not one containing a halogen.

Although it seems that the gases most likely to be encountered are mustard gas and the organic arsenicals such as Lewisite or the arsenical dusts, mixtures may occur. Hence, it is necessary to be prepared to identify a wider variety of poisonous gases, and, with this in view, the following notes have been put together. The tests or reactions are mostly well known, and have been collected from various sources, those that are applicable to minimal quantities being particularly selected. When larger quantities are available, identification by means of the usual physical

* H.M. Stationery Office, York House, Kingsway, W.C. Price 1s. 3d.

constants and major chemical reactions, such as are described by Sartori in his recent book,[1] should be fairly simple. It is hoped that the following notes will be of service should the necessity for such examinations unfortunately arise.

(1) CHLORINE (Cl).—The tests for this element are too well known to need any repetition, but it should be noted that impure phosgene or diphosgene gives most of the reactions of chlorine in solution, such as the *o*-tolidine reaction and the blue colour with aniline acetate paper.

Details for the preparation of a sensitive *o*-tolidine paper are given in a D.S.I.R. Leaflet (No. 10) on the Detection of Toxic Gases in Industry.[2] Another very sensitive test available for chlorine or bromine vapour in air is due to Eichler.[3] Resorufin in alkaline solution has an intense fluorescence which is changed or destroyed by halogens. A drop of a reagent consisting of 0·1 g. of resorufin and 1·5 g. of sodium carbonate in 100 ml. of water is added to 5 ml. of water, and the suspect air is passed through it. A blue colour (resorcin blue) is produced by chlorine or bromine, or, if the halogen is in excess, both the colour and the fluorescence are destroyed.

(2) PHOSGENE ($COCl_2$) is soluble in water and rapidly hydrolysed therein to hydrochloric acid, and so gives the usual colour with indicators such as methyl orange. Passed into a 1 per cent. solution of potassium iodide containing starch, a blue colour results. Traces of phosgene may be determined by bubbling a known volume of the air through 10 ml. of solution containing 1 ml. of 0·1 *N* sodium hydroxide solution and 5 ml. of alcohol. The liquid is then evaporated on the water-bath to 2 ml., acidified with acetic acid and evaporated to dryness, the residue is moistened and re-evaporated, and the chloride is titrated with *N*/40 silver nitrate.[4]

If chlorine is also present it may be removed at the outset by passing the gas through cotton-wool previously soaked with potassium iodide solution and dried. J. Studinger[5] and Kretov[6] quote the following test as specific for phosgene:

A filter-paper is soaked in a mixture of 5 ml. of a 0·5 per cent. solution of 1:3:6-nitroso-dimethyl-aminophenol and 2 ml. of a 0·5 per cent. solution of *m*-diethyl-aminophenol, both in xylene; this paper gives a green colour with traces of phosgene. If the paper has become dry it should be moistened with alcohol before use. Phosgene forms diphenylurea (m.p. 235° C.) when passed into an aqueous solution of aniline (Kling and Schmutz[7]). The reaction is sensitive and may be applied by bubbling the suspect air through about 3 ml. of a saturated aqueous solution of aniline; a white turbidity forms and then a crystalline precipitate, which may be collected and dried at 70° C.

A very sensitive drop reaction is described by Anger and Wang.[8] A granule of phenylhydrazine cinnamate is added to a drop of the solution of the suspect substance in chloroform or carbon tetrachloride and followed, after five minutes, by a drop of 1 per cent. copper sulphate solution; a red-violet colour of the diphenyl carbazide is produced in presence of phosgene. As little as 0·5γ can be detected. The test can also be applied by means of filter-paper impregnated with copper sulphate, dried, and dusted with the phenylhydrazine cinnamate; in presence of a drop of water phosgene produces the violet colour if the concentration is as little as 1:50,000.

(3) DIPHOSGENE ($COCl.OCCl_3$) reacts only feebly with cold water, but with hot water forms hydrochloric acid. It is decomposed on heating, or on contact with a porous material, into two molecules of phosgene. When the gas is passed into excess of sodium phenate solution a white precipitate of diphenylcarbonate, insoluble in cold water, m.p. 110–111° C., is formed. If the suspect gas is passed through a tube heated at 300–350° C. it is completely decomposed into phosgene and gives the reactions shown above (2).

(4) METHYL CHLOROFORMATE ($ClCOOCH_3$) is a volatile liquid boiling at 71° C.; it is not decomposed by cold water, but is hydrolysed by hot water or by alkali, with the production of methyl alcohol and hydrochloric acid; whereas the chloro-methyl chloroformates all produce chlorine as well as hydrochloric acid on hydrolysis, and therefore liberate iodine from potassium iodide. It may also be recognised by passing it into an alcoholic solution of aniline; hydrochloric acid is then produced. It does not liberate iodine from potassium iodide.

(5) CHLOROPICRIN ($CCl_3.NO_2$), known as PS., has a characteristic sweet smell; its vapour is insoluble in water and is not decomposed by it. Filter-paper impregnated with a petroleum spirit solution of Sudan red is turned a blood-red colour by it. On being passed through a tube heated to about 450° C. it is decomposed, and chlorine may be detected in the usual way; it gives the Beilstein halogen test quite easily. When chloropicrin is passed into an alcoholic solution of potassium iodide, potassium nitrite and potassium chloride are formed, and the former may be detected by the well-known Griess–Ilosvay reaction; the finding of nitrite is practically definitive of chloropicrin. Passed into 2 ml. of hot alcoholic potassium hydroxide solution containing a drop of aniline the characteristic smell of carbylamine appears. If a sufficient quantity is available the following test is useful:—A drop of the liquid is boiled with a 5 per cent. alcoholic potassium hydroxide solution, or the suspect air is bubbled through the hot solution and a few crystals of resorcinol are added; a red colour, due to the nitroso compound, is then obtained on the addition of sulphuric acid (Guillemard and Labat[9]).

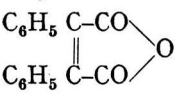
(6) BENZYL BROMIDE ($C_6H_5.CH_2Br$) AND XYLYL BROMIDE ($CH_3.C_6H_4.CH_2Br$). —These two gases are similar; they are only slowly decomposed by water, but are readily hydrolysed by alkali. When they are passed into an alcoholic solution of silver acetate a precipitate of silver bromide is immediately produced. When they are passed into a hot alkaline solution of potassium permanganate, benzoic or one of the phthalic acids, respectively, is formed. The acid may be isolated by acidifying and extracting with ether, and identified by the usual tests. Phthalic acid is quickly detected by heating the residue for a few minutes to 160° C. with resorcinol and conc. sulphuric acid; after cooling, an excess of sodium hydroxide produces fluorescein. Benzoic acid gives Mohler's reaction.

(7) BROMOACETONE (B.A.) ($CH_3.CO.CH_2Br$) AND BROMOMETHYLETHYL-KETONE ($C_2H_5.CO.CH_2Br$ and $CH_3CO.CHBrCH_3$) are similar in properties; they are slightly soluble in water and are not decomposed thereby. The vapour is quickly absorbed in warm 0·5 *N* alcoholic potassium hydroxide solution, forming potassium bromide and the hydroxy ketone. The ketone may be identified by the addition of a few drops of sodium nitroprusside solution to a solution of the gas in the alkaline hydroxide; acetone gives a red, and methyl-ethyl-ketone an

orange colour; the acetone colour is intensified on the addition of acetic acid. Another method is to pass the gas into sodium hydroxide solution, then add a few drops of an alcoholic solution of *o*-nitro-benzaldehyde, which combines with acetone to form indigo, or with methyl-ethyl-ketone to produce a brown colour. This test is not quite so sensitive as the nitroprusside reaction. If sufficient material is available, it may be combined with 2 : 4-dinitrophenylhydrazine to form the nitro-hydrazone. To 1 ml. of a 1 per cent. alcoholic solution of dinitrophenyl-hydrazine 1 drop of hydrochloric acid and few drops of the alcoholic solution of the substance are added. The mixture is kept at room temperature until crystals of the nitrophenylhydrazone separate; a few more drops of hydrochloric acid may help the crystallisation. The melting-point of the acetone compound is 148° C., and that of the methyl-ethyl-ketone compound 128° C.

(8) ETHYL BROMOACETATE ($CH_2Br.COOC_2H_5$) AND (9) ETHYL IODOACETATE (K.S.K.) ($CH_2I.COOC_2H_5$).—These products are slowly decomposed by water, forming bromo- and iodo-acetic acids, respectively. They are quickly absorbed by alcoholic potassium hydroxide solution, forming potassium bromide and iodide, respectively, together with glycollic acid. Glycollic acid is characterised by adding to the alkaline solution a small particle of guaiacol and then a few drops of sulphuric acid on warming, a violet colour is produced. It is pointed out, however, that the finding of iodide after hydrolysis is fairly certain to indicate the presence of K.S.K.

(10) BROMOBENZYLCYANIDE (B.B.C.) ($C_6H_5CHBr.CN$).—This compound when pure is a solid, but it may be dissolved or mixed with chloropicrin or other gas. It is not soluble in water, but readily so in organic solvents, and is quickly hydrolysed, even in the cold, by alcoholic potassium hydroxide, with the formation of potassium bromide and dicyanostilbene ($C_6H_5.C.CN)_2$. This, on boiling, gives off ammonia, and, if the solution is then cooled and acidified, a yellow precipitate of diphenyl maleic anhydride


(m.p. 156° C.) is obtained.

Concentrated sulphuric acid gives a deep red colour on warming with a tiny droplet of bromobenzylcyanide. A non-specific reaction for B.B.C. is the blood-red colour that it gives with Sudan red. A filter-paper lightly coloured by means of a solution of the dye in petroleum spirit gives this blood-red colour.* A similar reaction in a more sensitive form can be obtained by passing the gas through a plug of cotton-wool tinted with Sudan red by wetting the wool with the petroleum spirit solution and drying it. It should be noted that bromobenzyl cyanide, being really a nitrile, does not give a cyanide reaction after hydrolysis with alcoholic potash. Benzyl cyanide may, however, be present as an impurity.

(11) CHLOROACETOPHENONE (C.A.P.) ($C_6H_5.CO.CH_2Cl$) is soluble in most organic solvents, but is unaffected by water. It is hydrolysed at once by warm alkaline solutions and the chloride can be recognised. The gas passed into alcoholic ammonia forms indole, which can be oxidised to indigo by addition of perhydrol or recognised by the red colour produced on adding *p*-dimethylamino-benzaldehyde solution to the acidified liquid.

* This test is described by Ligtenberg, but I do not find that it works well.—H. E. C.

(12) DIPHENYLCHLOROARSINE (D.A.) ($[C_6H_5]_2$ AsCl) AND (13) DIPHENYLAMINECHLOROARSINE (D.M.) ($[C_6H_4]_2$. NH.AsCl).—Both substances are volatile solids, and are quickly hydrolysed by water, with the formation of hydrochloric acid with diphenylarsenious oxide and diphenylaminearsenious oxide, respectively. Hence they may be recognised by the Gutzeit test after decomposition with nitric acid and sulphuric acid in the usual way. To differentiate the amino-compound, a small quantity of vapour is passed into sulphuric acid, which gives a red colour with the diphenylamine compound, and a blue when a trace of nitrate is added. Both compounds may be distinguished from the corresponding cyanides by the absence of hydrogen cyanide in the products of hydrolysis. A shorter test for the arsenic is to pass the vapour into an acidified solution of potassium permanganate, which is decolorised; arsenic is then easily identified in the solution.

(14) DIPHENYLCYANARSINE (D.C.) ($[C_6H_5]_2$. AsCN) AND (15) DIPHENYLAMINECYANARSINE ($[C_6H_4]_2$.NH.AsCN).—Both compounds are only slowly affected by water, but are quickly hydrolysed by alcoholic potassium hydroxide, with formation of the corresponding phenyl or phenylamine arsenious oxide and potassium cyanide. Both absorb iodine quantitatively from alcoholic iodine solution. The cyanide produced on hydrolysis is recognisable by acidifying the alkaline solution and warming it while a piece of filter-paper, previously soaked in a mixture of benzidine and copper acetates, is held in the tube.* A blue colour is produced by cyanide. The Prussian blue reaction, obtained by adding a crystal of ferrous sulphate and a drop of ferric chloride solution, and then boiling and acidifying with hydrochloric acid, is more specific and very sensitive. Both compounds reduce an alkaline solution of potassium permanganate, and the arsenic can then be detected as usual by the Gutzeit test.

(16) DICHLORODIETHYL SULPHIDE (MUSTARD GAS) ($[CH_2.CH_2.Cl]_2S$).—This compound is hydrolysed in water to produce hydrochloric acid and thiodiglycol, so that a first indication is the colour change of an indicator such as methyl red. Studinger (*loc. cit.*)[5] describes several of the large number of tests which have been published for this gas. The following are specific:

A 0·1 per cent. solution of gold chloride is dried on filter-paper; a deep yellow spot or stain is produced on it by mustard gas. Grignard's test: 20 g. of sodium iodide, 40 drops of a 7·5 per cent. solution of copper sulphate, and 2 ml. of a 35 per cent. gum arabic solution are dissolved in 200 ml. of water. Air, thought to contain mustard gas, is slowly bubbled through 1 ml. of this reagent, or a drop of solution of the gas is added. A yellow colloidal precipitate of diiodoethyl sulphide is formed in presence of mustard gas. Quite a small quantity of dichlorodiethyl sulphide, when bubbled into 1 ml. of a 20 per cent. aqueous solution of sodium sulphide, quickly gives a precipitate of diethylenesulphide (m.p. 111° C.). When mustard gas is passed into 1 ml. of a freshly prepared alcoholic solution of β-naphthol mixed with an equal volume of 0·1 *N* sodium hydroxide a turbidity, due to dinaphthylthioether, is produced with as little as 0·06 mg. of the gas. Filter-paper, dipped into a 2 per cent. solution of sodium platinum iodide, is turned first purple, then blue, when exposed to air containing this gas.

* The method of making a sensitive benzidine copper acetate paper is described in the pamphlet on *Toxic Gases in Industry*, II, issued by H.M. Stationery Office. (*Cf.* ANALYST, 1938, **63**, 659.)

(17) CHLOROVINYLARSINE (LEWISITE) ($CHCl{:}CHAsCl_2$) has an odour of geraniums. It is rapidly hydrolysed by water, producing hydrochloric acid and chlorovinylarsenious oxide. Reactions for acid, chloride and arsenic will therefore be obtained. When Lewisite is passed into 1 ml. of a 15 per cent. solution of sodium hydroxide there are formed acetylene, sodium chloride and sodium arsenite. The acetylene can be recognised by suspending a piece of cuprous chloride paper above the alkali; a red stain is produced by acetylene. The arsenic is shown by a direct Gutzeit test. As by other chloroarsines, a white precipitate of the alkyl arsine sulphide is quickly produced on passing the suspect air or gas through a few ml. of water and then adding 3 drops of hydrogen sulphide water. Excess of hydrogen sulphide must be avoided, and then, according to Nametkin and Nekrassov,[10] the test is sensitive to 0·02 to 0·05 mg.

(18) ETHYLDICHLOROARSINE (DICK) ($C_2H_5AsCl_2$) AND (19) METHYL DICHLOROARSINE ($CH_3\ AsCl_2$).—Both compounds are quickly decomposed by water, just as is Lewisite, producing hydrochloric acid and the alkyl arsenious oxide. They both give the sulphide reaction with hydrogen sulphide, as described under Lewisite, but no acetylene is formed on absorption with sodium hydroxide. These two reactions therefore serve to distinguish the ethyl and methyl compounds from the vinyl compound. When these gases are passed into 1 ml. of mercurous nitrate solution just acidified with nitric acid, an immediate grey precipitate of metallic mercury is obtained from methyl dichloroarsine, and a white precipitate, changing slowly to grey, is produced by the ethyl compound.

(20) PHENYLCARBYLAMINE CHLORIDE ($C_6H_5.\ N.C.Cl_2$) is a slightly volatile oily liquid with an odour of onions; it is not hydrolysed by water and does not produce acid. Passed into hydrogen sulphide water it produces hydrochloric acid and phenylcarbylamine; hence it can be recognised by adding a few drops of hydrogen sulphide water to a benzene solution of the gas or benzene through which the suspect air has been passed. It gives reactions for chloride and phenylcarbylamine on absorption by alcoholic potassium hydroxide. Phenylcarbylamine chloride gives a Grignard reaction resembling that with mustard gas, but may be distinguished from that gas by the absence of acid and sulphur and by the other reactions described above. Ligtenberg[11] gives a test with Sudan red and ferric chloride diluted with chalk.

(21) METHYL (or ETHYL) CHLOROSULPHONATE ($CH_3.SO_3Cl$) is a volatile liquid usually admixed with dimethyl sulphate. It differs from the latter in that in water it is hydrolysed to methyl sulphate and hydrochloric acid. Thus it may be recognised by the liberation of this acid and the formation of potassium sulphate and chloride when aspirated through alcoholic potassium hydroxide solution.

GROUP REACTIONS.—In order to identify these gases most rapidly it may be convenient to apply certain group reactions.

A.—The following gases or vapours give rise to a halogen acid on contact with water, and so may be detected with an indicator, such as methyl red:—Chlorine. Phosgene. Diphosgene. Benzyl or Xylyl bromide (slowly). Diphenylchloroarsine. Diphenylaminechloroarsine (slowly). Methyl and Ethyldichloroarsine. Chlorovinylarsine. Dichlorodiethyl sulphide. Methyl and ethyl chlorosulphonate. Methyl chloro-formate (with hot water).

B.—The following, which do not quickly form an acid with water, are rapidly decomposed by alcoholic potassium hydroxide, giving an alkali halide:—Ethyl bromoacetate. Ethyl iodoacetate. Bromobenzyl cyanide. Bromoacetone. Chloro- and Bromoacetophenone. Phenylcarbylamine chloride. Chloropicrin (reacts only slowly). Diphenylaminechloroarsine.

C.—The following give hydrogen cyanide on hydrolysis with water, and may be detected by the Prussian blue reaction:—Hydrogen cyanide (possibly mixed with stannic salts). Cyanogen chloride (slowly hydrolysed in water, quickly by alkali). Diphenylcyanoarsine. Diphenylaminecyanoarsine.

