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An Investigation of Solanine Poisoning

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It is not always realised that the familiar potato plant (*Solanum tuberosum*) contains, in all its tissues, including the edible tuber, varying amounts of a poisonous gluco-alkaloid, solanine. It is well known that, under certain conditions, this alkaloid may accumulate in the tubers themselves, particularly when sprouting, in amounts which are definitely poisonous; hence most poisoning cases have been successfully traced to this cause. No case, however, appears to be on record, such as the one here recorded, in which an outbreak of solanine poisoning was traced to the young green shoots of the potato which had been consumed as a vegetable. This is the distinctive feature of certain cases in Cyprus and, so far as I am aware, there is no account of the use of young potato shoots as human food in other parts of the world.*

A review of the literature reveals the fact that authentic cases of solanine poisoning are not so rare as authorities appear to believe (*cf. Taylor's Medical Jurisprudence*).[2] In Great Britain, the most serious case of recent years occurred in Glasgow in 1917, and involved 61 persons. This case was investigated by Harris and Cockburn,[3] who concluded that the poisoning was the result of eating potatoes which, on analysis, proved to contain five or six times the amount of solanine of normal potatoes. Prior to this, Taylor[2] cites a very doubtful case in which two boys succumbed in 1902, but apparently no analysis of the potatoes in question was made. On the Continent, cases of mass poisoning are not infrequent. Autenrieth[4] mentions an outbreak of solanine poisoning which affected 673 soldiers in Strasbourg, and Pfuhl[5] describes in detail the poisoning by potatoes of 56 soldiers of the Berlin garrison in 1899. More recently, in the autumn of 1922, a serious epidemic broke out in Germany which was traced to the abnormal content of solanine in the potato crop of that year.[6,7] This was attributed to the excessive rainfall, but the evidence available is not conclusive.

* The leaves of the garden nightshade (*Solanum nigrum*) are said to be eaten, boiled, in the Isles of France and Bourbon, and in Hawaii Islands.[1]

Numerous determinations, principally by German investigators, have been made on the solanine-content of normal and abnormal potatoes, in the cooked and uncooked state, and on the sprouts and peelings. The range of variation in the findings is considerable, which may, perhaps, be accounted for by the use of different methods. These data have been summarised for comparison in Table I, and it has been found convenient to state the solanine-content as mgrms. per 100 grms. of material.

TABLE I

SOLANINE-CONTENT OF POTATOES

Material	Case	Amount found Mgrms. per 100 grms.	Observer	Reference
Peeled potatoes, Jan.–Feb.	—	2·4	Schmiedeberg and Meyer	*Arch. Exp. Path. Pharm.* 1895, **36**, 361
Do.	—	4·4	Do.	1895, **36**, 373
Unpeeled potato peelings	—	71·0	Do.	Autenrieth, *Detection of Poisons*, 1928, p. 448
Potato sprouts, 1 cm. long	—	500·0	Do.	
Peeled and uncooked potatoes	Berlin	38·0	Pfuhl	*Deut. Med. Woch.*, 1899, p. 753
Peeled and cooked potatoes	Do.	24·0	Do.	Do.
Peeled and uncooked (May)	Do.	6·0	Do.	Do.
Do (June)	Do.	6·4	Do.	Do.
Normal potatoes	—	1·7–10·6	Wintgen	*Z. Nahr. Genussm.*, 1906, **12**, 113
Table potatoes (aver. 18 var.)	—	12·5	von Morgenstern	*Landw. Vers. Stat.*, 1907, **65**, 300
Forage potatoes	—	95·8	Do.	Do.
Potatoes, raw	Glasgow, 1917	41·0	Harris and Cockburn	ANALYST, 1918, **43**, 133
Do. (from stock)		7·9		
Potatoes, 1922 crop	Germany, 1922	79·0	Griebel	*Z. Nahr. Genussm.*, 1924, **47**, 436
Potatoes, 1923 crop		5·0	Do.	Do. ANALYST, 1924, **49**, 486
Suspected potatoes	Germany, 1922	25·3–58·8	Bömer and Mattis	*Z. Nahr. Genussm.*, 1923, **45**, 288
Normal potatoes	—	2–10	Do.	*Ibid.*, 1924, **47**, 97