D.—The following will give an arsenic reaction when absorbed in alkaline permanganate solution:—Diphenylchloroarsine. Diphenylcyanoarsine. Diphenylamine-chloroarsine. Diphenylamine-cyanoarsine. Chlorovinylarsine. Ethyldichloroarsine.

E.—The following will give colours with conc. sulphuric acid:—Diphenylaminechloroarsine (red, cold). Bromobenzylcyanide (red, warm).

Consideration of the known types of gas, such as those dealt with above, indicates that the question of whether or not certain food is poisonous when taken internally will in practice usually resolve itself into the determination of the cyanide or arsenic content, and that for the purpose of assessing the harmfulness or otherwise the quantities might be considered in terms of hydrogen cyanide and arsenious oxide.

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11, BILLITER SQUARE
LONDON, E.C.3

October, 1939

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SOME FACTORS THAT AFFECT THE ACCURACY OF DETERMINATIONS OF THE THIOCYANOGEN VALUE

THE main object of the experiments described below was to find to what extent variations in the length of time allowed for the interaction of oil and thiocyanogen affect the magnitude of the thiocyanogen value.

Descriptions of determinations based on Kaufmann's method[1,2,3] indicate that the reaction periods employed by different workers differ considerably. In our experiments a series of determinations was made with each oil examined. Different periods of contact of oil and reagent, varying from one hour to twenty-four hours or more, were chosen in such a way as to facilitate the preparation of graphs showing how the thiocyanogen value varies with the reaction period. The method used was essentially that originated by Kaufmann. A series of determinations was also made with reagent solutions prepared with other solvents. These included an acetic acid reagent to which a mixture of definite proportions of pyridine and concentrated sulphuric acid had been added. None of the reagent solutions so prepared offered definite advantages over the simple acetic acid and acetic anhydride mixture of Kaufmann's process and the results obtained are not included in the table.

METHOD.—All apparatus was carefully dried previous to use. Glacial acetic acid and acetic anhydride were mixed in the proportion of 9 volumes to 1 volume and allowed to stand for at least a week. Lead thiocyanate (12·5 g.), which had been well dried over phosphorus pentoxide, was weighed into a brown reagent bottle, 500 ml. of the anhydrous acetic acid were added, and the mixture was kept for as long as possible before use. When the reagent was required 1·5 ml. of pure dry bromine was added, and the mixture was well shaken for an hour and then filtered through two thicknesses of oven-dried filter-paper into a brown bottle. Occasionally a second filtration was necessary. So prepared, the reagent was clear and colourless, or not more than faintly yellow, and about 0·12 *N* in concentration. Quantities of oil of from 0·1 to 0·14 g. were weighed into 250-ml. stoppered flasks. The temperature of the reagent was brought to 20° C., and 20 or 25 ml. were pipetted into the flasks. The proportions of oil and reagent were so adjusted as to provide at least 100 per cent. excess, and in most of the determinations not less than 200 per cent. excess, of thiocyanogen. It was found advisable to have at least 100 per cent., and preferably more than 150 per cent. excess. An excess greater than 200 per cent. did not appear to alter the rate of addition of thiocyanogen or the magnitude of the maximum value obtained. These observations are in agreement with Kaufmann's statements[4] concerning the proportion of reagent that is necessary. Most oils dissolve readily in the acetic solution, but care must be taken to ensure that all the oil dissolves. Carbon tetrachloride was not used in these experiments, but may be incorporated in the reagent. After being allowed to stand in the dark at room temperature for the appropriate time the reaction mixture was poured into 10 ml. of 10 per cent. potassium iodide solution, the reaction flask was well rinsed, first with potassium iodide solution and then with distilled water, and the whole was titrated with 0·05–0·055 *N* thiosulphate solution. It was not always possible to complete the determinations after definite time intervals, but the reaction periods are in terms of whole hours or are stated to the nearest whole hour. "Blanks" were pipetted at about the same time and kept for as nearly as possible the same period under the same conditions as the corresponding reaction mixtures.

Table I shows reaction periods and thiocyanogen values for various types of refined vegetable oils and Table II shows results for fish liver oils. The iodine value (Wijs) of each oil is also given.

TABLE I

THIOCYANOGEN VALUES

Hours	Olive	Olive	Tea-seed	Maize	Maize	Cotton-seed	Soya	Soya	Sesame	Rape	Raw linseed
1	—	—	66·3	71·7	70·2	62·3	73·6	74·2	72·9	71·8	92·4
3	—	—	—	72·8	71·8	62·5	76·3	77·0	73·3	72·2	106·4
5	70·1	72·1	—	71·0	71·9	63·0	77·0	78·0	73·4	—	108·5
6	—	72·3	—	—	—	—	—	—	—	77·0	109·0
7	—	—	69·7	73·2	71·9	—	77·7	79·3	73·5	—	—
9	70·0	—	69·3	73·1	—	—	—	79·6	—	76·0	—
10	—	—	—	—	—	64·4	—	—	—	—	—
13	—	—	70·7	—	—	—	—	—	—	—	—
15	70·9	—	—	74·6	—	64·0	77·8	80·2	74·9	77·6	114·3
16	—	71·2	—	—	72·4	—	—	—	—	—	—
18	—	—	70·4	—	—	—	—	—	—	—	—
20	—	72·1	—	75·0	72·6	64·4	77·0	80·5	75·2	78·5	113·5
22	—	—	—	—	—	—	—	—	—	—	113·6
24	71·0	71·8	—	74·6	72·7	66·1	78·6	81·3	74·9	78·7	112·2
28	71·5	72·5	—	—	—	—	—	—	—	—	—
IODINE VALUES											
1	87·0	85·2	80·6	112·5	110·9	107·7	129·6	132·6	111·3	101·5	180·6

TABLE II

THIOCYANOGEN VALUES

Hours	Cod-liver oil (Medicinal)	Cod-liver oil (Medicinal)	Cod-liver oil (Medicinal)	Shark-liver oil
1	80·8	80·7	—	72·9
3	89·6	—	—	82·8
5	92·5	92·1	91·6	86·2
7	94·4	93·4	96·6	86·7
9	96·5	94·2	—	86·9
13	—	96·4	—	—
15	98·9	97·9	—	89·4
20	98·3	—	98·8	90·9
22	—	98·4	96·9	—
24	99·6	97·9	98·3	88·4
30	—	98·9	—	—
IODINE VALUES				
1	160·7	163·0	167·2	146·4

Though the total number of oils examined was not large enough to justify definite generalisations, useful indications were obtained. From examination of graphs corresponding with the tables above and from the results of other experiments it is evident that olive oil, in which oleic acid constitutes 80 per cent., or more, of the total fatty acids, gives a maximum value (or a value which is nearly a maximum) in about 5 hours. The same is probably true of almond oil and other oils of somewhat similar composition, but for determinations made on these oils and on teaseed oil a 15-hour period is preferable. Examination of vegetable oils

which contain little or no linolenic acid but a high proportion of linolic acid relative to the percentage of oleic or other monoethylenic acid indicated that, although a maximum value may occasionally be obtained in 10 hours or even less, it is advisable to allow a contact period of at least 15 hours. Results for the more unsaturated oils were less satisfactory but maximum values were obtained in periods varying from 20 to 24 hours. (Kaufmann[5] allows 24 hours for determinations of thiocyanogen values of fish liver oils.)

In most cases, but especially when dealing with highly unsaturated oils, it was found that results obtained with reaction periods of more than 28 hours are liable to be very inaccurate. Stale reagent or reagent in which there is any precipitate should not be used. In our experience the activity of the reagent is not seriously diminished in 3 days, and good results are obtainable with reagent which is not more than 5 days old. It is, however, much preferable to begin determinations with reagent which is fresh or not more than 2 days old.

H. N. SHER
R. H. COYSH

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BATTERSEA POLYTECHNIC
LONDON, S.W.11

September 20th, 1939

A RAPID METHOD FOR THE VOLUMETRIC TITRATION OF COPPER IN BRONZE, ETC.

THE following method, though not so accurate as the electrolytic method, gives results sufficiently accurate for rapid routine control analysis. It is so speedy that it forms a suitable check on the electrolytic method when, as sometimes happens, there is not enough time for a duplicate electrolytic assay to be made.

METHOD.—One g. of bronze in drillings, millings or other divided form is weighed into a Philips beaker with a capacity of 800 ml. and dissolved in 10 ml. of a mixture of 250 ml. of strong hydrochloric acid and 50 ml. of strong nitric acid while covered with a watch-glass. The beaker is then kept on the coolest part of the hot-plate until the dense brown fumes have evaporated. The watch-glass and the inside of the beaker are rinsed, 50 ml. of cold water and 7 g. of urea are added, and the mixture is well cooled. A little starch solution and 5 g. of potassium iodide are then added (see Note), and the solution is titrated at once from a 100-ml. burette with thiosulphate solution.

NOTES.—The thiosulphate solution is made with 40 g. of sodium thiosulphate per litre, with about one g. of sodium carbonate per litre.

The 100-ml. burette has a spherical bulb of 50 ml. capacity above a stem consisting of an ordinary 50-ml. burette graduated from 50 to 100 ml.

The thiosulphate solution must be standardised under conditions identical with those in the assays. A convenient amount of copper for such a standard is 0·92 g. of copper of known purity.

It was found that the standardisation and the assay are influenced by the manner in which the potassium iodide is added, either as solid or as 50 per cent. solution. It is essential to titrate the solution as soon as possible after addition of the iodide.

RESULTS.—The following results, taken at random, show the accuracy of the method:

With solid potassium iodide:

1 ml. of thiosulphate	≡ 0·010424	g. of copper
,, ,,	≡ 0·010428	
,, ,,	≡ 0·010431	
,, ,,	≡ 0·010425	

With 50 per cent. potassium iodide solution:

1 ml. of thiosulphate	≡ 0·010438	g. of copper
,, ,,	≡ 0·010438	
,, ,,	≡ 0·010441	
,, ,,	≡ 0·010433	

BRONZES

Copper taken g.	Tin added g.	Copper found g.
0·9316	0·09	0·9312
0·9256	0·079	0·9260
0·9296	0·06	0·9291
0·9667	0·07	0·9667
0·9570	0·09	0·9576
0·9416	0·057	0·9413
0·9384	0·062	0·9376
0·9542	0·046	0·9540
0·9304	0·07	0·9302

GUN METALS (88/10/2)

Copper taken g.	Tin added g.	Zinc added g.	Copper found g.
0·8827	0·098	0·02	0·8828
0·8885	0·099	0·02	0·8891
0·8916	0·093	0·02	0·8912

In every instance the samples were synthetic alloys. The use of solid iodide appeared to give a sharper end-point.

URSULA F. WILLIS

THE MIDLAND LABORATORY GUILD (1928), LTD.
KING ALFRED'S PLACE
BIRMINGHAM, 1

September, 1939

THE FRENCH OFFICIAL METHOD FOR THE DETERMINATION OF FAT IN FLOURS, PASTRIES AND THE LIKE

IN two papers by M. Berlie on the determination of rancidity in flours and semolinas (Abst., ANALYST, 1934, **59**, 629; 1935, **60**, 181) reference is made to the French Official Method for determining fat in flours, breads, edible pastes, etc. This method is described in the *Service de la Répression des Fraudes*, but is not readily accessible in this country. As the method may be of use to analysts who are dealing with problems of rancidity in products of low fat-content, for which the usual methods of extraction are unsuitable, I have made the following translation of it.

FLOURS, BREADS, PASTRIES, EDIBLE PASTES, GROATS AND RASPINGS

Fatty substances.—The determination is made on 5 g. of flour weighed on a small scoop of silver-foil.

Apparatus.—A glass tube of the following dimensions is required: length, 24 cm.; external diameter, 19 mm. One end of the tube is drawn out so as to measure at the extreme tip not

more than 6 mm. in diameter. The other end is widened to facilitate the introduction of the sample.

Method.—A small ball of absorbent cotton-wool is placed in the drawn-out pointed end of the tube and lightly compressed by means of a glass rod. The 5-g. sample of flour is carefully introduced, in small quantities at a time, the tube being held vertically and the flour being allowed to fall into it from a height of 1 to 2 cm. The tube is then placed in a stand, an extraction flask, of 60 ml. capacity, is put underneath the drawn-out end, and ether is poured into the upper part of the tube, so as to fill it completely. The flour is allowed to soak up the ether, and as soon as the first drops fall into the flask the tube is corked. The rate of flow of the liquid is regulated by means of the cork, so as to obtain one drop in approximately 10 seconds. When all the ether has passed through the flour the extraction is complete. The drawn-out part of the tube, which always retains a little of the fat, is washed out with ether into the extraction flask. After evaporation of the solvent the flask is placed in an oven at 100° C. for an hour, and then cooled and weighed.

(NOTE.—The heating is omitted when rancidity is to be determined, and the specified solvent (alcohol, 30; ether, 30; chloroform, 40 per cent.) is substituted for ether.)

I have found this method simple to use, and, provided that care is taken, it is rapid and economical.

ENID A. M. BRADFORD

RESEARCH DEPARTMENT,
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WESTFIELDS ROAD
ACTON, W.3

August, 1939

Official Appointments

THE Minister of Health has approved the following appointments:

FRANCIS WILLIAM FREDERICK ARNAUD as Public Analyst for the Borough of Beckenham, as from October 1st, 1939 (September 29th, 1939).

FRANCIS WILLIAM FREDERICK ARNAUD as Public Analyst for the Borough of Chatham, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and JACK HUBERT HAMENCE as Joint Public Analysts for the Borough of Barking, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and JACK HUBERT HAMENCE as Joint Public Analysts for the Borough of Dagenham, as from October 1st, 1939 (September 29th, 1939).

BERNARD DYER and GEORGE TAYLOR as Joint Public Analysts for the Borough of Leyton, as from October 1st, 1939 (September 29th, 1939).

JOHN WALTER FLINT as Deputy Public Analyst for the County of Kent, as from October 1st, 1939, in addition to F. W. F. Arnaud (September 29th, 1939).

EDWARD HINKS as Public Analyst, and DANIEL DONALD MOIR as Deputy Public Analyst for the Borough of Sutton and Cheam, as from October 1st, 1939 (September 29th, 1939).

WILLIAM LINCOLNE SUTTON as Public Analyst for the Borough of Lowestoft, as from October 1st, 1939 (September 29th, 1939).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

KENT COUNTY COUNCIL

REPORT OF THE COUNTY ANALYST FOR THE QUARTER ENDED JUNE 30TH, 1939

PASTEURISED MILK.—Fifty-five samples, taken in the streets, were stated by the vendors to be pasteurised, although the milk was not sold as pasteurised or marked as such. Of these 55 milks, 9 had been inefficiently pasteurised.

LUNG MIXTURE.—A mixture sold by a chain stores, was stated to have the same composition as a well-known proprietary mixture, and its composition was disclosed at the time of sale. One of the ingredients that should have been present was Tinctura Camphorae Composita (33 per cent.), but it was entirely lacking. A summons was taken out under the Food and Drugs Act, and the vendors were fined £5 with £3 3s. costs.

SHODDY.—Only 3 of 46 samples contained excessive amounts of water (42·2, 34·0 and 28·0 per cent., respectively). In one instance where a farmer strongly objected to paying for wet shoddy, I advised that he was entitled to compensation in excess of the value of the deficiency of nitrogen. One-third of the shoddies were of rather poor quality and contained less than 6 per cent. of nitrogen. Sometimes a unit of nitrogen in a low grade shoddy costs more than a unit in one of high grade; no doubt this is connected with the railway charges which fall more heavily on the nitrogen unit in poorer shoddies.

HOUSE REFUSE.—Ground and treated house refuse is always damp and, in addition, contains nearly half its weight of useless mineral matter. I have found that the organic matter seldom exceeds 40 per cent. and much of this is in the form of coke, that is to say, partly burnt household coal. As large quantities of this treated household refuse are now being turned out from various centres its sale is being pushed by various types of advertising. One of the interested firms has undertaken manurial experiments, and the result of these will be known during the autumn. Meanwhile, if this material is purchased at all, it should be purchased in experimental quantities, so that its action on both the plant and the soil can be compared with that of other dressings. It is, of course, a fact that heavy yields of some crops can be obtained on old rubbish tips, but whether the refuse is worth its cost and the charges for carriage, cartage and distribution remains to be seen. However, considerable sums of money have been invested in plant to grind, screen and treat household refuse.

GUANO COMPOUND.—This contained 75 per cent. of its nitrogen in the form of sulphate of ammonia. The warranted composition, of course, did not convey to the purchaser the fact that such a large proportion of the fertiliser consisted of sulphate of ammonia. A calculation showed that the value of this compound was about £2 0s. 0d. per ton less than the price paid for it. This is another instance which shows the fallacy of buying this type of compound fertiliser without an enquiry into the amount of guano contained by the compound.

COMPOUND FISH MANURE.—This, too, should never be purchased unless a warranty is obtained with respect to its content of fish guano. Samples of compound fish manure examined during the quarter showed that in one instance 90 per cent. of the nitrogen was in the form of sulphate of ammonia. It is highly improbable that the purchaser would have been willing to pay the price asked for this compound had he known more about its actual composition.

WASTE FROM A BUTTON FACTORY.—This waste came from a factory manufacturing buttons from nuts. Analysis showed that, whilst it had not a very high nitrogen-content, it contained upwards of 90 per cent. of organic matter. Unfortunately, both the nitrogen and phosphoric acid contents were low, the former amounting to less than 1 per cent. and the phosphoric acid to 0·2 per cent. For fertilising purposes the waste would be of value to the farmers in the neighbourhood of the works where collection and carting expenses would be low.

COOKED FLAKED WHEAT.—It would seem to be most important that the flaked wheat should be submitted to a considerable amount of heat and this is not always done. Cooked flaked wheat is being fed to farm animals which hitherto have not received wheat as part of their ration, and in these circumstances it is necessary that producers of flaked wheat should take due precautions with regard to the cooking. F. W. F. ARNAUD

CITY OF LEEDS

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1938

LACTOSE IN CHEESE.—A complaint was received from a private purchaser that a sample of cheese contained glass. On examination there were found a large number of small wedge-shaped transparent crystals, composed, not of glass, but of lactose, constituting 1·5 per cent. of the total weight of the cheese. The cheese was a processed one, and no previous record of a similar occurrence can be found in the literature.