The present outbreak of solanine poisoning occurred in the Morphou district of Cyprus in May, 1932, and was traced to the use of young potato shoots and leaves, which had been consumed as a green vegetable. This remarkable practice is, of course, by no means general in the island, but appears to be confined to two areas—the Morphou and Lapithos districts—with some sporadic use in the Paphos

district. The custom is to collect the shoots about the time of flowering and to boil them for half an hour before consumption. Although some villagers declared that they habitually used such shoots as a vegetable whenever available, it appeared on investigation that the majority had had recourse to them only because of the present time of depression, aggravated by a season of severe drought, with resulting shortage of crops and greenstuff. In the case of habitual users of the potato shoots it is possible that some partial immunity may have been acquired from the toxic effects of the alkaloid. On the other hand, the abnormal climatic conditions prevailing last year may have resulted in an increase in the solanine-content of the plant. But, in view of the fact, to be considered later, that the solanine-content of the tubers was within normal limits, this does not appear to be probable. As soon as the true nature of this outbreak of poisoning had been ascertained, all concerned were officially warned against the danger of using potato plants as food; since then the practice has been discontinued, and no further illness has occurred.

Potato Plants as Food for Animals.—As already stated, in Cyprus the use of potato plants as human food is sporadic, and confined to certain areas. But, in spite of the general prejudice against the use of potato plants as food for animals, it is the general practice in the island to feed sheep, goats, and sometimes oxen, on potato plants which have commenced to wither. This system of animal husbandry is apparently successful only when the animals are allowed access to potato plants which are actually withering; but animals which have had access to the young growing shoots have paid the usual penalties of sickness and death. In the former case it may be that the animals have acquired some degree of tolerance to the alkaloid, or that the solanine-content of the leaves decreases as the plant withers, or, possibly, to both these factors. This system recalls the practice of the peasants in Hesse, quoted by Bryan-Brown,[8] where cows in winter are fed on yew leaves in gradually increasing amounts, and evidently acquire tolerance in some degree to the poisonous alkaloid, taxine, which they contain.

The potato is a crop of increasing value and importance in Cyprus. Normally, two crops are raised each year, namely, the winter crop from January to May, and the summer crop, which requires irrigation, from August to November. The variety principally grown is the Irish imported potato, which flourishes on the light red soils of the Messaoria plain. The Cyprus native potato, which is of small size, but of better flavour to some tastes, and commands a higher price, is now a diminishing crop, grown only in the mountain valleys. With the supply of water, many weeds are always to be found growing in the potato fields, and it has been observed that grazing animals appear to relish the withering potato plants better when eaten with the weeds. The leaves of the vine and the cotton plant, after the harvest has been taken, and sometimes mulberry leaves, are grazed by sheep, goats, and oxen, and are usually preferred to potato plants. The reason for the use of the potato and other non-forage plants as food for animals is, of course, the fact that no other greenstuff is available at that season of the year.

Feeding Experiments.—In order to study the effects of feeding animals with potato plants a feeding test was made on a group of 12 young adult albino rats (Wistar inbred stock acclimatised to Cyprus), and a control group of the same

number, comparable with it in type, weight and sex. Both groups received a basal diet of bread and milk, and, in the case of the experimental group, young potato shoots *ad lib.* of the same variety as had been concerned in the poisoning cases investigated, in place of the lettuce or other salad plant given to the controls. Unfortunately, since the rats definitely declined to eat the plants after the first days, the experiment could not be continued. On the first day an average of 1·5 grm. per head was consumed, on the second day 0·5 grm., still less on the third day, and nothing at all on the succeeding days. Even when kept fasting for 24 hours the rats refused the shoots, whether young plants or old, and one of the group died and was partly devoured by the remainder. The basal diet was then restored, and, since the rats still declined the shoots completely, after the eighth day the experiment was abandoned. During the same period the controls made normal gains in weight.

It is perhaps significant that such an omnivorous feeder as the rat will not accept potato shoots.

CASE HISTORY.—Previous to the eight cases medically treated, and discussed in some detail below, about 50 cases of more or less severe sickness of the general nature of gastro-enteritis had occurred during May in different villages of the Morphou district. Potato shoots had been consumed in all cases. All of them recovered, mostly without medical treatment.

A Greek family of eight persons, consisting of six adults (ages from 16 to 52) and two children (ages 4 and 9), on the evening of May 28, 1932, partook of a meal made up of broad beans and young potato shoots with native bread and olive oil. Four of the adults also had a little black wine. The broad beans and potato shoots had been boiled in water for about half an hour, after which the water was drained off and a little vinegar and lemon juice were added. The meal was freely partaken of by all the family.

Apparently there was no sickness during the night, the first symptoms being observed about 8 a.m., *i.e.* 12 hours after ingestion of the meal. The observed symptoms, which were more or less exhibited by all eight persons, were those of a gastro-enteritis, and included headache, severe colic-like pains in the stomach and abdomen, hot skin, fever, rapid pulse, vomiting in some cases, in others nausea only, diarrhoea (with blood and mucus), great weakness and depression. The increased temperature, which was amongst the earliest symptoms, ranged from 38° C. to 40° C. (100·4° F. to 104° F.), and the pulse rate varied between 100 and 110.