CURDS ADULTERATED WITH FLOUR.—A formal sample was found to have been made from skimmed milk and adulterated with 1·8 per cent. of flour.

HYPOPHOSPHITE WINE DEVOID OF HYPOPHOSPHITES.—A medicated wine purporting to contain hypophosphites was found to be devoid of hypophosphite. The sample was a sweet red wine containing 28·5 per cent. of proof spirit and 1·5 per cent. of malt extract. The manufacturer was summoned for giving a false warranty to the retailer and was fined 40s. including costs. C. H. MANLEY

METROPOLITAN BOROUGH OF WOOLWICH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1938

OF the 833 samples of food and drugs examined 506 were purchased informally.

HOT MILK MADE FROM MILK POWDER.—A sample of hot milk taken at a café was found to be a fluid made from machine-skimmed milk powder and water. The sample was deficient in fat to the extent of 93 per cent., and the sp.gr., freezing-point, and proportion of five other constituents were outside the normal range for fresh milk. The figures were as follows:—Fat, 0·21 per cent.; solids-not-fat (including 5·33 per cent. of milk sugar), 10·86 per cent.; proteins, 4·14 per cent.; mineral matter, 0·92 per cent.; citric acid, etc., 0·47 per cent.; sp.gr. at 15·5° C., 1·0415; freezing-point (Hortvet), −0·620° C. The nitric nitrogen (0·0004 per cent.) corresponded with the proportion of nitrates (0·45 per 100,000) in a sample of tap water obtained from the supply at the premises where the "milk" was purchased, thus confirming the amount of tap water added to the milk powder. On being summoned, the defendant admitted the offence and was fined £1 with £1 1s. costs.

CHEESE CONTAINING LACTOSE CRYSTALS.—A sample of bread-and-butter and cheese consisted of five slices of white bread spread with butter and with cheese. A variation in the quantities of ingredients used in the manufacture of the cheese (which was sold, not as cheese, but under a fancy name) led to a complaint that it

contained broken glass. Analysis showed that particles, 1/16″ to 1/8″ long, were present. They were sharp, brittle and tasteless, rhombic prisms, and proved to be crystals of α-lactose hydrate, which had presumably formed gradually as the cheese slowly lost water by evaporation. Correspondence with the manufacturers confirmed the inference that an excessive amount of lactose had been used, and that the water-content had fallen from 55 to 45 per cent. The total lactose-content was 11·1 per cent. expressed as hydrated lactose.

H. AMPHLETT WILLIAMS

Report of the Government Chemist upon the Work of the Government Laboratory

FOR THE YEAR ENDING MARCH 31ST, 1939*

THE chemical work for the various Government Departments has been carried out as before (*cf.* ANALYST, 1938, **63**, 887) at the laboratory at Clement's Inn Passage, Custom House, Geological Survey Museum, Park Royal, and Deptford. The total number of samples examined including those dealt with at the Chemical Stations was 555,045, a decrease of 7504 on the previous year. The chief decreases were in wines, imported beer and samples under the Safeguarding of Industries Act, and increases are noted in samples of tobacco, War Office samples and tea.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter.*—The proportion of water varied from 12 to 16·8 per cent.; 39 samples contained over 16 per cent., 526 between 15 and 16 per cent., 232, 14 to 15 per cent., 39, 13 to 14 per cent., and two, 12 to 13 per cent. The Reichert–Meissl value was under 24 in one sample; 24–26 in 39 samples; 26–28 in 149 samples; 28–30 in 275 samples; 30–32 in 279; 32–34 in 95 samples.

Margarine.—Eight of 127 samples had over 16 per cent. of water.

Cheese.—Water varied from 26·5 to 57·8 per cent.; fat from 9·2 to 39·6 of the cheese, or 19·7 to 59·6 per cent. of the dry matter.

Sheep Dips.—Of the 34 samples examined, only one would not have satisfied the Ministry's requirements when prepared as directed.

Sea Water.—The salinity of 6682 samples of sea water, including 2618 from the Fishery Board for Scotland and 498 taken by the Admiralty, was determined, and the data sent to Copenhagen. In 593 samples the proportion of dissolved oxygen was also determined.

Water and Pollution of Rivers.—To ascertain the condition of fishing streams from the point of view of fish life, 85 samples of river water were examined.

Fertilisers and Feeding Stuffs Act, 1926.—Two fertilisers (compound fertiliser and basic slag) were alleged not to conform with the statutory statements supplied with the articles; a bone meal was alleged to contain an excessive proportion of sand. Eleven feeding stuffs (ground oats, linseed cake, white fish meal, 2 meat and bone meals and 6 feeding meals) were examined. The ground oats contained tapioca starch; the linseed cake contained cyanogenetic glucosides capable of yielding hydrocyanic acid; the white fish meal contained an excess of salt and a deficiency of oil; the six feeding meals were alleged not to conform with the particulars given in the statutory statement. The results obtained confirmed those of the Agricultural Analysts, except that the basic slag and two feeding meals were found to agree with the Statutory Statement within the limits of variation allowed.

* Obtainable at H.M. Stationery Office, York House, Kingsway, W.C.2. Price 9d., postage extra.

Agricultural Produce (Grading and Marking) Act.—National Mark Schemes.—The 265 samples of flour examined included 85 Yeoman flours. Samples of malt extract, and malt extract with cod-liver oil numbered 6; of cider, 137; of perry, 6; of honey, 170. The cheese grades remain as last year, except that the Cream Cheese Regulations, 1938, specify one grade made from cream and containing not less than 60 per cent. of butter-fat on the cheese. Nine hundred and fifty-six samples of cheese were examined, including 266 Cheshire, 64 Stilton, 272 Cheddar, 13 cream, 66 Caerphilly, 209 Lancashire, 55 Wensleydale, 6 Leicester, and 5 Derby cheeses. One hundred and forty-two samples of water from the intakes and water-cress beds were examined.

Land Fertility Committee.—In connection with the scheme for improvement of the soil 139 samples of lime and basic slag were examined.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples examined in connection with duty on beer was 42,293. Of these, 475 were of materials used for brewing. Of 3784 samples taken as a check on declarations of gravity, 46 were found to be under-declared. To check dilution, 692 samples of beer were examined; in 17 samples there was evidence of dilution, and in 5 dilution was equivalent to the addition of over 3 gallons of water per barrel. Of the 15,541 samples of beer examined for drawback, only 46 were found to be over-declared. In the examination for arsenic 29 of 2067 samples contained arsenic slightly in excess of the recommended limit.

Cocoa and Chocolate.—The total number of samples was 12,403. The import samples included 1147 additionally examined for spirit, and coconut oil (liable to Ottawa duty) had to be tested for in 1623 samples.

Dangerous Drugs Act.—Fifty-five samples of suspected goods were examined, and of these, 4 were Indian hemp, and one dried rolls of citrus fruit smeared with traces of opium.

Hydrocarbon Oils Duty.—The standard cone and needle penetration tests remain as before. The total number of samples examined for the presence of hydrocarbon oil was 12,979, of which 5711 were from imported and 7268 from exported goods, and of these 8834 were hydrocarbon oils and the remainder such composite goods as enamels, paints, garage preparations, road dressings, insecticides, printing inks, etc.

Hydrometers and Graduated Vessels.—The accuracy of the various vessels issued to the Customs and Excise Officers was tested, 2506 tests being made. Approximately 1250 Tate saccharometers have now been calibrated and issued.

Safeguarding of Industries Act, 1921.—Listed imported chemicals and substances containing the chemicals are subject to duty, and 6662 such samples were examined.

Silk and Artificial Silk.—Of the total 19,487 samples examined, 7746 were from imported articles concerning which the proportions, if any, of real or artificial silk had to be ascertained; also whether or no the natural gum of silk had been removed from the fibre.

Spirits.—Samples examined included 776 of wood naphtha, other crude methyl alcohol and mineral naphtha; 206 of pyridine and dyes intended for use in the manufacture of methylated spirits (only 4 of the samples were condemned), and 3534 of special denaturants. Gins and liqueurs were tested for strength and character (3313), and of these, 2800 were also tested for sugar and saccharin; 134 samples of 14,448 of exported spirituous preparations were found to be over-declared. The 12,549 samples of imported spirits were mostly sent for determination of their obscuration. Two of 42 samples of imported methyl alcohol were found to be liable to duty owing to potability.* One sample of fusel oil of 21 import samples contained excess ethyl alcohol, as did 5 of 43 samples from British distilleries.

*Methylic alcohol purified so as to be potable is liable to duty as spirits (Finance Act, 1920).

Sugar, Glucose and Saccharin.—The samples of sugar, including 567 from beet sugar factories, numbered 22,064, and sweetening material 52,891, of which 46,183 were from imported goods. Saccharin was found in many of the 90 samples of imported substances specially examined for its presence, and 529 samples of saccharin and articles containing it were analysed for drawback.

Tea.—Of a total of 14,845 samples of tea examined, 95, representing 269 packages, were reported against, 20 on account of the presence of foreign substances, and 75 as unfit for human consumption. To guard against the presence of adulterants or exhausted leaves, 581 samples of exported tea were examined.

Tobacco.—The number of samples examined during the year again showed a further increase, and reached 207,024 (201,751 in 1938–9). The samples are taken for detection and prevention of adulteration (almost non-existent in this country); for determination of appropriate rate of duty and drawback; to ensure that manufactured tobacco for home consumption complies with the requirements of the tobacco laws; for effective control of denaturing waste tobacco used for agricultural and other purposes.

Food and Drugs Acts.—Eight samples of food were examined consisting of milks alleged to be deficient in fat or non-fatty solids, one "appeal to cow" milk, one tea alleged to contain foreign matter, and four jams alleged to be deficient in fruit. All the results were in agreement with those put forward by the prosecution, except that the proportion of foreign matter in the tea was less than alleged, and that one jam could not be stated to be deficient in fruit.

Ministry of Health.—*Condensed Milk.*—Of 128 samples, 10 were reported against; in four the quantity of whole milk to which the contents of the tin were supposed to correspond was over-stated, and in addition 2 samples were deficient in milk-solids or both fat and milk-solids, and 6 samples were wrongly labelled.

Preservatives.—Of 1240 samples of imported dairy produce and 630 of other food substances, including pulped fruit, vegetables in brine, fruit juices, cornflour, etc., 29 were reported against. Of these, 27 contained sulphur dioxide; one sample of liquid egg-yolk contained boric acid, and one of soda fountain preparation contained benzoic acid either contrary to Regulations or in excess of permitted quantities.

Office of Works.—Four samples of water were examined bacteriologically in connection with chlorination of bathing water in the Serpentine and St. James's Park Lake, and 73 samples with a view to securing safe supplies for Government institutions, training camps, etc. D. G. H.

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

CHLORINE

Occurrence.—Dangerous concentrations may be encountered in alkali (electrolytic) works, bleaching works, chemical works, dye-making and dye-using works, tanneries, tinplate works, water purification works, etc.

Poisonous Effects.—Acute poisoning by chlorine is unusual, as the gas can be recognised by its odour and irritant qualities even in low and harmless concentrations. It can be recognised by smell in as low a concentration as 1 part in 1 million parts of air.

* Leaflet No. 10. H.M. Stationery Office, July, 1939. Price 3d. net.

The effects of various concentrations in air are as follows:

Parts by vol. (approx.)	Mg. per litre (approx.)	Duration of exposure	Effect
1 in 1000	3·17	Brief exposure	Rapidly fatal—by asphyxia
1 in 10,000	0·32	Few seconds	Intolerable
1 in 20,000	0·16	Thirty minutes	Very dangerous, owing to acute pulmonary oedema
1 in 100,000	0·03	Sixty minutes	Bronchitis
1 in 1,000,000	0·003	Prolonged exposure	Permissible

METHOD OF DETECTION.—A test suitable for industrial use must be capable of detecting at least 1 part of chlorine in 1,000,000 without requiring an inconveniently large sample. The only known test that is sufficiently sensitive depends on the interaction of chlorine and a dilute solution of *o*-tolidine to form a yellow compound, which can be estimated colorimetrically. This method has therefore been adopted as the standard industrial method. The test-papers are approximately one-tenth as sensitive to nitrous fumes as to chlorine.

The test is applied by drawing samples of the air, by means of a hand-pump of definite capacity, through a bubbler containing *o*-tolidine solution until the depth of colour produced is equal to that of one of a series prepared from potassium dichromate solution. From the number of strokes required the concentration is obtained by reference to a table.

Apparatus.—The method of sampling the air, the arrangement of the bubbler, and the type of pump are described and illustrated (*cf.* ANALYST, 1938, **63**, 659; 1939, 279).

Preparation of Reagent.—One g. of *o*-tolidine (specially purified—m.p. not lower than 130°–131° C.) is dissolved in 100 ml. of conc. hydrochloric acid (of reagent quality), and the volume is made up to 1 litre with water.

Preparation of Standard Colours.—One g. of potassium dichromate (of reagent quality) is dissolved in 1 litre of water. A series of standards is then made by diluting the following quantities of the 0·1 per cent. solution to 10 ml. in tubes of exactly the same bore as the bubbler.

Standard	Vol. of 0·1 per cent. dichromate solution diluted to 10 ml.
No. 1	5 ml.
„ 2	3 „
„ 3	2 „
„ 4	1 „

If kept in well-sealed bottles in the dark, the standards should not change in six months.

Application of Test.—Ten ml. of the *o*-tolidine solution are measured into the side-arm test-tube of the apparatus, and the tube is connected with the pump, the valves of which have previously been tested. The delivery tube must be approximately central, and must on no account touch the side of the test-tube.

Pumping of the atmosphere to be tested shall be carried out with slow strokes (approximately 10 seconds per stroke), and be continued until the depth of colour developed (if any) is approximately equal to that of one of the standards. The bubbler is then removed and immediately compared, by transversely transmitted daylight, with the standard tube. Other methods of comparing the colours may be used such as a comparator with coloured glasses as standard, a photo-electric colorimeter, or an optical density meter.

The concentration of chlorine corresponding with the standard used and the number of strokes made is then read from the following table:

Number of strokes	Standard No. 1	No. 2	No. 3	No. 4
2	1/16,000	1/27,000	1/40,000	1/80,000
5	1/40,000	1/67,000	1/100,000	1/200,000
10	1/80,000	1/130,000	1/200,000	1/400,000
20	1/160,000	1/260,000	1/400,000	1/800,000
25	1/120,000	1/330,000	1/500,000	1/1,000,000

Where a test is required on air from a space not readily accessible, or where there is a possibility of a highly toxic concentration of chlorine being present, the air should be sampled from a distance. In the procedure described for this purpose the apparatus is connected with the space to be tested by means of glass tubing (approx. 0·25 in. bore) with rubber connections. When the sampling tube has been filled in this way with the atmosphere under examination, the bubbler is restored to the circuit, and a test is made in the usual manner. Approximately, one stroke of the pump is made per 12 feet of extension tube.

FIRST AID.—In cases of acute gassing with chlorine the patient should be removed to the fresh air and kept warm and at rest, pending the arrival of a doctor. If breathing is weak or stops, artificial respiration must be begun at once and continued for several hours even after it may seem to have failed.

Home Office

REPORT OF THE CHIEF INSPECTOR OF FACTORIES FOR THE YEAR 1938*

IN this Report H.M. Senior Medical Factory Inspector (Dr. J. C. Bridge) discusses the question of health risks in chemical industry.

LEAD POISONING.—Since lead poisoning became notifiable, nearly forty years ago, the cases have fallen from well over a thousand to less than one hundred per annum. Although only seven cases of lead poisoning in white lead works were reported, this number was greater than for many years. Five of these cases occurred at one factory where a new process had recently been started. In a number of instances it was found that lead paint was being applied by means of a spray, but, after representations had been made, the brush method was used.

MERCURIAL POISONING.—One case occurred in the manufacture of thermometers. The man, who had been employed for eight years, was a confirmed nail-biter. The other case was that of a female worker, aged 28, who had been employed for four months in assembling electric meters.

ARSENICAL POISONING.—In the three cases reported, dermatitis was present in addition to gastro-intestinal symptoms. One of the cases occurred in the manufacture of an insecticide containing calcium arsenate, and the other two in the manufacture of sheep dip containing sodium arsenite.

ANILINE POISONING.—Four of the nine reported cases were unusually severe, necessitating absence from work for two or three weeks or longer; aniline oil was responsible for two of these cases, *p*-nitro-chlorobenzene vapour for the third, and *p*-toluidine for the fourth. In this last case the methaemoglobinaemia called for a blood transfusion. The remaining five cases, which were slight, were caused by trinitrotoluene at a shell-filling factory.

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price 2s. 2d.

Investigation of a case of "leucopenia" showed that the boy in question, aged 17, had been employed as a cellulose sprayer for about 14 weeks, and that during part of his time he had used a cellulose solution containing as much as 30 per cent. of benzene, while the other cellulose paint which he had sprayed contained toluene.

HYDROGEN ARSENIDE POISONING.—Three cases of toxic jaundice were caused by arseniuretted hydrogen evolved from cadmium residues in a chemical works.

CHLORINATED NAPHTHALENE WAX.—Three fatal cases of jaundice were investigated in which there was exposure, in varying degree, to fumes from chlorinated naphthalene wax.

CHROME ULCERATION.—The number of notified cases increased from 101 in 1937 to 115 in 1938, the main increase being in connection with the process of anodic oxidation. An unusually high number of cases occurred at one factory where there was some deterioration in the plant. New methods of crystallisation, to avoid handling the chrome products, were considered, and a fortnightly, instead of a monthly, medical examination of the workers was instituted.

EPITHELIOMATOUS ULCERATION.—The relatively low figures for gas works (12 cases with one death) may be due to a more prolonged contact with the carcinogenic agent being necessary than when there is tar distillation. The comparative figures of 1934 to 1938 appear to bear out the suggestion that there is a tendency in recent years for the disease to manifest itself at an earlier age and after a shorter period of service than formerly, but it is more probable that periodical medical examination and ray treatment leads to a number of cases that have not yet assumed malignancy being included in the returns.

DANGEROUS DUSTS.—Not many years ago asbestos dust, which is now recognised as highly dangerous, was regarded as innocuous. On the other hand, substitution of a relatively harmless dust for a harmful one is a valuable means of protection. It is gratifying, therefore, to be able to report excellent progress in the substitution of alumina for flint in one of the processes of the pottery industry.

DYE WORKERS' BLADDER CANCER.—Five cases of papilloma of the bladder in workers engaged in synthetic dye manufacture came to the knowledge of the Department. As usual, most of the workers had come into contact with more than one dyestuff intermediate, but three were known to have had substantial contact with β-naphthylamine. In two cases no contact with this chemical could be traced, both men being employed mainly, if not solely, in the manufacture of auramines, which involved contact with various intermediates derived from dimethylaniline. The onset of the disease in all cases occurred prior to 1938, and in one case as early as 1931.

POISONING BY FUMES AND GASES.—Of the 190 cases reported, 98 were due to carbon monoxide, 10 to hydrogen sulphide, 17 to chlorine, and 14 to nitrous fumes. Three cases of ammonia poisoning were caused by an escape of fumes from refrigerator plant. One case of gassing by trichloroethylene was due to escape from a dry-cleaning plant, and a case of phosgene poisoning was probably due to formation of phosgene while a fire was being extinguished with a patent extinguisher. During the past few years several complaints have been received about the irritating nature of acrolein fumes intermittently evolved, and at one large foundry simple canister respirators have been worn four or five times a day for ten minutes at a time with satisfactory results.

DERMATITIS.—There were 2195 cases of dermatitis voluntarily reported, as compared with 1985 cases in 1937. Among the new causative agents is ultramarine, to which two cases were attributed. In each case the length of exposure was four years.

A suitable "barrier substance" against dermatitis has been found, but is being put to further practical tests in various factories before the prescription is issued.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1938

THE Government Analyst (Mr. Kenneth Wallis) reports that the number of samples and specimens examined for 27 Government Departments and various private firms and individuals was 8939 as compared with 8774 in 1937. These included 1994 samples from the Director of Medical Services, 1876 from the Comptroller of Customs, and 2035 exhibits from the Commissioner of Police.

POISONING CASES.—Eighteen cases, involving the examination of fifty exhibits, were received. The principal poisons found were corrosive sublimate, acriflavine, tartar emetic, Jeyes' fluid, zinc sulphate and potassium cyanide.

OBEAH.—From time to time cases of obeah (witchcraft) are still brought before the Courts. Thirty exhibits were submitted in connection with four cases. They included skull, powdered skull, vegetable powders, oil, mercury, copper sulphate, resin, dried manure and bone.

FOOD AND DRUGS.—Of the 4876 samples submitted under the Food and Drugs Ordinance, 415 were reported as adulterated and prosecutions followed. The percentage of adulteration was 8·5 as compared with 6·7 in 1937.

Milk.—Of 4212 samples examined, 399 were adulterated, 220 being deficient in solids-not-fat and 179 in butter-fat. Special raids are unexpectedly carried out by the Police Department and Public Health authorities on Sundays and public holidays and after official hours. The number of samples so analysed was 1036, of which 102 were adulterated, the percentage adulteration being 10·1 as compared with 9·4 on ordinary weekdays.

British Standards Institution

HANDBOOK OF INFORMATION*

INCLUDING ANNUAL REPORT, 1938–1939

THIS Handbook, published July, 1939, contains 115 pages, and includes a Chart of Organisation, General Council, Divisional Councils, Industry Committees and Aims and Objects of the Institution.

Also, lists of British Standard Methods of Test used in B.S. Specifications. New and Revised British Standards in Course of Preparation. British Standards: Numerical List; Subject Index. Dominion and Foreign Standards Organisations. Government Department Co-ordinated Specifications.

THE following Table has been issued:†

NO. 860—1939. TABLE OF APPROXIMATE COMPARISON OF HARDNESS SCALES.

In view of the fact that to an increasing extent the "Brinell," "Diamond Pyramid" and "Rockwell" tests are being used in different works or laboratories for measuring the hardness of the same material, there has been a general demand for some means of correlating the most used A, B and C scales of the Rockwell test with those of the other tests.

Investigations show that there can be no general theoretical relationship between these scales, and empirical formulae devised from experiments only hold closely for materials of approximately similar composition and in a given condition. *Variations* in the empirical relationships result if the conditions as regards composition, heat-treatment and cold work differ appreciably, and also if different loading ratios are selected in the Brinell test. On the other hand, groups of materials similar as regards composition, cold work, etc., when tested by any of the above methods, may give fairly close comparisons.

* British Standards Institution. Publications Dept., 28, Victoria Street, London, S.W.1. July, 1939. Price 1s. 6d.

† Publications Department, 28, Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

The Table is therefore a general approximation. It is issued solely as an indication of the order of the relationship between the three systems of Hardness Readings, and must not be used as a standard for the conversion of hardness values given on one scale in any British Standard to those of another scale.

The Diamond Pyramid Scale has been taken as the basis of reference, and the most probable comparative values have been adopted from published experimental results.

This Table requires reference to the following British Standards:

No. 240. Methods and Tables for Brinell Hardness Numbers.
No. 427. Tables of Diamond Pyramid Hardness Numbers.
No. — *Direct Reading Hardness Test (Rockwell Principle).

*In preparation.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Colorimetric Determination of the Preservative Value of Hops. A. A. D. Comrie. (*J. Inst. Brewing*, 1939, **45**, 336–341.)—Ferric chloride has been found to possess certain disadvantages as a colour-matching agent in the colorimetric determination of the preservative value of hops, and a 0·001 *N* solution of iodine with potassium iodide is proposed in its place. The method has been re-studied with this solution as colour-matching agent, and a slightly modified procedure is described. In determining the relation between colour value, in terms of 0·001 *N* iodine, and preservative value it has been found that the colour value is proportional to an average of $\alpha + \beta/5{\cdot}5$ for some standard English varieties (where α and β represent α- and β-resins), and to an average of $\alpha + \beta/4{\cdot}4$ for some American varieties, the actual value varying slightly from hop to hop. For "Brewers' Gold," the only member of the new hybrids to be studied, the colour value is proportional to $\alpha + \beta/3$. Three distinct standards are therefore proposed for use in the colorimetric determination of the preservative values, expressed as $10(\alpha + \beta/3)$, of these three classes of hops. The effects of using such fixed standards on the accuracy of the method, as applied to different hops with varying β-resin content, is discussed, and it is pointed out that the errors involved will be small. The method is rapid and requires only the simplest of apparatus and reagents. To obtain the hop colour a 5 per cent. extract in 90–100 per cent. alcohol is made, 1 ml. is diluted to 50 ml. with alcohol, 15 ml. of this are placed in a 25-ml. measuring flask, 1 ml. of uranium nitrate solution (1 per cent. in alcohol with 0·5 per cent. of pyridine) is added, and the mixture is made up to the mark with alcohol. This gives a 0·05 per cent. solution, which is generally convenient for matching with the standard colour value, *i.e.* the colour given by 0·8 mg. of hop resin or its equivalent as matched with 0·001 *N* iodine. If the calibration value of the hop colorimeter tube is x, the concentration (per cent. of hop) of the hop solution tested is C, and the depth (in mm.) of the hop solution tested is D, the preservative value of the hop is given by the general expression $80x/\text{C.D}$. This value will be approximate, for it is based on average results, from which individual hops will deviate, from the brewers' point of view; however, an approximate measure is all that is needed. D. R. W.

Preliminary Investigation of the Lichthardt Test for the Detection of Caramel in Cider Vinegar and Distilled Vinegars. F. E. Cook and H. Miller. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 588–593.)—The Lichthardt test (*J. Ind. Eng. Chem.*, 1910, **2**, 389) was applied to pure cider vinegars and distilled vinegars to which caramel had been added. The reagent was prepared as follows:—Exactly 4 ml. of sulphuric acid (sp.gr. 1·84) were added to 9·8 g. of tannic acid dissolved in 294 ml. of water, and the mixture was diluted to 490 ml. with water. This reagent (5 ml.) is added to 5 ml. of vinegar and, according to the original method, the mixture should be heated gently until the precipitate first formed is nearly dissolved and then set aside for 12 hours. A brown precipitate adhering closely to the bottom of the test-tube indicates caramel; a flocculent precipitate is disregarded. Experiments showed that often no precipitate was formed whether the vinegar contained caramel or not, and the effect of variations in the degree of heat applied was investigated. Some caramels gave no immediate precipitate when the reagent was added. Uncontrolled heating gave unsatisfactory results, and temperatures of 50° C. and above interfered with the formation and settling of the precipitate. Temperatures up to 48° C., maintained for not more than 4 minutes, did not interfere with the formation and settling of the precipitate, but showed no specific advantage over temperatures of 30° to 40° C. Some vinegars which had darkened in colour after standing for 3 or 4 months gave slight precipitates where previously they had given none. One sample gave a slight precipitate under all conditions of the test, and the results of Amthor's test for caramel were also inconclusive. A precipitate allowed to form undisturbed would spread itself over the side walls and bottom of the tube, but a slight twist of the tube would cause it to settle to the bottom. No precipitate adhering firmly to the walls was noted, and very little difference was found between precipitates obtained from vinegars containing caramel and those obtained in absence of caramel. The precipitate produced when caramel had been added to the vinegar was slightly less flocculent and less easily disturbed than the smaller precipitate produced when no caramel had been added. It may be the intention of the original method that the mixture of vinegar and reagent should not be heated unless a precipitate has formed. The method is considered sufficiently promising to warrant further investigation of the conditions in which the precipitates can be distinguished. A. O. J.

Observations on the Colorimetric Method for the Determination of Vanillin. A. L. Curl and E. K. Nelson. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 684–688.)—Results obtained by the colorimetric method for the determination of vanillin (*Methods of Analysis, A.O.A.C.*, 1935, 307) were much higher than those obtained gravimetrically, and a colorimetric determination made upon the residue from the gravimetric extraction showed that a substance that was not vanillin reacted with the reagent. Similar discrepancies were found with extracts of Bourbon, Java, Mexican, South American and Tahiti vanilla beans as with the Puerto Rico vanilla first used. The effect of changes in the ratio of neutral to basic lead in the basic lead acetate reagent was investigated, and it was found that the ratio should not be much greater or less than 3 to 1. A ratio of 6·3 to 1 was unsatisfactory, especially if the vanilla contained much resin, since the interfering

substances were not completely precipitated and high results were obtained. On the other hand, a ratio of 1·2 to 1 caused precipitation of some vanillin and led to low results. The basic lead acetate used for preparation of the reagent should therefore be assayed, and if the ratio of neutral to basic lead is much greater than 1 to 1, the material should be rejected. The preservation of standard vanillin solutions used in the colorimetric method was investigated. A standard vanillin solution kept in a partly filled bottle increased in apparent strength, probably by oxidation. A full bottle kept in a refrigerator gave the same results as the fresh solution. Folin and Denis (*J. Ind. Eng. Chem.*, 1912, **4**, 671; Abst., ANALYST, 1912, **37**, 501) state that in the colorimetric method, with the standard set at 20 mm., no readings should be accepted as final if they fall much outside the limits of 15 to 30 mm. A 20 per cent. sodium carbonate solution, as recommended by Snell (*Colorimetric Methods of Analysis*, 1937, **2**, 86), was found preferable to the saturated solution. In making the gravimetric determinations, extraction with ammonia (designed to separate vanillin from coumarin) was omitted. Petroleum spirit extracts of the crude vanillin residues were made, and the insoluble impurities were deducted. When the extraction with ammonia was not omitted the results were, on the average, about 2·1 per cent. lower. A. O. J.

Volatile Oil in Sage. J. F. Clevenger. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 683–684.)—Most of the sage leaves used in the United States are grown in Jugoslavia and imported from Trieste. These are known as Dalmatian sage (*Salvia officinalis*). A certain amount of Greek sage (*Salvia triloba*) is imported from Athens. The characteristics of the volatile oils of the two species determined by the methods outlined in *Methods of Analysis, A.O.A.C.*, 1935, 447 *et seq.*, are as follows, the first number (*a*) referring to Dalmatian and the second (*b*) to Greek sage:—yield of volatile oil (ml. per 100 g.), (*a*) 1·2 to 2·3; (*b*) 2·1 to 2·6; sp.gr. (25°/25° C.), (*a*) 0·917 to 0·937; (*b*) 0·907 to 0·918; $[\alpha]_D^{25}$, (*a*) +3·8 to +13·5; (*b*) −4·1 to −21·0°; n_D^{20}, (*a*) 1·461 to 1·469; (*b*) 1·466 to 1·473; acid value, (*a*) 0·9 to 3·5; (*b*) 0·57 to 1·75; ester value, (*a*) 10·8 to 28·74; (*b*) 13·0 to 25·2. The difference in optical rotation of the two kinds of oil provides a valuable means of distinguishing them. Coarsely-ground sage leaves when stored in an open shallow pan in the laboratory for 7 months lost about 25 per cent. of their content of volatile oil. A. O. J.

Preservation of Pharmacopoeial Paraldehyde: Detection of Resorcinol. J. S. Toal. (*Pharm. J.*, 1939, **143**, 226–227.)—In an investigation on the effect of preservatives on the keeping properties of paraldehyde, it was necessary to test for the presence of resorcinol. This was successfully accomplished by a modification of Carrobio's test (*Boll. chim. farm.*, 1906, 365; *Yearbook Pharm.*, 1907, 133). Ten ml. of the paraldehyde to be tested were shaken for about a minute with 2 ml. of 0·1 per cent. zinc sulphate solution to which 4 drops of conc. ammonia solution had been added. After standing for half-an-hour the aqueous layer separated with a deep-blue colour when resorcinol was present. Under these conditions the test is sensitive to 10 parts of resorcinol per million. F. A. R.

Verbenin, a Glycoside from *Verbena officinalis*, which Promotes Milk Secretion. K. Kuwajima. (*Tohoku J. Exp. Med.*, 1939, **36**, 30–43.)—A glycoside, to which the name "verbenin" has been given, has been obtained

from the powdered root of *Verbena officinalis* L. by extraction with hot ether. The aqueous solution of the residue obtained on cooling the hot ethereal solution was filtered and evaporated, and the residue was taken up in hot alcohol. On diluting the alcoholic solution there separated a substance which by fractional crystallisation from absolute alcohol could be separated into a major portion crystallising in platelets, and a minor portion forming needle-shaped crystals. The former is chiefly responsible for the action of the root in promoting the secretion of milk. The m.p. of the plate-shaped crystals, which constitute the new substance verbenin, is 179° C. The needle-shaped crystals, which appear to be identical with the verbenalin of Bourdier (*cf. Abderhalden, Biochemisches Handlexikon*, Berlin, 1911, **2**, 681) and of Holste (*Z. exp. Path. u. Therap.*, 1918, **19**, 483), melt at 177° C. Both glycosides, which have a very bitter taste, dissolve easily in water and absolute alcohol, sparingly in ether, and very difficultly in chloroform, the aqueous solutions being neutral. Both reduce Fehling's solution and ammoniacal silver nitrate solution on warming, particularly after treatment with hydrochloric acid, but not in the cold. On prolonged boiling with dilute sulphuric acid both give bright yellow amorphous precipitates, and when they are heated with acetic acid and phenylhydrazine light red-brown precipitates gradually separate. Injected into guinea-pigs, small quantities of verbenin have an exciting action, and large quantities a paralysing effect, on the sympathetic nerve endings of the mucous membrane, the heart, and the blood vessels. In very large quantities the glycoside paralyses the central nervous system. With milk-yielding animals quantities of verbenin which do not cause any other appreciable changes bring about a marked increase in milk secretion, which continues for some time. After entry into the blood verbenin appears to become fixed and gradually destroyed in certain tissues. E. M. P.

Exalgin, its Identification and Detection in Mixtures. A. Denoël. (*J. Pharm. Belg.*, 1939, **21**, 691–695, 709–711.)—Exalgin (*N*-methyl acetanilide) is frequently present in mixtures containing also one or more of the other antipyretics, acetanilide, phenacetin, antipyrine and pyramidone, and it has been difficult hitherto to detect its presence in such instances. The behaviour of a solution of exalgin towards various reagents was therefore studied, and compared with that of the four other compounds. In general, phenacetin and acetanilide did not give precipitates with the reagents used, whereas antipyrine gave precipitates with all, pyramidone with most, and exalgin with about two-thirds. The compounds obtained by treating exalgin with potassium ferrocyanide, gold chloride, iodine in acetic acid, potassium iodate (or bromate) in hydrochloric acid, and Reinecke's salt formed crystals of characteristic appearance when examined under the microscope. These reagents are therefore suggested for identifying exalgin. Exalgin can be separated from phenacetin and acetanilide by extracting 1 g. of the mixture with 5 ml. of cold water. The solubilities of phenacetin, acetanilide and exalgin are respectively 1 in 1400, 1 in 230 and 1 in 60. Exalgin can be characterised in the filtrate by any of the tests mentioned above (with the exception of the last), which give negative responses with phenacetin and acetanilide. In the examination of mixtures of exalgin and antipyrine it is essential to

remove all the antipyrine before attempting to test for exalgin. This can be done in three different ways. In the first method 10 ml. of a solution containing 0·5 g. of the mixture are shaken with 20 ml. of Lugol's solution,* and filtered after standing for 30 minutes. The filtrate is decolorised with sodium thiosulphate solution, made alkaline and extracted three times with ether. The combined ethereal extracts are filtered and evaporated. The residue contains no antipyrine. In the second method a solution of 0·2 g. of the mixture in 10 ml. of cold water is shaken with 50 ml. of 1 per cent. picric acid solution for 5 minutes and filtered. The filtrate is made alkaline and extracted with ether, and the ethereal extract is evaporated. The residue obtained is used for the test. In the third method a solution of 0·2 g. of the mixture in 10 ml. of water and 2 ml. of 10 per cent. sulphuric acid is shaken with 20 ml. of 40 per cent. ammonium thiocyanate solution for 5 minutes and the mixture is filtered through a sintered-glass filter. The filtrate is made alkaline and extracted with ether, and the extract is evaporated. The residue is used for the test. Of these methods, the first and the third are preferred. Exalgin is detected in the residues by any of the five reagents described above. When exalgin occurs in a mixture with antipyrine and pyramidone, it can be freed from both these substances with Lugol's solution as described above, and the residue used for testing for exalgin. F. A. R.