There was some irritation of the throat, and breathing appeared difficult. The majority were drowsy and apathetic, and one person (a girl) had convulsions. In individual cases the face was somewhat cyanosed, and the conjunctivae were yellow, but these were symptoms observed later. Enlargement of the pupils was not reported. The patients were kept in bed, and by the morning of the fourth day all, with one exception, who had died in the meantime, showed definite improvement. Vomiting had ceased, the fever and diarrhoea had abated, and eventually there was complete recovery.

The fatal case occurred with the oldest sufferer, aged 52, a man of strong physique. After the onset of the symptoms already described he passed into a

semi-conscious condition. The eyes became abnormal and the face cyanosed. He suffered considerably, and was given injections of emetine and morphia. The medical officers in attendance suspected an infection, probably dysentery. However, bacteriological examination of the fresh faeces did not disclose dysentery bacilli in this and other cases. The sickness was not complicated by malaria or enteric, since the blood tests for these diseases were negative. In spite of some apparent recovery on the second day, the man died 44 hours after ingestion of the fatal meal. According to the *post-mortem* report nothing very characteristic was seen at the autopsy. The stomach was inflamed, and the intestinal tract more so, while the blood was more fluid than normal. The other organs were apparently normal, and death was described as due to syncope.

As poisoning was not suspected at the time of autopsy, no viscera were sent to the laboratory for analysis. However, from the failure of Meyer[9] to detect any appreciable quantity in the excreta of a dog fed with 0·1 grm. of solanine for 10 days, and the failure of Harris and Cockburn[3] to find solanine in the bowel-contents in their fatal case in man, it would seem that the prospects of isolating small quantities of the alkaloid from viscera are at present not encouraging. The problem is obviously one for further investigation. Samples of the foodstuffs consumed at the last meal were analysed for inorganic poisons, but with completely negative results. The potato shoots (Irish) in question were then examined qualitatively for solanine by digesting the finely-minced material with very dilute acetic acid, followed by filtration and extraction of the filtrate with pure hot amyl alcohol. On standing, the amyl alcohol extract set to a jelly.[10] From this characteristic behaviour it was concluded that the alkaloid, solanine, was present in the potato shoots, possibly in considerable amount. A quantitative determination of the solanine present was then made.

METHODS.—The methods available for the estimation of solanine have been critically studied by Bömer and Mattis.[11] These authors found the methods of Schmiedeberg,[12] Meyer[9] and Morgenstern[13] to be unsatisfactory, and accordingly devised an improved technique which, with a few modifications, was followed in this work. With careful control concordant results are obtained. About 250 grms. of potato shoots or tubers, free from disease, were taken for analysis. The material was first finely minced by twice grinding it in a mincing machine, and an equal weight of distilled water was added. After standing half an hour at room temperature the liquor was pressed out through fine muslin, and the residue was re-extracted four times with equal quantities of distilled water containing acetic acid in the proportion of 2 c.c. per litre. After each extraction the mixture was allowed to stand for half an hour at room temperature before expression of the liquid. The extracts were combined, and the chlorophyll was allowed to deposit by standing overnight. The solution was then filtered by decantation, and the clear, light brown filtrate was rendered slightly alkaline with ammonia and kept alkaline throughout the subsequent evaporation to dryness on the water-bath. Pure silver sand, in the proportion of 5 grms. per hundred grms. of solanine-containing material, was added in place of kieselguhr, which was not available. The dry residue was carefully scraped off, ground up in the mortar, and extracted in a Soxhlet apparatus for six hours with pure 95 per cent.

alcohol. The material was then taken out, re-ground, and again extracted for a further period of six hours.

The alcohol was removed by evaporation of the extract on the water-bath, and the dark-brown residue was taken up in 100 to 150 c.c. of distilled water, made slightly acid with acetic acid, and filtered. The residue was tested for solanine by re-extraction and addition of alkali, and, if none was found, it was discarded. The filtrate was made slightly alkaline with ammonia and warmed for a short time until the crude solanine separated out as a mass of gelatinous flocks. The deposit was filtered off, washed with a little 2 per cent. ammonia and purified by solution in dilute acetic acid, re-precipitation with ammonia, washing, and, finally, drying in the oven at 100° C. Usually the second precipitate was almost colourless, but, in the case of solanine from potato shoots, a second purification was necessary. Bömer and Mattis allow a correction factor of 2·75 mgrms. per 100 c.c. of solution, including washings, in order to allow for the solubility of the alkaloid in dilute ammonia. This factor has been applied to the results obtained in this investigation, which are summarised in Table II.