Determination of Amidopyrine in Presence of Antipyrine and Caffeine. F. C. Sinton and F. A. Rotondaro. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 678–680.)—Caffeine and antipyrine can be extracted quantitatively with chloroform from an aqueous solution containing 3·5 to 5 per cent. by weight of sulphuric acid. The aqueous residue is then made ammoniacal, and the amidopyrine is completely extracted with chloroform. The following procedure was found satisfactory for a solution containing 3 g. of amidopyrine, 2 g. of antipyrine and 0·5 g. of caffeine in 100 ml.:—The sample (10 ml.) was mixed with 5 ml. of sulphuric acid (10 per cent. by weight) and extracted with five 25-ml. portions of chloroform. The extracts were washed with 5 ml. of 3·5 per cent. sulphuric acid. The residue, after removal of chloroform by evaporation, was dried at 80° to 100° C. for 10 minutes and weighed. The combined aqueous residue and washings were made alkaline with ammonia, and the amidopyrine was extracted with chloroform, dried at 80° to 100° C. and weighed. If the original aqueous solution is saturated with anhydrous sodium sulphate before extraction, the concentration of acid necessary to effect complete separation is higher (10 per cent.) but less critical. The sodium sulphate appears to depress the ionisation of the acid, and the 5 ml. of acid added should contain 30 per cent. by weight of sulphuric acid. This method might presumably be applied to the determination of amidopyrine in admixture with other drugs. A. O. J.

Estimation of Small Quantities of Arsanilic Acid in Tryparsamide. C. A. MacDonald and J. G. Reynolds. (*Pharm. J.*, 1939, **143**, 222.)—The method proposed for the estimation of arsanilic acid in tryparsamide is a modification of the limit test described in the B.P. Addendum, 1936. Exactly 0·5 g. and 1·0 g. of tryparsamide are weighed into two test-tubes and dissolved in 6·0 ml. of

* A 5 per cent. solution of iodine in 10 per cent. potassium iodide solution.

water. Each tube is cooled below 5° C. and 2·5 ml. of 4 per cent. sodium nitrite solution are introduced into each, followed by 5 ml. of 10 per cent. hydrochloric acid. The contents of each tube are mixed and poured into 10 ml. of a cooled solution of β-naphthol, and the colour is measured in red units in the 1-cm. cell of a Lovibond tintometer. The amount of arsanilic acid present is calculated from a graph prepared in a similar manner with the aid of solutions of pure atoxyl of known strength. The colour develops its maximum intensity within a few minutes and remains unchanged for several hours. The quantity of sodium nitrite is the critical factor, since increasing amounts augment the colour produced from a fixed amount of arsanilic acid, whereas an insufficient amount gives almost the same colour when the amount of arsanilic acid is increased many fold. Satisfactory results were obtained with tryparsamide containing arsanilic acid of the order of 0·05 per cent. A serious anomaly in the Pharmacopoeial test was revealed, for whereas a sample containing 0·02 per cent. of arsanilic acid will just fail to satisfy the official test, a sample containing 0·05 per cent. will apparently fulfil the official requirements. The reason for this is that insufficient sodium nitrite is employed in the B.P. test, and the full colour development does not take place in the tube containing the larger amount of tryparsamide, so that this may actually be paler in colour than the other tube containing the smaller amount.

F. A. R.

Riboflavin in Liver Extract.—G. E. Shaw. (*Pharm. J.*, 1939, **143**, 222–223.)—A fluorometric method of estimating lactoflavin after conversion into lumiflavin by irradiating its alkaline solution has been developed. Exactly 1 ml. of the liver extract to be tested is measured into a 50-ml. separating funnel and mixed with 1 ml. of *N* hydrochloric acid and then with 10 ml. of acetone. The mixture is repeatedly extracted with 10-ml. portions of chloroform, acetone being added when necessary, until the lower layer ceases to give a blue fluorescence when examined in "black light." The combined lower layers are repeatedly extracted with 5-ml. portions of water until no more fluorescing material can be removed. The chloroform solution is discarded. The aqueous extracts are combined, extracted with chloroform to remove any blue fluorescing material, and transferred to a distillation flask, together with the upper layer from the original extraction. Acetone is removed by heating at 35° to 40° C. under reduced pressure, and the solution is made just alkaline to phenolphthalein and diluted to 30 ml. It is then transferred to a shallow evaporating dish, mixed with an equal volume of *N* sodium hydroxide solution, and exposed to unfiltered ultra-violet light for a suitable time. (An S.500 Hanovia analytical lamp for 10 minutes at a distance of 18 in. was satisfactory.)

The irradiated solution is transferred to a 200-ml. separating funnel, made faintly acid to phenolphthalein by addition of a 20 per cent. solution of citric acid, and extracted with 10-ml. portions of chloroform until no more green fluorescing material is removed. The combined chloroform extracts are diluted to a suitable volume, and the fluorescence of 10 ml. is compared in a test-tube with standard lumiflavin tubes. To prepare these standards, a series of 10 dilutions of riboflavin, from 0·1 to 1·0 mg. per 100 ml., is made, 1 ml. of each is diluted with 4 ml. of water

and 5 ml. of *N* sodium hydroxide solution, and the mixture is irradiated as described above. Each is then acidified to phenolphthalein and extracted with chloroform. The combined extracts are diluted to 20 ml., and 10 ml. are sealed up in non-fluorescent glass test-tubes. Figures varying between 6 and 1·8 mg. per 100 ml. were obtained for 8 preparations for oral administration, and 16 to less than 0·1 mg. in the same volume, for 11 parenteral preparations. F. A. R.

Biochemical

Distribution of Bromide and Chloride in Tissues and Body Fluids. E. G. Weir and A. B. Hastings. (*J. Biol. Chem.*, **1939, 129**, 547–558.)—Contradictory reports on the distribution of bromides between the blood and various body fluids and tissues after bromide administration having been published in the literature, a re-investigation of the problem was deemed desirable, and especially a critical examination of the methods used for determining bromides in such materials. The research involved the administration of sodium bromide to anaesthetised dogs and the subsequent analysis of blood, body fluids and tissues. Samples of blood and tissue were obtained and prepared for analysis according to the methods described by Hastings and Eichelberger (*J. Biol. Chem.*, **1937, 117**, 73), but an examination of the electro-titrimetric method used by Hastings and van Dyke (*J. Biol. Chem.*, **1931, 92**, 13) for the determination of bromides proved that the method was inaccurate when small amounts were present, owing to the fact that these workers used tungstic acid filtrates of cells which contained organic material capable of reacting with silver. The following modified method was therefore devised to overcome this difficulty:—The halides of the dried fat-extracted tissue (about 0·4 g.) obtained after the determination of water and fat, were converted into silver salts by digestion with excess of silver nitrate solution and nitric acid (*cf.* Sunderman and Williams, *J. Biol. Chem.*, **1931, 92**, 99). The mixture of silver halides formed was allowed to settle to the bottom of the Pyrex tube in which the digestion was carried out, and the supernatant liquid was drawn off by a pipette. The precipitate was washed with distilled water until the solution was free from silver. The digestion-tube was then attached to a series of three absorption vessels, and the washed silver halides were decomposed in the tube by adding 0·1 g. of manganese dioxide and 3 ml. of conc. sulphuric acid and boiling the mixture for 30 to 40 minutes. The mixture of chlorine, bromine, hydrogen chloride and hydrogen bromide produced was absorbed in 15 ml. of a 0·1 *N* sodium sulphite solution in 4 *N* sodium hydroxide solution contained in the receiving vessels. When the distillation was complete, the contents of the receivers were washed into conical flasks, neutralised to methyl orange with conc. nitric acid and treated with hot saturated barium nitrate solution to remove sulphate ions. The solution was made up to 100 ml. and filtered, and 50 ml. of the clear filtrate were used for the electrometric titration of the bromide. The subsequent procedure was identical with that described by Hastings and van Dyke, except that the titration was carried only to the bromide end-point. Total halides, and thus chlorides by difference, were determined by adding 3 ml. of water to the mixture remaining in the digestion-tube after decomposition of the silver halides, and adding a drop or

two of potassium oxalate solution if the resulting solution was pink, followed by 3 ml. of 10 per cent. ferric alum solution. The silver ion was titrated with 0·02 *N* ammonium thiocyanate solution. When known amounts of bromide were added to tissues and body fluids, it was found that a slight end-point correction was necessary to yield correct results, but total halide recovery in tissues and body fluids was satisfactory without correction. The results obtained were uniformly consistent among themselves and in agreement with the recent results of Wallace and Brodie (*J. Pharmacol. and Exp. Therap.*, 1939, **65**, 220). F. A. R.

Colorimetric Estimation of Phosphorus in Complex Mixtures. G. Barac. (*Bull. Soc. Chim. Belg.*, 1939, **48**, LII–LIII.)—The colorimetric method devised by Bell and Doisy (*cf.* ANALYST, 1921, **46**, 13) for the estimation of the total phosphorus in biological fluids, has been found to give satisfactory results with faeces. The method is specific for phosphate phosphorus. With a Pulfrich photometer as little as 4γ can be measured in a 3-cm. cell, and up to 300γ in a 0·5-cm. cell. A loss of as much as 35 per cent. of the phosphorus was experienced when an attempt was made to decolorise simple aqueous solutions with animal charcoal, but the loss was avoided altogether by using a trichloroacetic acid solution. By suitable modifications it was found possible to apply the method to the estimation of phosphorus in different states of combination. The powdered dried faeces were extracted with chloroform to remove phospholipoids, and the residue was allowed to stand for several hours in contact with trichloroacetic acid. The filtrate, after being decolorised with animal charcoal, was used for the estimation of the total phosphate, whilst the amount of inorganic phosphate was measured in the solution obtained after igniting the trichloroacetic acid extract, and the amount of organic phosphate was obtained by difference. Lipoid phosphorus was estimated in the residue obtained by evaporating the chloroform extract, either after ignition or after hydrolysis with hot acid. The method fails to give satisfactory results with substances of the type of casein, for the sum of the phosphorus present in the three forms mentioned above did not amount to more than 50 per cent. of the total phosphorus. The remainder was characterised by its solubility in warm alkali solution and was estimated after oxidation with nitric-perchloric acid mixture. F. A. R.

Recent Investigations on Bilirubin. G. Barac. (*Bull. Soc. Chim. Belg.*, 1939, **48**, LIII–LIV.)—The simplest method of estimating bilirubin is direct colorimetric measurement in an alkaline solution, but the method suffers from the grave disadvantage that alkaline solutions of bilirubin are rapidly oxidised, even when prepared and stored in the dark. The oxidation was not inhibited by formaldehyde, thiosulphates, hydrosulphites or antioxidants, such as polyhydric phenols. It was found, however, that a small amount of ascorbic acid stabilised the alkaline solution, and this observation was applied with complete success to the colorimetric estimation of bilirubin. Thus the addition of 200 mg. of ascorbic acid to a solution of 5 mg. of bilirubin in 1 ml. of 0·01 *N* sodium hydroxide solution prevented any loss of colour during 72 hours. The use of such a solution also enabled the absorption spectrum in both the visible and the ultra-violet regions of the spectrum to be studied without difficulty. F. A. R.

Determination of Phenol and related Compounds in Tissues. W. Deichmann and H. W. Scott. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 423–424.)—The phenolic compounds in tissues have been separated into (1) volatile compounds, and (2) acidic, neutral and basic non-volatile ether-soluble compounds. The phenolic substance in each was estimated colorimetrically as phenol. An aqueous extract of at least 20 g. of the ground tissue was treated with Folin–Wu reagent, allowed to stand for at least 15 minutes to precipitate the proteins, and filtered. A measured volume of the filtrate was acidified in a 250–ml. distillation flask with conc. hydrochloric acid (1 ml. per 25 ml. of filtrate) and steam-distilled at constant volume in an all-glass apparatus into 2 ml. of 4 per cent. sodium hydroxide solution (A). The distillate, measuring approximately 270 ml., was concentrated on a hot plate to 8 or 10 ml. After concentration of the distillation residue to 100 ml. and filtration, the three non-volatile fractions were separated as follows: *Acidic.*—The solution was extracted five times with ether, and the combined ethereal solutions were extracted with 5 ml. of (A) and 20 ml. of water. If the extract was not alkaline, the extraction was repeated with the same solution after addition of another 2 ml. of (A). The ethereal solution was extracted four times more with 0·5 per cent. sodium hydroxide solution (B), and the combined alkaline extracts, after removal of the remaining neutral compounds by two extractions with ether, were neutralised (to litmus) with 10 per cent. hydrochloric acid (C) and evaporated to 5 or 8 ml. *Neutral.*—The original ethereal solution, together with the two ethereal extracts of the alkaline solution, were mixed with 5 ml. of water containing a drop of (C), and the ether was evaporated on a water-bath kept below 80° C. *Basic.*—The acid solution which was previously extracted with ether was made just alkaline to litmus with (A), and extracted five times with ether, and the combined extracts were treated in the same way as the previous ethereal extract. The phenol in all four fractions was determined as follows:—The concentrated solution was filtered into a graduated 50-ml. cylinder and made up to 20 ml. with the washings of the flask and filter. To this, and to 20 ml. of standard phenol solution, were added 1 ml. of a 25 per cent. solution of sodium acetate in a 0·5 per cent. (aqueous) solution of gum acacia, 2 ml. of Moir's reagent (D) and, after 1 minute, 4 ml. of 20 per cent. sodium carbonate solution (E). (The reagent (D) was prepared daily from a solution of 1·5 g. of *p*-nitroaniline in 40 ml. of (C), diluted to 500 ml. Seventy-five ml. of this were treated with 0·75 ml. of 10 per cent. sodium nitrite solution.) After 3 minutes the solutions were compared colorimetrically. The neutral fraction, which was very weak, was compared in test-tubes with a series of standards containing from 0·000 to 0·015 mg. of phenol in 20 ml. For the other fractions, 20 ml. of the standard solution contained 0·015 mg., and a colorimeter was used. E. B. D.

Carbamido Diacetyl Reaction. A Test for Citrulline. W. R. Fearon. (*Biochem. J.*, 1939, **33**, 902–907.)—A method of detecting citrulline (α-amino-δ-carbamidovaleric acid) in proteins is of some importance biochemically in relation to nitrogen metabolism, since citrulline is an intermediate between ornithine and arginine. A number of aldehydes that yield coloured condensation products with ureas were rejected as reagents for citrulline on account of their giving even more

intensely coloured products with tryptophane. Diacetyl in strongly acid solution, however, yielded, with substituted ureas, products which were converted into orange or red pigments on careful oxidation, and tryptophane and substituted guanidines did not give colours with this reagent. The guanidines gave colours with diacetyl in alkaline solution only. Diacetyl monoxime was found to be superior to diacetyl itself in the test, and the oxidation was most conveniently carried out with potassium persulphate. About 2 ml. of the protein solution are treated with at least 4 ml. of conc. hydrochloric acid and 3 to 5 drops of 3 per cent. aqueous diacetone monoxime solution. The mixture is boiled for 30 seconds, allowed to cool, and then carefully oxidised by adding 1 to 3 drops of 1 per cent. potassium persulphate solution or of 0·01 per cent. hydrogen peroxide solution. A carmine red colour develops if citrulline or a similar carbamido-compound is present. The colour deepens on standing or on warming gently. A slight excess of the oxidising agent rapidly bleaches the pigment in hot solution. The reaction will detect as little as 0·01 per cent. of citrulline. The time of boiling must be reduced when large amounts of carbohydrate are present, as, for instance, with dried milk powder, for such substances readily form furfuraldehydes which react with tryptophane giving violet pigments. It is useful to check the absence of this reaction by making a control test without the addition of diacetyl monoxime, though it should be noted that some samples of caseinogen from sour milk may contain diacetyl or acetoin, and so give a positive reaction even when no reagent has been added. Urea itself gives a bright yellow colour, deepening to orange on oxidation, and the reaction will detect 0·1 mg. of urea in 2 ml. of solution. Semicarbazide gives a colour in absence of an external oxidising agent, and the pigment gradually separates out as a dark red precipitate. Compounds that behave like citrulline are: methylurea, butylurea, phenylurea, β-naphthylurea, dimethylurea (symmetrical and unsymmetrical), allantoin, and all higher proteins examined (ovalbumin, seralbumin, seroglobulin, caseinogen, lactalbumin, fibrin, edestin, gluten, mucin). Commercial peptones and gelatins give the reaction with varying degrees of intensity. The test is negative with ammonium salts, hydrazine, carbamate, cyanate, acetamide, acetylurea, diphenylurea (unsymmetrical), guanidine, methylguanidine, creatine, creatinine, glycocyamine, uroxamic acid, uric acid, indole and all amino-acids examined other than citrulline. F. A. R.

Colorimetric Estimation of Tocopherol (Vitamin E). III. Estimation of Tocopherol in Blood-serum. A. Emmerie and C. Engel. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 895–902.)—Tocopherol, like vitamin A, cannot be extracted directly from serum by shaking with ether. Digestion with a solution of alkali cannot be employed to convert the tocopherol into an ether-extractable form, as considerable loss of activity occurs, the loss being greater the higher the temperature, the longer the treatment, and the stronger the alkali solution employed. Although tocopherol is stable to heating with hydrochloric acid, digestion of the serum with pepsin and hydrochloric acid did not effect recovery of added tocopherol. The following procedure was therefore adopted:—To 10 ml. of the serum in a 250-ml. separating funnel were added, with gentle shaking after each addition, 5 ml. of aqueous 0·2 *N* potassium hydroxide solution, 15 ml. of

37 per cent. formaldehyde solution (neutralised to phenolphthalein) and 15 ml. of ethyl alcohol. Fifty ml. of peroxide-free ether were then added, and the mixture was thoroughly shaken and allowed to stand. The aqueous layer was extracted twice more with 50 ml. of ether after the addition of 10 ml. of ethyl alcohol each time. The combined ethereal extracts were washed first with 25 ml. of 2 per cent. potassium hydroxide solution, then with 25 ml. of 1 per cent. sulphuric acid, and finally several times with water. The extract was dried over anhydrous sodium sulphate, mixed with 10 ml. of benzene, and evaporated under reduced pressure in an atmosphere of carbon dioxide. A further 10 ml. of benzene were added to the residue in the flask, and the mixture was again evaporated. The residue (a very small drop) was taken up in 5 ml. of pure benzene and filtered through a column (30 × 12 mm.) of purified "Floridin XS" earth (*cf.* ANALYST, 1939, **64**, 446). The column was washed with 25 ml. of benzene and the filtrate evaporated under reduced pressure. Acetyl-tocopherol is also extracted by this procedure. The residue in the flask was then dissolved in 5 ml. of the reagent mixture (1 ml. of dipyridyl solution, 1 ml. of ferric chloride solution and 5 ml. of benzene are made up to 25 ml. with ethyl alcohol), and the colour of the mixture was measured after 10 minutes in a Pulfrich photometer (*cf.* ANALYST, 1939, **64**, 216). The recovery of tocopherol, added in amounts of from 25 to 272γ to 10 ml. of serum, was 98 to 100 per cent. Applied to the serum of different groups of vitamin E-deficient rats (checked biologically), the method showed that administration of tocopherol or of acetyl-tocopherol gave rise to an increased tocopherol-content of the serum. It should be noted that acetyl-tocopherol does not react with the reagent prior to hydrolysis, which was effected by heating at 72° to 74° C. with methyl alcoholic potassium hydroxide solution for 10 minutes, diluting with water and extracting with three 50 ml.-portions of ether. In estimating the acetyl-tocopherol content of an unknown sample, a compromise has to be sought between the quantity of alkali necessary for saponification and the concentration necessary to reduce destruction of the tocopherol to a minimum. F. A. R.

Colorimetric Determination of Nicotinic Acid with 1-Chloro-3.4-dinitrobenzene. M. Covello. (*Boll. Soc. Ital. Biol. Speriment.*, 1938, **13**; *Chim. e Ind.*, 1939, **21**, 493.)—A method for the determination of small quantities of nicotinic acid in biological materials depends on the reaction between 1-chloro-3.4-dinitrobenzene with substances containing a pyridine nucleus, to give products which with sodium hydroxide form derivatives with an intense red colour. The material containing nicotinic acid is fused with 1-chloro-3.4-dinitrobenzene for half-an-hour at 160° C. The intensity of the resulting colour can be measured in a colorimeter with a photo-electric cell. The author has used the method for determining nicotinic acid in urine. E. M. P.

Bacteriological

Microbiological Examination of Frozen Egg Products. R. Schneiter. (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 625–628.)—The presence of large numbers of viable organisms in frozen egg products indicates the use of poor quality stock, unsatisfactory manufacturing processes or insanitary plant conditions. A high

incidence of coliform organisms and haemolytic types may, in addition, be a danger to health. For the sampling of the canned material it is recommended that three cores be removed from the container by means of a sterile electric drill. The thawed material (5 g.) is transferred under aseptic conditions to a glass-stoppered bottle containing 45 g. of sterile physiological saline solution and a tablespoonful of glass shot to promote thorough distribution by shaking. From this tenfold dilution serial dilutions may be made from one-hundredth to one-hundred-millionth concentration. Duplicate inoculations are made on nutrient agar or dextrose agar plates with 1-ml. portions of dilutions from one-thousandth to one-millionth concentration, one set being incubated for 3 days at 20° to 30° C. and the other for 3 days at 37° C. The plates incubated at the lower temperature give the higher counts. To determine the incidence of coliform organisms, fermentation tubes of lactose broth are inoculated with 1-ml. portions of dilutions of a tenth to a hundred-millionth concentration and incubated at 37° C. for 24 to 48 hours. From all lactose broth cultures yielding gas, streak cultures are made on Levine's eosin and methylene blue agar plates and incubated at 37° C. for 24 to 48 hours. Nutrient agar cultures are prepared by inoculation from colonies of the coliform type and are incubated for 24 hours at 37° C., and these purified cultures are subjected to Kovac's test (indol production), the methyl red and the Voges–Proskauer tests, and Koser's test (utilisation of sodium citrate as the sole source of carbon). Haemolytic types are isolated by inoculating Petri plates with 1-ml. portions from dilutions of one-hundredth to one-millionth concentration. Veal infusion agar containing 6 per cent. of defibrinated horse, sheep or rabbit blood is poured over the plates. The agar is cooled to 40° C., and the blood (0·6 ml. per 10 ml. of medium) is added immediately before pouring. The plates are incubated for 24 hours at 37° C. For counts of anaerobic organisms, tubes of chopped meat medium are inoculated with 1-ml. portions of dilutions from a tenth to a hundred-thousandth concentration and incubated at 37° C. for 3 days. Direct microscopical counts may be made on dried smear preparations of 0·01 ml. of the tenth or hundredth dilutions spread over an area of 1 sq.cm. Veal infusion agar is made by infusing 500 g. of lean veal with a litre of water in the refrigerator overnight, straining, removing fat, and adding 1 per cent. of peptone (Difco), 0·5 per cent. of sodium chloride and 1·5 per cent. of agar. The reaction of the medium is adjusted to *p*H 7·6. To prepare Holman's cooked meat medium, 500 g. of ground fresh lean beef is infused overnight in the refrigerator with a litre of water, 5 g. of bacto-peptone are added to the heated strained infusion, and then, after filtration of the mixture, 5 g. of sodium chloride are added. Normal sodium hydroxide solution is added until the medium is alkaline to phenolphthalein, and the liquid is re-heated and filtered. The pressed-out beef remaining from the infusion is distributed into tubes, approximately 2 g. being placed in each with 10 ml. of the cleared alkaline broth. The final reaction after sterilisation should be *p*H 7·2 to 7·4. Before use the tubed medium is boiled for at least 10 minutes and cooled quickly to expel adsorbed oxygen. Dextrose agar is made by adding 1 per cent. of dextrose to standard nutrient agar. The other media and tests mentioned are those described in *Standard Methods of Water Analysis*, American Public Health Association, 8th Ed., 1936. A. O. J.

Lobsters and Gastro-Enteritis. Some Experiments on Cooking and Sterilisation. H. M. Royds Jones. (*Lancet*, **1939**, **14** (ii), 738–9.)—Two outbreaks were previously described by the author, the first involving 152 and the second 49 patients. Investigation of the last one revealed the fact that the lobsters were of large size and were placed in boiling water and cooked for 40 minutes, after which the claws were cut off, the body was split longitudinally, the gut removed by the cook's fingers, and the body was cut up into portions for service. It is suggested that the contents of the gut were not completely sterilised by the process of cooking, and that the cook's fingers became soiled by the contents of the gut and conveyed the specific micro-organisms to the fleshy parts. To test this point, six lobsters from the same batch were cooked in the same way, and the contents of the gut were examined bacteriologically. *B. coli* and *B. proteus* were isolated, proving that complete sterilisation was not effected. A similar test was carried out by Professor Eyre, and *B. coli*, *B. proteus* and *B. aerogenes* were again recovered. Experiments were then made to ascertain the length of time required for boiling in order to secure sterilisation of the contents of the gut of lobsters weighing 2 lb. It was found that when the lobsters were plunged into boiling water 45 minutes' boiling from the time the water again reached boiling-point was usually sufficient, and that the flavour of the lobsters was not thereby impaired. A further experiment was made to ascertain the temperature to which the interior of lobsters is raised by boiling for different lengths of time. The lobsters were taken out, one at a time, the head was broken off, two thermometers were plunged down the neck into the interior of the flesh, and the temperature recorded, the lower reading being taken. The results are given in tabular form as follows:

Number and weight of lobsters	Duration of boiling, minutes	Temp. °C.
5 (1 lb. 4 oz. each)	10	82·0
	15	84·5
	20	86·6
	25	85·5
	30	89·0
5 (2 lb. each)	25	79·0
	35	91·0
	40	87·5
	47	90·0
	60	91·0

Number and weight of lobsters	Duration of boiling, minutes	Temp. °C.
11 (2 lb. each)	5	60·0
	10	76·5
	15	76·5
	20	82·0
	25	87·5
	30	82·0
	35	90·5
	40	85·0
	45	90·5
	55	95·5
	75	95·5

It is recommended that the usual time of boiling, *viz.* 25 to 30 minutes, should be extended to 45 minutes for 2-lb. lobsters, and that if there is any doubt how long they have been cooked, it is safer to eat small 1-lb. lobsters or to re-cook larger ones. D. R. W.

Varieties of Yeasts and Bacteria in Fruits. A. Romwalter and A. V. Király. (*Archiv. f. Mikrobiologie*, **1939**, **10**, 87; *J. Inst. Brewing*, **1939**, **45**, 355.)—The isolation of living bacteria from the inner structures of fruit, seeds and plant tissues and from sap is recorded. This raises the question whether methods in common use for the sterilisation of fruit and vegetables are efficient. In the

experiments described whole gooseberries were washed with a 0·2 per cent. solution of chlorine and stored for one month. The fleshy portions were found to contain many germinating yeast cells, and carbon dioxide was slowly evolved; an alcoholic odour was also noticeable. In living fruit such fermentation does not occur during ripening and sugar formation. Similar results were obtained with fruit washed in a fairly strong solution of chlorine and subsequently in a 2·5 per cent. solution. Several varieties of yeasts were identified. D. R. W.

Bactericidal Efficiency of certain Aniline Dyes. F. W. Tilley. *J. Agric. Res.*, 1939, **58**, 941–946.)—In connection with investigations concerning the hog cholera virus, hog cholera vaccine, stained antigen for the detection of pullorum disease of fowls, and Bang's disease in cattle, the author has carried out a number of tests on the efficiency of aniline dyes as bactericidal agents. The test organisms used were *B. coli*, *B. pullorum*, *B. suipestifer*, *B. typhosum* and *Staphylococcus aureus*, all being Gram-negative except the last. The dyes used were auramine O; the following derivatives of triphenyl methane: basic fuchsin, malachite green, Hofmann's violet, methyl violet, crystal violet, and victoria blue; other dyes, including ethyl green and ethyl violet, thiazine and diazo dyes. The organisms were exposed to the action of these dyes, with and without the addition of phenol, *o*-cresol, sodium carbonate, borax and disodium phosphate, for periods ranging from 5 to 60 minutes. The results of these tests are recorded and may be summarised as follows:—The thiazine and azo dyes were shown to be very ineffective, as was also ethyl violet. Ethyl green (ethylated crystal violet) was tenfold less effective than crystal violet. Basic fuchsin showed comparatively low bactericidal activity. The addition of phenol or ortho-cresol to crystal violet or methyl violet greatly increased their bactericidal activity with Gram-negative bacteria but showed little or no increase with Gram-positive bacteria. The addition of phenol or ortho-cresol to brilliant green or malachite green had little, if any, effect. The addition of sodium carbonate to aqueous solutions of crystal violet increased their bactericidal efficiency to a pronounced extent. The addition of sodium borate or disodium phosphate to such solutions produced little or no effect, but in contaminated hog blood mixtures crystal violet in dilutions of 1000 to 2000 with 0·02 molar disodium phosphate was uniformly effective, with 0·02 molar borax usually effective, and with 0·02 molar sodium carbonate uniformly ineffective.

D. R. W.

Effect of Radiant Energy on Thermophilic Organisms in Sugar. H. H. Hall and J. C. Keane. (*Ind. Eng. Chem.*, 1939, **31**, 1168–1170.)—Results obtained in the Bureau of Agricultural Chemistry, U.S.A. Dept. of Agriculture, show that the spores of a thermophilic organism which spoils canned food, *B. stearothermophilus* Donk, are killed in dry white sugar by radiant energy rays, most of which are in the region 253·7$m\mu$, and that enhanced lethal action is obtained when the sugar crystals are kept in constant motion in the sugar granulator. For this purpose, twenty-four 30-inch lamps were installed in the sugar outlet end of a granulator. Under these conditions an average of 47·8 per cent. of the spores were killed by irradiating eight successive batches of sugar. No immediate or delayed physical or chemical changes were noted in the irradiated

sugar, and no residual lethal power was retained by the sugar. There was no increase in the spore counts of irradiated samples during storage. The results indicate the possibility of sterilising white sugar and other ingredients of food by irradiation.

Organic

Modified Beilstein Test for Halogens in Organic Compounds. D. F. Hayman. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 470.)—The Beilstein test for halogens in organic compounds often gives results indicating the presence of small amounts, even when halogen is absent, for example, with certain types of pyrimidines, pyridines and oxyquinolines. The following modification, which has been used for five years by the author, has never given a positive test in absence of halogen except with material containing copper. A section of Monel metal tubing, 0·9 cm. in external diameter, is heated to bright redness with a fishtail Bunsen burner, and the compound under examination is brought into the flame on a platinum loop or spoon within 1 cm. of the under side of the tube. In presence of halogen a flare of colour between green and blue is produced. The rate of decomposition, and therefore the type of the colour tint, varies with the compound analysed. With experience, the halogen may be estimated to within 20 per cent. of its actual amount; the method is valuable as a rough quick control of the course of a reaction. E. B. D.

Benzyl-isothio-urea as a Reagent for the Identification of Organic Acids. S. Veibel and K. Ottung. (*Bull. Soc. Chim.*, 1939, **6**, 1434–1435.)—The use of benzyl-isothio-urea hydrochloride, previously suggested as a reagent for the identification of organic acids (Veibel and Lillelund, *Bull. Soc. Chim.*, 1938, **5**, 1153) has been extended to the 15 acids shown in the table, in which some properties of the salts are summarised.

Acid	m.p.	Weight g.	0·098 *N* HCl ml.	Molecular weight calc.	Molecular weight found	Acid or neutral salt
Malic (*d*, *l*)	159–160	0·0840	7·34	466·4	463·6	neutral
Mucic	194–195	0·2404	17·89	542·4	544·4	—
Monochloroacetic	159–160	0·1581	12·24	260·6	261·4	—
Dichloroacetic	178–179	0·2565	17·57	295·1	295·8	—
Trichloroacetic	148–149	0·1709	10·53	329·5	328·2	—
α-Bromopropionic	158–159	0·2367	15·04	319·1	318·4	—
Azelaic	163–164	0·1260	9·82	520·4	519·6	—
o-Toluic	145–146	0·2151	14·38	302·2	302·6	—
p-Hydroxybenzoic	143–145	0·1923	12·84	304·2	303·2	—
α-Hydroxynaphthoic	158–159	0·2878	16·40	354·2	355·0	—
β-Hydroxynaphthoic	216–217	0·2950	16·90	354·2	353·4	—
Phthalic	157–158	0·2007	16·29	498·4	499·2	—
Isophthalic	215–216	0·1207	7·32	332·4	334·2	acid
Terephthalic	202–206	0·1244	10·10	498·4	499·2	neutral
Pyromucic	211–212	0·2112	15·40	278·2	277·6	—

It has not been found possible to prepare the salts of the following: glycine, taurine, phenylalanine, tartaric acid, citric acid, and ethylene-tetracarboxylic acid; the salt of isophthalic acid can be isolated only with difficulty. The authors regard their method as better than the similar one proposed by Donleavy (*J. Amer. Chem. Soc.*, 1936, **58**, 1005). E. M. P.

New Method for the Identification of Ethers. P. P. T. Sah. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 758–760.)—Aliphatic ethers can be identified by subjecting them to pyrolysis and identifying the resulting carbonyl compound by some suitable reagent, such as *o*-tolylsemicarbazide (Lei, Sah and Shih, *J. Chinese Chem. Soc.*, 1935, **3**, 246–250), *p*-tolylsemicarbazide (Sah and Lei, *J. Chinese Chem. Soc.*, 1934, **2**, 167–172), *m*-nitrobenzhydrazide (Meng and Sah, *Science Reports, National Tsing Hua University*, 1934, A II, 345; Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 759), or *p*-chlorobenzhydrazide (Shih and Sah, *Science Reports, National Tsing Hua University*, 1934, A II, 353). The procedure is as follows:—One to 2 ml. of the ether is dropped from a dropping funnel into a small distillation flask heated in an oil-bath to a temperature about 20° C. above the b.p. of the ether. The vapour evolved is conducted through a quartz or copper tube heated to 500° C., and the products are passed through a water condenser and collected in a wash-bottle containing 0·2 g. of the reagent dissolved in 10 ml. of 95 per cent. ethyl alcohol, the flask being immersed in a freezing-mixture. The last traces of vapour are collected by the application of mild suction. The contents of the bottle are boiled gently for 10 minutes under reflux in an Erlenmeyer flask. After filtration, the hot filtrate is diluted with an equal volume of water, and the crystalline precipitate, which separates on cooling, is filtered off with the aid of suction and re-crystallised from 50 per cent. or 95 per cent. ethyl alcohol. The melting-points and crystalline forms of the derivatives are determined. With mixed ethers, such as alkyl-benzyl ethers, the pyrolysis products, which contain two hydrocarbons and two carbonyl compounds, are collected in a clean bottle, and the lower-boiling fraction is separated from the benzaldehyde by fractional distillation and identified. The author gives the melting-points of semicarbazones and benzoylhydrazones obtained from the pyrolysis products of 12 ethers.

E. M. P.

Saccharolactone as a Reagent for Precipitating certain Amines. A. C. Kurtz and D. W. Wilson. (*J. Biol. Chem.*, 1939, **129**, 693–699.)—Saccharolactone in conc. alcoholic solution reacts with certain amines at room temperature to give sparingly-soluble *N*, *N'*-substituted saccharamides, which after recrystallisation have sharp, characteristic melting-points that enable them to be readily identified. The following is a list of the amines that gave such well-defined saccharamides, together with their m.p.:—methylamine 188° C., ethylamine 174° C., *n*-propylamine 179° to 181° C., isopropylamine 176° to 178° C., *n*-butylamine 178° C., isobutylamine 159° C., *n*-amylamine 173° to 174° C., isoamylamine 138° C., *n*-heptylamine 174° to 176° C., ethanolamine 129° to 130° C., benzylamine 200° to 201° C., *β*-phenylethylamine 185° to 186° C., tyramine 204° C., and piperidine 191° C. The last-named is the only secondary amine that gave a precipitate. In the series of primary amines tested, the symmetry of the molecule was found to be of great importance in determining precipitability. Thus *n*-butylamine was precipitated immediately, isobutylamine only after 30 minutes, and secondary butylamine not at all; *n*-amylamine and isoamylamine rapidly formed precipitates, whereas 2-methyl-*n*-butylamine did not give a precipitate after several days. The reagent can thus frequently be employed for the separation of amines which otherwise can be separated only with great difficulty. F. A. R.