TABLE II

SOLANINE-CONTENT OF *S. tuberosum*

Expt.	Variety	Plant tissue	Place of growth	Altitude Feet	Solanine-content per 100 grms. Mgrms.
1	Irish imported	Shoots	Plain	500	48·9
2	Do.	Potatoes	Do.	Do.	9·1
3	Do.	Shoots	Mountain Valley	3,500	38·6; 37·1
4	Do.	Potatoes	Do.	Do.	2·7
5	Do.	Shoots	Mountain Side	4,400	29·4; 28·6
6	Do.	Potatoes	Do.	Do.	8·1
7	Cyprus Native	Shoots	Troodos Foothills	3,000	27·0
8	Cyprus Native	Potatoes	Do.	Do.	5·6

REACTIONS.—The solanine isolated was identified by its physical properties and its behaviour in certain colour-tests. The lack of uniformity, described by different authors in certain of the colour-tests, is probably explained by the presence of impurities in the product tested. It is noteworthy, however, that the colour reactions of solanine from different sources appear to be different as, for example, in the case of solanine-S isolated from *Solanum sodomeum*. The solanine in these experiments had a bitter taste and an irritating effect upon the throat. The colour-tests for solanine are also given by solanidine, the product of the hydrolysis of solanine. The following tests were made:—

1. Dissolved in hot amyl alcohol, or ethyl alcohol, the solution of the alkaloid set to a firm jelly on cooling. This reaction is very characteristic.
2. With selenic-sulphuric acid reagent (0·3 grm. of crystalline sodium selenate, 8 c.c. of water, and 6 c.c. of concentrated sulphuric acid), a characteristic raspberry-red coloration was produced. The appearance of the colour is favoured by gentle heat and the reaction is very sensitive.

3. With Fröhde's reagent (sodium molybdate in sulphuric acid) the colour of the solution was first reddish-yellow, slowly changing to cherry-red, deep violet, and finally, red-brown.
4. The vanadic-sulphuric acid reagent (0·1 grm. of ammonium vanadate in 100 grms. of concentrated sulphuric acid), gave an orange-yellow, changing to a clear red and, lastly, to different shades of violet.
5. With sulphuric acid in alcohol (9 c.c. of absolute alcohol and 6 c.c. of concentrated sulphuric acid) the colour was pink, changing to red (*cf.* Henry[14]). Warming favours the appearance of the reaction.
6. Concentrated nitric acid gave a light brown coloration which changed to red, slowly on standing, and quickly on warming.
7. A solution of antimony trichloride in pure dry chloroform (vitamin reagent) gave, on standing, a deep red colour with solanine.

Discussion.—Some points of interest emerge from consideration of these data. From Table II it is seen that the solanine-content of the tubers of all the plants examined was within the limits for normal potatoes suggested by Bömer and Mattis,[11] that is, 2 to 10 mgrms. per 100 grms. They can therefore be regarded as normal potatoes. As regards the green shoots of the potato plant, the solanine-content of plants growing in the plain, as compared with that of plants growing in the mountains, is striking. The results, in fact, indicate that the solanine-content of the potato shoots diminishes as the altitude increases, at least in the case of the imported Irish potato, which is that principally grown in the island. The Cyprus native potato is now grown only on the foothills and in the mountain valleys, but not on the plain. It was, therefore, not possible to make a corresponding comparison, but a specimen growing on the foothills of the southern Troodos range had only about half the solanine-content of Irish potato shoots growing on the plain. Although many more data are desirable, the results clearly point to the influence of climate, as conditioned by altitude, in that a diminishing amount of the alkaloid appears to be present in the shoots of the same variety of potato plant as one moves from the plain to the mountain.

The amount of solanine found in the Irish potato plants consumed in these cases of poisoning is more than 5 times the quantity found in the tubers of the same plants. This, and the fact that the green plants were partaken of freely, together with the symptoms observed, leaves no doubt that this outbreak was caused by the consumption of young growing potato plants, which have been shown to contain large amounts of solanine. Since a warning was issued against this dangerous practice no further cases have been reported. As regards the minority of habitual consumers of potato shoots, an acquired immunity from the toxic effects of the alkaloid is the most likely explanation. In this connection it is perhaps noteworthy that, in recent investigations on the precursor of vitamin *C*, Laland[16] considers that potatoes, amongst other vegetables and fruits, contain traces of another alkaloid, narcotine (20 kilos. contained 12 mgrms. of narcotine).

Many factors have been regarded as influencing the solanine-content of the potato, and most of the investigations have been made on the tubers themselves.