Antioxidants for Castor Oil. G. O. Inman. (*Ind. Eng. Chem.*, 1939, **31**, 1103–1104.)—It is not uncommon for the acid value of castor oil that has been used as a lubricant to increase in two years by oxidation from 2 to over 35, and for the oil to become green through its action on a brass lubricator. The results of the experiments made to find an inhibitor that would prevent the oxidation of castor oil have confirmed the conclusion of Mattill (*J. Biol. Chem.*, 1931, **90**, 141), that if a phenolic compound contains two hydroxyl groups in the ortho or para position it will have a high antioxygenic action, whilst the corresponding meta isomer will be inactive. Thus hydroquinone and catechol are strong antioxidants, whilst their *m*-isomer, resorcinol, is a weak pro-oxidant. Pyrogallol is a strong anti-oxidant. All three cresols are mild pro-oxidants, but the *m*-isomer is stronger than the other two. *o*-Nitrophenol is a slightly stronger pro-oxidant than *p*-nitrophenol. Benzyl alcohol is a weaker pro-oxidant than the three cresols.

Inorganic

Determination of Cadmium in Silicate Rocks. E. B. Sandell. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 364–365.)—The method involves differential extraction of metals with carbon tetrachloride in presence of dithizone, and ultimate determination of cadmium colorimetrically with dithizone. It is applicable to traces of cadmium in presence of small amounts of the heavy metals. A 0·5-g. sample of the powdered rock is dissolved, as far as possible, in a platinum dish, in a mixture of 1 ml. of 70 per cent. perchloric acid, 5 ml. of hydrofluoric acid and a little water. The liquid is evaporated to dryness; the residue is successively treated with 0·5 ml. of perchloric acid and then with a little water, with intervening evaporation to dryness, and is finally dissolved, as far as possible, in 6 ml. of 1 : 5 hydrochloric acid. Ten ml. of sodium citrate solution (10 per cent.) and 0·1 g. of hydroxylamine hydrochloride are added, and the solution is rendered slightly ammoniacal. [Main solution.] Any precipitate is filtered off and fused with sodium carbonate, and the extract of the melt is acidified with hydrochloric acid and rendered ammoniacal after addition of a few ml. of the sodium citrate solution and a little hydroxylamine hydrochloride. [Subsidiary solution.] The main solution is extracted by shaking for one minute with successive quantities of 5 ml., or less, of a 0·02 per cent. solution of dithizone in carbon tetrachloride until the carbon tetrachloride layer shows a greenish colour. The subsidiary solution is similarly extracted. The combined dithizone—carbon tetrachloride extracts are washed by shaking with 5 ml. of water, and the solvent layer is then shaken with two successive 5-ml. portions of 0·01 *N* hydrochloric acid. Zinc, lead and cadmium dithizonates are thus decomposed, the metals entering the aqueous phase as chlorides; copper and cobalt remain in the carbon tetrachloride. The aqueous phase is transferred to a stoppered glass colour-comparison tube, and 2·5 ml. of 25 per cent. sodium hydroxide solution are added, followed by 1 ml. of a 0·001 per cent. solution of dithizone in carbon tetrachloride (this weak dithizone should be shaken, before use, with 10 ml. of redistilled water and 2 ml. of 25 per cent. sodium hydroxide solution, in order to free it from colour.) The non-aqueous layer is thoroughly shaken, and, immediately after, its colour is compared with that

of standards prepared in a similar manner from, for example, 0, 0·05, 0·1, 0·15γ of cadmium in 0·01 *N* hydrochloric acid. In test experiments 0·1 per cent. of zinc in the sample gave distinctly less colour than that produced by 0·05γ of cadmium. Nickel interferes if present in more than traces, but tin, bismuth, silver, thallium and manganese in small amounts are without effect. S. G. C.

Colorimetric Determination of Nickel as Nickel-Ammonia Complex Ion. G. H. Ayres and F. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 365–367.)—The transmission of the blue nickel-ammonia complex was measured by means of the Yoe photo-electric colorimeter. This enabled amounts of nickel giving a feeble blue colour, difficult to match by visual inspection, to be estimated. The ammonia concentration should be 1·5 *N*; larger amounts of ammonia produce violet coloured solutions offering less sensitiveness in determination. Identical transmissions were obtained in ammoniacal solutions prepared from nickel sulphate, nitrate and chloride; ammonium salts had only a slight effect. As little as 5 mg. of nickel per litre can be detected; the highest accuracy is obtainable with 500 to 1500 mg. per litre. The method is, in general, subject to interference by the same ions as affect other colorimetric methods for nickel. Preliminary separation of nickel by precipitation with dimethylglyoxime is advised; the precipitate is decomposed by heating with nitric acid, yielding a solution of nickel nitrate. S. G. C.

Colorimetric Method for the Determination of Rhenium. J. J. Hoffmann and G. E. F. Lundell. (*U.S. Bureau of Standards; Chem. Trade J.*, 1939, Aug. 25, 168.)—A method for the separation and colorimetric determination of rhenium and molybdenum has been based on differential reduction with mercury. When a dilute hydrochloric acid solution of the two metals is shaken with mercury, potassium thiocyanate and ethyl ether, only the molybdenum is reduced to a form that produces an ether-soluble coloured compound with thiocyanate. The colour of the ethereal extract is proportional to the quantity of molybdenum. On adding stannous chloride to the acid solution remaining after the extraction of molybdenum a yellow to yellowish-red ether-soluble compound is produced, and this can be used for the colorimetric determination of rhenium. As little as 0·001 mg. of rhenium can be detected in presence of 10 mg. of molybdenum. Very few elements interfere, and practically all can be eliminated by a simple distillation.

New Indicator for the Argentometric Determination of Chlorides. E. Percs. (*Ber. Ungar. Pharm. Gesellsch.*, 1939, 449; *Pharm. Weekblad*, 1939, **76**, 1238.)—The indicator consists of a saturated solution of trithionine monopicrate in a mixture of methyl alcohol and acetone; this solution is red-violet in colour, but turns blue when the silver salt is produced. For the titration, a solution containing the equivalent of 0·03 g. of chloride is acidified with nitric acid, and 5 ml. of carbon tetrachloride and 8 to 10 drops of the indicator solution are added. The mixture is then titrated with a 0·1 *N* solution of silver nitrate until the colour of the water layer changes from red-violet to ultramarine. J. G.

Determination of Sulphides by means of Potassium Ferricyanide. G. Charlot. (*Bull. Soc. Chim.*, 1939, **6**, 1447–1451.)—The method depends on the oxidation of soluble sulphides by potassium ferricyanide, with precipitation of sulphur, in a medium buffered to *p*H about 9·4.

(1) *Potentiometric determination.*—The titration is carried out in a tube closed with a 4-bored stopper, the holes carrying a platinum electrode, a calomel electrode, and tubes for the passage of hydrogen through the solution. Into the tube there are introduced 20 ml. of a buffer solution (70 ml. of conc. ammonia and 50 g. of ammonium chloride per litre) and hydrogen is bubbled through for 5 minutes. Ten ml. of the sulphide solution are then added and there is introduced gradually an approximately *N*/10 potassium ferricyanide solution (standardised iodimetrically in presence of a zinc salt by Kolthoff's method, *Z. anal. Chem.*, 1921, **60**, 454), the potential being determined after each addition of the ferricyanide. A curve of the potential in centivolts is plotted against the number of ml. of ferricyanide solution added, and a sharp inflexion point gives the end-point of the titration. The sulphide-content can be calculated from the equation

$$S'' + 2Fe(CN)_6''' \longrightarrow S + 2Fe(CN)_6''''.$$

(2) *Determination by means of ferrous dimethylglyoxime.*—Twenty ml. of the buffer solution are just coloured by adding a few drops of the indicator solution (1 ml. of *N*/50 ferrous sulphate solution, 4 to 5 ml. of saturated alcoholic dimethylglyoxime solution [about 1 per cent.], and 0·5 ml. of conc. ammonia). Air-free hydrogen is passed through for 5 minutes, and the solution to be titrated is then added. The ferricyanide solution is run in, the end-point being the permanent disappearance of the pink colour. To obtain the correct result 0·06 ml. must be subtracted from the volume of ferricyanide solution added, but if the titration is carried out in air, aerial oxidation is sufficient to cancel out this correction. If the sulphide solution is strongly alkaline, sufficient ammonium chloride to react with the free alkali is added.

Determination in presence of sulphite.—Twenty-five ml. of the buffer solution and enough *M*/2 barium chloride solution to precipitate the sulphite are introduced into a flask (50 ml. of barium chloride solution will precipitate completely 10 ml. of saturated sodium sulphite solution). Hydrogen is passed through the liquid for 5 minutes, a few drops of the indicator are added, the mixture is left for 10 minutes for the precipitate to settle, and the liquid is titrated. The determination may be made without any particular precautions in presence of thiosulphates. E. M. P.

Ferrous-Molybdate Reagent for Detection of Small Amounts of Phosphorus, Silicon and Arsenic. J. H. van der Meulen. (*Rec. Trav. Chim. Pays-Bas*, 1939, **58**, 841–846.)—*Reagent.*—Twenty ml. of *M* sodium molybdate solution (242 g. of $Na_2MoO_4.2H_2O$ per litre) are diluted to 900 ml., 40 ml. of acidic *N*/10 ferrous sulphate solution (27·8 g. of $FeSO_4.7H_2O$ per litre of *N* sulphuric acid) are added gradually with shaking, and the whole is diluted to 1 litre. *Use.*—On adding 1 ml. of water containing a small amount of phosphoric acid to 5 ml. of the reagent a greenish colour is produced; the further addition of 0·25 to 0·5 ml.

of alkali fluoride solution produces a deep blue colour; sensitiveness: 0·005 mg. of phosphoric acid. A similar reaction is obtained with arsenic acid, arsenious acid (the formation of the blue colour being rather slower with arsenious acid) and silicic acid, but not with pyrophosphoric acid. The development of a blue colour with silicic acid can be prevented by the addition of fluoride and a little mineral acid to the test solution *before* it is mixed with the reagent.

Silicomolybdic acid reagent for pyrophosphoric acid.—A one-tenth gram-molecular amount of sodium molybdate and a 1/120th gram-molecular amount of sodium silicate are dissolved in 500 ml. of water, 21·7 ml. of 10 *N* sulphuric acid are added, and the mixture is heated on a water-bath until a test sample fails to produce a blue colour with ferrous sulphate solution, after which it is diluted to 1 litre. For use, 0·25 ml. of this reagent is diluted with 10 ml. of water and 0·25 ml. of acidic ferrous sulphate solution (*N*/10, in *N*/10 sulphuric acid) is added. Small amounts of pyrophosphoric acid produce an immediate blue colour, whilst phosphoric, arsenic, arsenious and silicic acids give no colour. S. G. C.

Microchemical

List of Micro-methods for the Determination of Calcium and Phosphate. R. S. Manly. (*Mikrochem.*, 1939, **27**, 145–153.)—A reference list of 27 methods for the determination of calcium and 47 methods for the determination of phosphorus, for less than 1 mg. of the constituent determined, is arranged in order of decreasing quantity of the constituent required. The table is given under the following headings: amount of calcium (or phosphorus) required, constitution of precipitate, principle, special apparatus, special reagents, accuracy or deviation from theory (per cent.), precision or deviation from mean (per cent.), application, comment. J. W. M.

Collected References. Some Micro-methods for the Examination of Beer. G. Ghimicescu (*Mikrochem.*, 1939, **27**, 197–210.)—Methods are summarised for the determination of the following in samples of beer:—carbon dioxide, nitrogen, ammonia, nitrate, ash, alkalinity of ash, dried extract, total acidity, volatile acids, non-volatile acids, lactic acid, glycerol, maltose, dextrose, chloride, sulphate (total, organic and inorganic), phosphate (total, organic and inorganic), boric acid, and total and free sulphurous acid. Twenty-four references are given. J. W. M.

Determination of Anthraquinone-1,8-disulphonic Acid in Presence of other Anthraquinone Sulphonic Acids and Sulphuric Acid. W. Seaman. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 465–469.)—When a mixture of sulphuric acid, anthraquinone-1,8-disulphonic acid (I) and anthraquinone-1, 5-disulphonic acid (II) is treated under standardised conditions with barium chloride solution, the barium salt of (I), which is precipitated, can be readily distinguished from those of the other acids by microscopic examination between Nicol prisms under suitable illumination. It appears as glistening specks or prisms according to the size of the crystals. As the small and large crystals appear to be formed in some constant proportions, a linear relationship may be determined between the count of crystals

and the percentage of (I), within certain percentage limits; hence (I) may be determined quantitatively. The method was worked out in detail for mixtures containing 20 per cent. of sulphuric acid, 0 to 20 per cent. of (I) and 80 to 60 per cent. of (II).

The influence of anthraquinone-2,6-disulphonic acid (III), anthraquinone-2,7-disulphonic acid (IV) and anthraquinone-2-monosulphonic acid (V) on the determination was investigated. The barium salt of (III) forms anisotropic needles, which are counted with (I), but results are not additive; (IV) and (V) may cause low values for (I). It might be possible to determine anthraquinone-1-sulphonic acid in presence of anthraquinone-2-sulphonic acid by a similar method. For the analysis, a percentage/count curve is drawn based on the barium salts of such acids as would be present in the sample analysed, and the percentage corresponding with the count of the sample is calculated from the curve. The original paper gives full details of the preparation of pure reagents and solutions for the plotting of this curve, the precipitation of the salts, and the counting of crystals.

E. B. D.

Micro-determination of Veronal in Blood and Spinal Fluid. R. Fischer. (*Mikrochem.*, 1939, **26**, 255–263.)—At least 2 ml. of blood are mixed with an equal volume of water and treated with an acid buffer solution (1 per cent. sodium phosphate with 0·4 ml. of *m*-phosphoric acid and 0·05 g. of potassium cyanide; *p*H=3·3–3·5) to prevent the separation of proteins, and the veronal is extracted with purified ether. The extract is dried with sodium sulphate, purified with magnesium oxide and charcoal and filtered. The precipitate is washed, and the filtrate is concentrated, evaporated to dryness and sublimed between 90°–150° C. on to a weighed coverslip. The purity of the product is ascertained by microscopic examination before re-weighing the coverslip. The sublimation apparatus used is the author's electrically heated apparatus with an automatic regulator, which combines a melting-point and sublimation block (*Mikrochem.*, 1934, **15**, 247; Abst., ANALYST, 1935, **60**, 123). The limits of error range between 2·5 and 6·7 per cent. for blood and between 2·5 and 4·8 per cent. for spinal fluid, on amounts of veronal ranging from 70 to 300γ. A method is described for the separation of veronal from succinic acid by adsorption on alumina followed by washing with ether containing 20 to 30 per cent. of alcohol.

J. W. M.

Iodimetric Micro-determination of Potassium in Serum. S. Dénes. (*Mikrochem.*, 1939, **26**, 277–281.)—The method gives results that agree with those obtained by Kramer's method to within about 2 per cent. without removal of albumin. A sample of about 0·5 ml. of serum is treated with 1 ml. of Kramer–Tisdall's sodium cobaltinitrite reagent; after 1 hour, 1 ml. of water is added, and the precipitate is centrifuged and washed. It is then taken up in 3 ml. of 0·01 *N* permanganate solution and 0·5 ml. of 20 per cent. sulphuric acid, and the solution is heated for 2 minutes on a water-bath. After cooling, 1 ml. of 10 per cent. potassium iodide solution is added, and the liberated iodine is titrated with 0·01 *N* thiosulphate solution.

J. W. M.

New Test for Thallium. H. Jurány. (*Mikrochem.*, 1939, **27**, 8–13.)—Thallium is precipitated by potassium mercury iodide, $K_2(HgI_4)$, as an orange-yellow crystalline precipitate; under the microscope the crystals appear as yellow rectangles or rods, often grouped together to form crosses or star-shaped clusters. The crystals belong to the tetragonal system with straight extinction, and are optically positive. *Limit of identification*, 0·1γ of thallium; *concentration limit*, 5γ of thallium per ml. Silver, lead, stannous tin and tervalent arsenic interfere with the reaction, but the elements of the ammonium sulphide group, alkaline earths and alkalis do not. During the course of the work three new crystalline compounds formed by $K_2(HgI_4)$ with lead ions, with caesium chloride, and with a mixture of the chlorides of caesium and rubidium were discovered; a brief description is given of these. J. W. M.

Physical Methods, Apparatus, etc.

Quantitative Spectrographic Analysis of Solder, Spelter, and Magnesium and Aluminium Alloys. J. A. C. McClelland and H. K. Whalley. (*Spectrochimica Acta*, 1939, **1**, 21.)—The spectra of the samples are excited by the spark method, a circuit with a condenser of 0·005μF, and an inductance of 0·125 or 0·25*m*H being used. A special jig is described for accurate setting up of the electrodes. The spectrograms are examined with a photometric apparatus incorporating a photo-electric cell. The determinations are made by the use of modifications of Gerlach's internal standard method. The authors describe two methods, *viz.* the variant and the constant exposure method. Details are given of the general procedure to be adopted in carrying out either of these two methods, but no analytical tables are given for any of the specific impurities that are being determined. A study is made of the accuracy and reproducibility of the methods, and it is concluded that extensive use in routine work indicates that an accuracy within ± 5 per cent. of the amount of the constituent determined may justifiably be claimed. The following details of technique are found to be of importance. (*a*) In every instance the standards are chosen from alloys of composition similar in all respects to the samples to be analysed. (*b*) A preliminary period of sparking is given to free the surface of the electrodes from incidental impurities, and to bring the surfaces into a steady sparking condition. By this means the initial variation of the relative line intensities in the spectrum caused by preferential volatility and oxidation of certain constituents is minimised. (*c*) Variation of electrode size is found to be much less important in those instances in which the minor constituents have no marked preferential volatility. A tabular summary is given of the alloys examined; this includes a list of the impurities determined, circuit details, exposure times and the lines used as internal standards (*cf. J. Soc. Chem. Ind.*, 1937, **56**, 177T, 438T.) B. S. C.