Thus, unripe potatoes were found to contain more solanine than the same variety when ripe, and smaller ones than large ones (Bömer and Mattis).[11] At one time the question of soil was considered to be of importance, especially in Germany, which produces the largest potato crop in Europe. It was thought that tubers grown in sandy soil were richer in solanine than those, for example, from humus soil. Again, the question of manuring was thought to be of importance (*cf.* Morgenstern).[13] However, later work by Showalter and Hartmann (1924),[7] and by Bömer and Mattis (1924),[11] showed that there is no apparent connection between the type of soil or system of manuring and the solanine-content. According to Morgenstern, moisture would appear to diminish the solanine-content of the resulting potatoes, but, on the other hand, Showalter and Hartmann, and Griebel attribute the excessive content of solanine in the 1922 crop in Germany to the abnormally heavy rainfall of that year. However this may be, there can be little doubt that the action of light, in a way unexplained, increases the solanine-content of the tuber. According to Weil,[16] two of the bacteria present in the black spots of old potatoes have the power of producing solanine.

Solanine first appears to increase during the germination, passing into the sprouts, and increasing with the growth of the plant. The course of events, as suggested by Morgenstern, would then seem to be for the plant to withdraw the alkaloid from the older shoots to the young growing shoots. It is thus suggested that solanine may play the rôle of a natural protector of the plant, especially of the young growing parts. This interpretation would account for the fact, observed in Cyprus, that animals, when turned into potato fields as the plants have commenced to wither, consume the plants, if not with enthusiasm, at least without apparent toxic effect.

In conclusion, I wish to record my thanks to Dr. G. C. Strathairn, Director of Health, Cyprus, for permission to publish the results of this investigation.

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Discussion

The PRESIDENT remarked that it seemed somewhat strange that potatoes in certain states (old potatoes, green potatoes, etc.) were often described as highly toxic to stock. Many hundreds of tons had been used as stock feed, and he had never actually known of any stock poisoning. Of course, it could be argued that the potatoes used for feeding were often cooked, and much of the solanine dissolved out, but, on the other hand, a large number of these potatoes were used uncooked, and, therefore, stock did consume this vegetable with its full content of solanine, and, so far as he knew, without detriment. During the war a circular was issued, stating that potatoes were an injudicious feed for horses, and setting out the maximum amount that should be given. However, potatoes had been given to horses in limited quantities without bad results.

Mr. C. E. SAGE said that cases of solanine poisoning were not infrequent, but he knew of no fatal one, caused by eating the bright red berries of *Solanum dulcamara*, which grew plentifully in this country. *Solanum nigrum*, which had white flowers and black fruits, were sometimes eaten by country children, but he had never met with any casualties. Until recently the fruits of *Solanum carolinense* were used in America for the preparation of a tincture for medicinal use. It grew plentifully as a weed in the Southern States, and the orange-coloured fruits were known as Sodom apples. The alkaloids, *solanine* and *solanidine*, existed in the fruits, and, as the negroes had used it for a long time as a remedy for falling sickness, the alkaloid could not be particularly toxic, although it was undoubtedly potent. *Solanum chenopodium* was a native of Queensland, and some thirty years ago he had isolated the alkaloid solanine from it. In Brazil, *S. aculeatissimum* was the plant yielding Sodom apples. It also contained solanine. With all these sources of solanine, and with potatoes and tomatoes containing it, there seemed to be no great danger from its toxicity. The leaves of *S. nigrum* were boiled and eaten in the Hawaii Islands, and the fruits known as "fox's grapes" could be eaten in small quantities without any harmful effects. With sprouting potatoes it did not seem beyond the bounds of possibility that some product of decomposition might have caused the illness of people recorded in the paper.

Mr. W. PARTRIDGE said that his only experience in the determination of solanine was in connection with a case in which it was alleged that potatoes had been tampered with and had caused illness. He had used the Meyer process, as outlined by Harris and Cockburn (ANALYST, 1918, **43**, 133), but with the improvements (including the correction for solubility in ammonia wash-water) of Bömer and Mattis (ANALYST, 1924, **49**, 284). The potatoes in question, substantial areas of which were green, contained 19 mgrms. of solanine per 100 grms. Taking the attitude that normal potatoes contained about 2 mgrms., and never more than 8 mgrms. per 100 grms., and that 25 mgrms. per 100 grms. were known to be dangerous, he had felt justified in associating the symptoms, minor though they were, with green potatoes.

Mr. E. M. HAWKINS remarked that there seemed to be something in the wisdom of old-fashioned country folk. Thirty years ago when, fresh from the town, he went to live in a rural district, the old country folk instructed him that a potato which was allowed to get green through exposure above the earth was likely to be dangerous to human beings and to animals, and he, therefore, never used them. He thought it significant, in the Glasgow case, that more solanine was contained in potatoes which were green from exposure to sunlight than in the white tubers, and the paper certainly bore out this same contention.

The Estimation of the Fineness of Grinding of Chocolate by Microscopical and Tasting Methods

By H. M. MASON, M.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, December* 3, 1932)

Introduction.—In the preparation of chocolate it is desirable to reduce the size of the particles of sugar and cocoa matter to such a degree that roughness or grittiness is not noticed when the chocolate is being masticated. Further, it is generally agreed that the cocoa flavour is realised more fully when the particles are highly refined. A standard of fineness is, therefore, expected by the consumers of the chocolate, and the aim of the manufacturer should be so to control the milling process that the chocolate is reduced to the required standard of fineness, and not beyond, as this would be wasteful of time and energy.

In order to adjust the milling process to the public requirement, it is necessary to have some definite information as to the degree of fineness which can be detected and appreciated by the consumer. Thus, if it could be proved that particles smaller than 100μ maximum length cannot be detected by tasting, a qualitative microscopical examination of the chocolate is all that is necessary to ensure that this limit of refinement has been reached.

Qualitative microscopical examination of a number of proprietary brands of chocolate showed that the sizes of the particles varied between greater than 200μ and less than 1μ, and those containing the largest particles were decidedly gritty when eaten. Further, since the result of a simple qualitative examination could not be connected with the texture of the chocolate when tasted, it was decided to make a more elaborate estimation of the size and distribution of the particles and to compare the results with the average opinion of a number of trained tasters. For this purpose a quantitative microscopical method of estimating the fineness of the chocolate was worked out, and it was found that the result could be conveniently expressed in the form of a numerical quantity which is termed the "micro value." Samples of chocolate, the micro values of which had been determined, were submitted to trained tasters, and the two sets of results were compared and used for fixing standards intended for controlling the mills.

Descriptions of the microscopical and tasting tests of chocolate are given below, and the technical applications of the microscopical method are discussed.

Microscopical Investigation of Particle-size and Distribution in Chocolate.—The standard textbooks on chocolate manufacture all refer to the use of microscopical methods in connection with the fineness of chocolate, but, in my opinion, none of the methods pays sufficient attention to the effects of both size and frequency of the particles. The average size of the ten largest particles

may be an indication of texture, but the number of large particles in unit mass is a much more definite indication.

To obtain this information, a definite quantity of material must be examined, and, further, this quantity must be large enough to ensure that the largest particles present are seen.

This condition is not usually satisfied by a single preparation having a field density convenient for examination, under a $\frac{7}{8}$-inch cover-slip.

After various methods of obtaining definite quantities of chocolate for microscopical examination had been tried it was decided to adapt the lycopodium method, described by Wallis (ANALYST, 1919, **44**, 321, and later communications), to our requirements. This method depends on the uniform dispersion of the pollen grains in a liquid medium. If a 1 per cent. suspension of lycopodium in water is examined microscopically, the number of pollen grains per field indicates the quantity of the preparation under examination.

If definite weights of lycopodium and chocolate are dispersed together in oil, the number of pollen grains per field indicates the weight of chocolate represented by one field, and observations on the properties of the chocolate may be made quantitatively. One advantage of this method over dilution methods and micro weighings is due to the even distribution of the grains, for when variations in the thickness of the observed film cause variations in the density of the field, the lycopodium is affected equally with the other substance, and the two counts are proportional.

The adaptation of Wallis's method involved preliminary experiments to fix the details of manipulation, as, for example, the quantity of chocolate which need be examined, convenient field densities, and the relative proportions of lycopodium and chocolate, for the accuracy of the results depends very largely on these details. Sugar particles can be examined in a suspension in oil, which dissolves cocoa fat and enables uniform dispersion to be produced by shaking, but cocoa particles are best counted in an aqueous suspension of the defatted chocolate.

ESTIMATION OF FINENESS BY THE MICROSCOPICAL METHOD.—The method can be most easily described if we divide it into three sections, *viz.*, the preparation of the suspensions, the method of counting the particles, and the calculation of the results.

Preparation of Suspensions.—The complete test requires two suspensions, one in mineral oil and one in water for the enumeration of the sugar and cocoa particles, respectively.