Longitudinal Scattering of Light (Plotnikow Effect) and its Importance in Biology. M. E. Jörg. (*Fundamenta Radiologica*, 1939, **4**, 9–17.)—The nature of the Plotnikow effect is outlined (*cf.* Mitchell, ANALYST, 1935, **60**, 454).

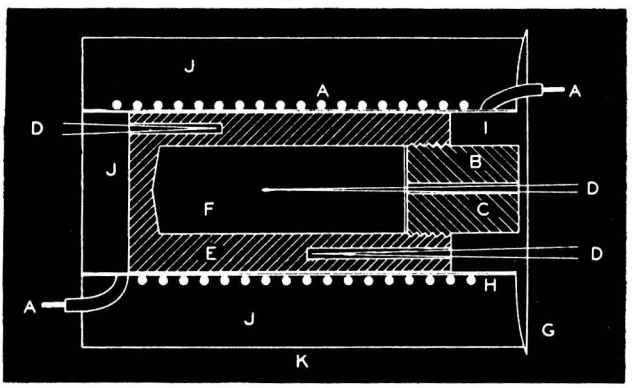
The magnitude of the effect depends on, and may be used to indicate the nature of, the molecular state of the substance producing it, and details are given of two applications of this nature, in which the scattering of ultra-violet, violet, blue, green and infra-red radiations (wave-lengths, 318, 375 to 400, 450, 519 to 590 and 740 to 1000$m\mu$, respectively) were measured. The necessary radiations were isolated by means of filters in the usual way, the source for all except the ultra-violet rays being a cinematograph arc-lamp (100 volts, 40 amps.), provided with impregnated carbons and a water-cooled housing. A diaphragm and an aplanatic microscope condenser (aperture, 1·4) were used to obtain an intense parallel beam of light, and this was directed on to a 10- or 20-cm. layer of the solution to be tested, which was contained in a glass cell with plane parallel walls. The usual type of Plotnikow screening-tube was used for obtaining the scattered light (*cf.* Mitchell, *loc. cit.*) and a Wratten filter (No. 87) served to isolate the infra-red radiations used for this purpose. The aurora produced by the scattering was photographed on a Kodak panchromatic plate, which was developed with pyrogallol (6 minutes at 17° C.), and fixed and washed in the usual way. The apparatus was tested with hexane (which has no scattering capacity), and under these conditions no aurora was produced after an exposure of 90 minutes, although some slight trouble was experienced from the Foucault-lens effect of the walls of the containing-vessel. The diameters of the aurora were measured by means of a photo-electric scanning device, the electrical impulses from which were translated (through the medium of the oscillations of a galvanometer-mirror and a revolving drum carrying a light-sensitive paper) into a continuous record. Curves relating the diameters of the aurora and the wave-lengths of the exciting radiations could then be drawn. Water taken from the surface of the Sargasso sea was tested (1) after filtration through filter-paper, (2) after four subsequent ultra-filtrations through a Bechhold collodion-cellulose acetate filter, (3) after boiling followed by a fifth ultra-filtration, and (4) after distillation. After the first ultra-filtration 0·4 per cent. of organic matter was present, but none was detectable after the fifth ultra-filtration. The results indicated a considerable scattering capacity after simple filtration throughout the whole spectral range, but especially with ultra-violet rays. After the first ultra-filtration the scattering was less, especially for the ultra-violet rays, and the three following ultra-filtrations resulted in further rapid decreases, except for the infra-red range; the diameters of the aurora falling in this instance only from 15·32 to 15·20 mm. After boiling and the fifth ultra-filtration the scattering of the infra-red rays was reduced to 15·18 mm., and, except for a slight scattering of green rays (8·2 mm.), no Plotnikow effect was apparent with the other regions of the spectrum tested. After distillation there remained only a slight scattering (9·5 mm.) of the infra-red rays. Photographs of the corresponding aurora are reproduced in the paper. When dust-free water was distilled three times in a vacuum, a similar result was obtained (*i.e.* a scattering of diameter 8·18 mm. in the infra-red region only, which is known as the "limiting dispersion"). The results indicate that the characteristic colour, viscosity and physical properties of the Sargasso sea-water are due to organic substances of high molecular weights, which cannot be removed completely by successive ultra-filtrations. Similar experiments were made with a synthetic resin, prepared from

urea, glycerin and an aliphatic aldehyde, in the fluid, viscous and solid states. In none of these was there scattering of the ultra-violet, violet or blue rays; scattering of the green rays was very weak, 9·23 mm., and very weak for the three states, respectively, whilst the scattering of infra-red rays corresponded with auroras of diameters 9·2, 12·3 and 9·2 mm., respectively. These results confirm the view that in the first stage, when the resin is fluid and optically-clear, long-chain molecules have only started to form by polymerisation, and that this process is completed in the second stage; the third (*i.e.* hardening) stage corresponds with the formation of cyclic compounds from these molecular chains (*cf.* following abstract). J. G.

New Optical Method for the Measurement of the Rate of Coagulation of Blood. P. Gjurić and J. Plotnikow. (*Fundamenta Radiologica*, 1939, **4**, 92–95.)—The longitudinal scattering of light (the Plotnikow effect, *cf.* preceding abstract) of blood plasma increases with the lapse of time to a limiting value, at a rate which can be measured by photo-electric methods (*loc. cit.*). The curve relating the Plotnikow effect and the time may therefore be used to follow the course of the coagulation of blood. In an explanatory note Plotnikow points out how the method may be used to follow other processes involving polymerisation reactions; to establish whether these reactions are mono- or bimolecular in type; also to measure their reaction-velocities and the effects on them of temperature, catalysts, etc. The difference in this respect between long-chain macro-molecules and suspended particles, and the difficulties of interpreting results obtained with mixtures of these, are also pointed out (*cf.* preceding abstract); the macro-molecules may give a clear solution (as with blood plasma and certain synthetic resins), and yet produce a marked Plotnikow effect, especially towards infra-red radiation. Similarly, the effect is characteristic of highly-viscous substances, whether organic or inorganic, but it is not as yet possible to deduce an exact and generalised correlation between the magnitude of the effect and the structure of the substance producing it; this applies particularly to short-chain molecules. With molecules in which the chain structure is particularly long the scattered light may itself undergo a "bending" effect (known as "scattering reflection"), and when such light strikes a substance having a different degree of opacity or scattering capacity as compared with its surroundings, it is possible to produce an image of the substance in question on a photographic plate (*cf.* L. Freund, *id.*, 1938, **2**, 100). An example of an application of this modification of the method is given by M. Jörg (*Photog. Korresp.*, 1938, **74**, Sept.); it refers to a hunt for a man with star-shaped tattoo mark. This mark had been rendered invisible to the eye and to the usual methods of detection (*e.g.* photography with a panchromatic plate) by the browning effect produced by exposure to ultra-violet light. The actual tattoo mark, however, was still in existence under the skin, and the method outlined above enabled it to be detected. Other applications are indicated. J. G.

Exothermal Decomposition Temperature of Wood. K. A. Kobe and F. L. Goin. (*Ind. Eng. Chem.*, 1939, **31**, 1171–1172.)—An apparatus has been devised to determine the effect on the exothermal decomposition temperature of

wood caused by impregnating it with inflammable organic solvents such as gasoline kerosene, light and heavy motor oils and creosote. In a recent legal case the point was made that wood so impregnated had a much lower exothermal decomposition point than untreated wood. In the procedure described the lowest temperature at which the temperature of the wood will rise above the retort temperature, when heated in absence of air, is termed the "exothermic point." The retort, E, used, consisted of steel shafting (2 in. × 5 in.) in which a hole, F (1 in. × 4½ in.), was drilled. The outer end of the hole was threaded to take a plug in which was drilled an opening for a thermo-couple. The lower and upper portions of this hole were filled with steel, a rectangular opening (1 in. × ⅜ in.) being left, into which the test specimen of spruce wood was fitted tightly. The retort was fitted



closely into a metal sleeve, H, which was covered with mica and wound with resistance wire to form a heating element, A. This was placed inside a can, K, and insulated with magnesia, J, except at the outer end, where the can cover, G, left a dead air space, I. More resistance wire at this end of the heating element gave a uniform temperature along the retort. The temperature of the wall was measured in two places by means of thermo-couples, D, and the temperature of the wood was measured with another thermo-couple placed in the centre of the test specimen. The heating rate was controlled by variable resistances in series with the heating element. The retort was heated rapidly to about 250° C., and maintained at that temperature until the wood temperature was within 20° C. of the wall temperature. The rheostats were then adjusted until a rise of 2° C. in the temperature of the retort wall was recorded. Readings were taken every minute on each of the three thermo-couples. In the first few minutes of the test the temperature of the wood rose above that of the retort wall, increased at the same rate as the wall temperature, and then began to fall to the temperature of the wall. The temperatures of wall and wood were plotted against time, and the point of intersection of the two curves was taken as the exothermal decomposition temperature. The following results were thus obtained with spruce; the impregnated specimens showed uniform staining with the liquid when cut in half.

Treatment of sample	Weight before treatment g.	Weight after treatment g.	Gain Per Cent.	Weight after charring g.	Loss Per Cent.	Temperature of decomposition ° C.
As received ..	4·538	—	—	3·348	26	273
Oven-dried ..	4·945	4·545	−8·1	3·535	29	276
Dioxane	4·456	5·325	19	2·350	47	275
Gasoline	4·215	4·587	8·1	1·955	54	363
Kerosene	5·044	6·262	24	3·875	23	266
Light motor oil ..	4·198	5·935	41	2·900	31	267
Heavy motor oil ..	4·542	7·065	56	3·779	20	272
Creosote	4·430	6·765	52	2·965	33	284

Moisture had no appreciable effect on the result, for the oven-dried sample decomposed within 3° C. of the sample containing 10 per cent. of moisture. Removal of moisture with dioxane and impregnation of the wood with that substance, itself containing 36 per cent. of oxygen, had no effect on the exothermal point. Volatile liquids, such as gasoline and kerosene, lowered the exothermal point, which, however, increased with the b.p. of the liquid. Creosote increased the exothermal point.

Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Fourth Edition. By Sir J. F. THORPE, C.B.E., D.Sc., F.R.S., and M. A. WHITELEY, O.B.E., D.Sc., F.I.C. Vol. III. Pp. 608. London: Longmans, Green & Co. Price 63s.

This volume starts with chemical calculations and chemical warfare, includes long major articles on cyanides, chlorine, crystallisation, corrosion, deuterium and diazo compounds, and ends with one on diffusion. It provides a truly remarkable amount of information on these and a wide range of other topics, some of which have not appeared in earlier editions. The editors have most delightfully disarmed all reviewers and critics by their very apt Foreword taken from Dr. Samuel Johnson's preface to his famous Dictionary in 1755. The great doctor counted himself among the unhappy mortals who write dictionaries, but by his work he joined the immortals; if Sir Jocelyn Thorpe and Dr. Whiteley have not yet attained to that felicity they have at least assured for their names a lasting place in the annals of industrial chemistry by producing a dictionary which to chemists is as essential as ever Johnson's was to savants of his time.

Chemical calculations are well known in some circles, but little valued, even shunned, in others; hence it is useful to have a selection of time-saving methods of much practical value simply explained. Chemical warfare and its defence, over the familiar initials J.D.P., is of such obvious interest that no commendation is needed. The articles on chlorine and on cyanides have been largely rewritten by F. Holt and G. E. Wainwright, respectively; both are concerned with fundamental products of greatly increased importance in our industry, and these have been the subject of many patents and new processes, all the most important of which are skilfully summarised.

Colorimeters and comparators form the subject of a well-written monograph by

J. Guild; it is of much interest to the analyst in view of the increasing applications of colorimetric methods in various branches of our work. Then, as a chemical antidote to any who may think they have had an overdose of physics, one may turn to an account of colour and chemical constitution—a subject that has gone out of fashion of late—and a brief but comprehensive survey of co-ordination compounds by G.T.M. and F.H.B.

Cryoscopy is perhaps among the articles to which many analysts will turn. In addition to the familiar Beckmann apparatus, it describes the more elegant micro and semi-micro methods of Rast, which deserve to be more widely used; some of us would have liked to see mention of Hortvet's method, as that, too, can be applied to many things besides milk.

Mention may be made of the up-to-date monograph on Deuterium if only because its study is now being so actively pursued and because it affords so useful an indicator to the course of organic reactions and of biological metabolism. But it is hopeless to attempt to comment on even the major articles, for there are about 250 which may be so described. The reviewer has pored over the new volume, tested it on such subjects as he was able to, and consulted it on the day-to-day problems of the practising chemist. He finds it full of valuable information, for few of the articles can be read without learning something hitherto unknown or unrealised. It is singularly free from misprints and enhances the traditions of its predecessors. Thorpe's Dictionary is a necessity on our book-shelves, and we are indebted to its authors, contributors and publishers for keeping it so thoroughly up-to-date and authoritative. H. E. Cox

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Editor-in-Chief, JOHN R. JOHNSON. Pp. 105. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1939. Price 8s. 6d. net.

The nineteenth volume of this well-known series has now been issued. It is, in arrangement and appearance, identical with its predecessors. Details of thirty preparations are given together with some additions and corrections for preceding volumes. An index for Volumes X–XIX inclusive is also provided.

Many of the preparations involve either cyclic or heterocyclic compounds, and some of the reactions afford good examples of ring closure or rupture. Among the more noteworthy preparations may be mentioned that of the useful reagent phenacyl bromide, the hydroaromatic-aromatic compound phenyl cyclohexane, and *para*-dinitrobenzene, the preparation of which gives an interesting use of hydroborofluoric acid in the replacement of the amino group by the nitro group. Some interesting iodo compounds are also dealt with.

In conclusion, it may be stated without reserve, that Volume XIX of Organic Syntheses is a worthy member of this series. HAROLD TOMS

SOIL ANALYSIS. By C. HAROLD WRIGHT, M.A., F.I.C. Pp. x + 276. Second Edition. London: Thomas Murby & Co. Price 12s. 6d. net.

Five years ago the first edition of "Soil Analysis" was published, and the comparatively early appearance of the second edition denotes that analysts have

found the former work to be valuable. The work has only been extended by forty pages, but these additional pages do not represent all the new matter incorporated, because some methods have been omitted and the space occupied by processes now considered to have a greater value or to have wider application.

Mr. Wright has had the assistance of a considerable number of acknowledged experts in the production of this work, and, therefore, its revision before publication has been placed before highly qualified analysts, many of whom devote a considerable portion of their time to soil study.

The first revision noted is that of the chapter dealing with the mechanical analysis of soils, and the author has here had the assistance of Dr. G. W. Robinson. The methods of dispersion agreed to internationally at Versailles in 1934, and at Leningrad in 1930, are given in detail, and these are now of considerable importance. The section on hydrogen ion concentration has largely been reproduced, but the quinhydrone electrode has been more clearly and carefully explained, and articles on glass and antimony electrodes have been added. Methods for the determination of various metals occurring in soils are given and, as alteration of details in a number of instances has been made, enquiry has undoubtedly taken place since the appearance of the first edition. From the description of processes involving the use of cobaltinitrite for the determination of potassium both gravimetrically and volumetrically, it would appear that the author favours one or the other of these as a method to be employed. However, throughout the book, although he has had considerable experience in the examination of soils, he invariably refrains from suggesting which of the processes given should be used for a determination, but he does usually indicate the advantage that one method may have over another.

The original section of the book which dealt with the very important processes for the determination of nitrogen in its various forms of combination, was, in my opinion, too short for it to give an analyst even an insight into the varied methods applicable. This part of the book has now been extended and the subject given the attention that it deserves.

We are apt to forget that for a process to be of use to the practical man the results obtained by it must have a practical interpretation. The results given by some old processes may not attain to high scientific accuracy, but they were capable of translation, so that the best agricultural procedure was indicated. In this connection it was with a little concern that it was noted that one old, but largely used and valued, process for the estimation of lime requirement of soils was not even mentioned in the present book. Possibly the author is correct in limiting his outlook generally to processes complying with modern scientific outlook, but, even though there may be much to recommend these processes, it may need some years of experiment before the laboratory results can be correlated with farm results.

The first edition I welcomed, as it brought together so much scattered information, and I hold the same view now. The serviceability and utility of the second edition is unquestioned.

F. W. F. ARNAUD

THE CHEMICAL FORMULARY. Vol. IV. Editor-in-Chief, H. BENNETT. Pp. 632. London: Chapman & Hall, Ltd. 1939. Price 25s. net.

The previous volumes of this publication were issued between 1934 and 1936, and the contents of these, together with those of the present one, have been submitted to a board of editors, the members of which are engaged in educational or industrial work. Thus the text, which comprises several thousands of formulae for preparations applicable to a wide range of uses, together with the methods used in compounding them, may be relied upon as practical and trustworthy.

A lengthy introduction provides much sound information on the general principles involved in the methods used in compounding preparations of all kinds, together with a series of varied recipes for easily prepared mixtures. The next and principal portion of the volume is devoted to a miscellaneous collection of formulae arranged under some twenty headings covering a very extensive field. Most of the preparations given are of recent origin, since many of the components have been available only during the last few years whilst other formulae are derived from European, Canadian and American patents. In the preface the editor states that, in addition to the usual purposes of these volumes, they may serve to make chemistry useful and interesting to students by teaching them to prepare adhesives, insecticides, etc., but surely the sections devoted to pyrotechnics and explosives would prove far more attractive to the majority of pupils.

It would appear that the American definition of the term "Cosmetic" is very different from that adopted in this country, since under this heading we find such diverse matters as moth balls, lavatory deodorants and tobacco pipe cleaners. As many of the substances included in the various formulae are given their trade names, an extensive list of firms supplying these, both in the United States and elsewhere, is given at the end of the volume, and this is followed by a comprehensive and accurate index in which, however, more cross-indexing would have been advantageous. There are a few typographical errors, but these are of minor importance. The volume is a valuable and up-to-date compilation which will prove of service in many domestic and industrial activities and will, in addition, indicate to the chemist substances for which search should be made when analysing a preparation outside the range of his usual practice. T. J. WARD