The oil suspension is prepared by mixing in a test-tube 0·5 grm. of chocolate, 0·1 grm. of lycopodium, and, approximately, 10 c.c. of colourless mineral oil. The chocolate should be in the form of thin parings from the edge of the sample, and should be free from lumps. The test-tube is closed with a cork, shaken, warmed sufficiently to melt the cocoa butter, and the shaking is continued until the suspension is quite even and contains no visible masses of chocolate. Occasionally it is found that the chocolate is not completely broken up by this treatment, but the difficulty is easily overcome by shaking the mixture with 1 c.c. of petroleum spirit before the addition of the mineral oil. On standing, the particles remain in

suspension for a few minutes, but it is advisable to give the preparation a good shake before preparing the slide.

The suspension in water is prepared by placing 2·5 grms. of chocolate in a test-tube, and, after removal of the fat, 0·1 grm. of lycopodium is added, and the mixture is shaken up with about 8 c.c. of water containing 2 drops of 2 *N* sodium hydroxide solution, which helps to break up aggregates of the cocoa particles. The fat is rapidly removed by treatment successively with trichorethylene and ether, each liquid being separated by centrifuging and decantation.

The ether is driven from the residue by warming and stirring the mass with a glass rod, and the fat-free residue then falls to a fine powder. Microscopical examination of the decanted liquids shows nothing but very minute particles, which can be ignored.

Microscopical Examination.—To facilitate counting, the microscope eyepiece is fitted with a scale ruled in 0·5 mm. squares, and the lenses are selected and the draw-tube so arranged that each eyepiece scale division is equivalent to 0·1 mm. on a stage micrometer. This arrangement is convenient for the counting of large particles, for those measuring 100μ fill one eyepiece scale division. For counting particles measuring 25μ the adjustments are so made that each eyepiece scale division is equivalent to 0·05 mm. on the stage micrometer, or, 25μ equals half a scale division:—The magnifications are approximately 70 and 140 diameters.

The preparation of the suspension for microscopical examination depends on the quantity of material which must be examined in order to ensure that the large particles, if present, are seen, and our preliminary experiments indicated that two preparations are necessary. For the counting of the particles measuring 50μ and upwards, we find it convenient to use 4-inch squares of plate glass which should be smooth, level and free from scratches. Six or seven drops of the suspension are placed in the middle of one plate, and, when a similar plate is used as the cover glass, the preparation spreads to a circle of about three inches diameter.

The smaller particles are counted on an ordinary slide, and a single drop of suspension, just sufficient to fill the $\frac{7}{8}$-inch cover-glass when gently pressed into position, serves for this purpose.

The object of the counting is to find the number of sugar or cocoa particles of some definite size and the number of lycopodium spores in an equal number of fields.

For this purpose, when the plate is being used, ten fields, spaced as suggested by Wallis, are examined for the lycopodium count, and 40 fields, in which the material is distributed evenly over the field, are examined for sugar particles measuring 100μ upwards and 50μ upwards. These observations do not take as long a time as might be expected, as the number of large particles is usually small.

In the examination of the slide, ten fields are examined and the lycopodium spores and sugar particles measuring 25μ and upwards are counted on the same fields.

The plate and the slide are also used when the cocoa particles are examined in the aqueous suspension.

In this way the number of lycopodium spores in ten fields is determined, the number of sugar particles of definite size in the same number of fields is

estimated, and the number of sugar particles equivalent to 100 lycopodium spores can then be calculated. By this means the counts in the plate and the slide are made comparable.

The number of particles may be expressed in any convenient way, and, in order to avoid the use of too many ciphers, our calculations are in units of 100,000 particles.

This arrangement produces figures which are easy to understand.

The results of examination of a very coarse specimen of chocolate are given in Table I.

TABLE I

ENUMERATION OF SUGAR PARTICLES

Suspension: 0·5 grm. of chocolate and 0·1 grm. of lycopodium in 10 c.c. of oil.

		Number of particles in		Ratio n	Units per grm. of chocolate
		40 fields	10 fields		
Plate.	Lycopodium	—	671	—	—
	$<100\mu$	16	4	0·60	1·13 (n_1)
	$<50\mu$	229	57	8·5	15·98 (n_2)
Slide.	Lycopodium	—	145	—	—
	$<25\mu$	—	189	130	244·4 (n_3)

Calculations.—One hundred lycopodium spores weigh $1{\cdot}064 \times 10^{-6}$ grms., and are equivalent to $5{\cdot}32 \times 10^{-6}$ grms. of chocolate.

If n is the number of sugar particles equivalent to 100 lycopodium spores, the number of particles per grm. of chocolate is $188000n$, and, as each unit represents 100,000 particles, the number of "units" per grm. of chocolate is $1{\cdot}88n$.

The microscopical examination thus provides us with three figures representing the approximate size distribution of the largest sugar particles in the chocolate, but these figures are not suitable for comparison with the quality of the chocolate for eating.

For technical purposes it is an advantage if the results of the test are expressed as a simple number.

The generally accepted statement that the palate is not sensible to particles smaller than 25μ, having been confirmed, it was decided to express the results in terms of the number of units of 25μ particles which would be present if the larger particles were reduced to this size. This is termed the micro value. On the assumption that a particle of 100μ diameter produces 64, and a particle of 50μ diameter produces 8 particles of 25μ diameter, the equivalent can be calculated from the following formula:

Let n_1, n_2 and n_3 be the number of units of 100μ, 50μ, and 25μ particles, respectively, per grm. of chocolate.*

$$\text{Micro value} = 64n_1 + 8(n_2 - n_1) + (n_3 - n_2)$$
$$= 56n_1 + 7n_2 + n_3.$$

In the above example the micro value is $63{\cdot}3 + 111{\cdot}9 + 244{\cdot}4 = 419{\cdot}6$.

* To simplify the counting, each "unit" includes all particles larger than the stated size; hence the number of 100μ units must be subtracted from the number of 50μ units before the latter can be calculated to the equivalent number of 25μ units, and the number of 25μ units counted must be corrected in a similar manner.

The distribution of the sugar particles of various sizes in four typical specimens of chocolate is shown in Table II.

TABLE II

NUMBER OF SUGAR PARTICLES PER MGRM. IN TYPICAL CHOCOLATES

Grade:—	Coarse	Medium	Fine	Superfine
100μ	40	Nil	Nil	Nil
100–50μ	720	230	25	Nil
50–25μ	9130	8050	4530	1880
25–10μ	—	66200	66900	45600
10–5μ	—	124500	100900	95600
Visible, less than 5μ	—	448000	360000	147000

These figures are only approximate, owing to the difficulty of counting the smallest particles and the large factor used in the calculation.

For industrial research purposes the distribution of the cocoa particles was determined in the same way, but, as the sizes of these particles were found to have practically no effect on the fineness of the chocolate as estimated by tasting, the cocoa counts are omitted from the factory control tests.

The time required for the complete investigation of the sugar and cocoa particles is roughly two and a half hours, but a routine test of the sugar particles only can be made in twenty minutes.

When very rapid tests are required, as, for example, when the correct setting of machinery is doubted, an experienced worker, by preparing a plate and slide according to the above instructions so as to obtain the correct field density, can tell, without counting the particles, whether the chocolate conforms to the standard. Even in a qualitative test it is essential to examine sufficient fields to ensure that the quantity of chocolate seen is large enough to include the large particles which may be present.

The minute quantities of material used in quantitative microscopical work are apt to upset the sense of proportion of the observer, and it may be of interest to note the quantities concerned in these experiments. When using the plate test, 0·175 mgrm. of chocolate are examined and a single field represents 0·0044 mgrm.; with a $\frac{7}{8}$-inch cover-glass, the corresponding quantities are 0·012 mgrm. and 0·0012 mgrm.

ESTIMATION OF FINENESS BY TASTING.—To test the sensitiveness of the average palate to variations in particle size, five batches of chocolate, which had been refined to different degrees, were submitted to fifteen trained tasters.

Samples were tried in pairs, each specimen being compared twice with each of the other specimens, and the order in which the tasting was done was reversed in the second test. The identification marks of the samples were changed in all the tests. The tasters were asked to say which of the two samples was the finer, and to place the samples in the appropriate class of a range including very coarse, coarse, medium, fine and superfine.

The order in which the samples were submitted was so arranged that the easier comparisons were made first, and the more difficult ones were made after the tasters had become experienced in applying the test.

More than six hundred reports included some in which obvious mistakes had been made in reporting the results, but these mistakes were neither corrected nor confirmed, so that the loss in accuracy was balanced by the fairness of the test.

As the results of the tests indicated that the tasters found it easier to distinguish differences in the coarse samples than in the fine ones, it was decided to allow 0, 1, 2, 4, and 5 marks, respectively, for the classes mentioned above. The number of marks scored by each sample in all the tests, expressed as a percentage of the maximum marks obtainable, represented the tasters' opinion on the texture of the chocolate.

The replies to the question, as to which of the two samples was the finer, were worked out to the percentage number of times each sample was selected.

The "micro value" of each batch of chocolate was determined, and the results of the two types of test can be compared by reference to Table III.

TABLE III

COMPARISON OF MICRO VALUE WITH TASTING-TEST RESULTS

	Micro value	Marks fineness Per Cent.	Marks selection Per Cent.
No. 1. Very coarse ..	167·0	26·3	6·0
No. 2. Coarse	116·8	58·9	39·5
No. 3. Medium.. ..	101·5	65·7	45·8
No. 4. Fine	51·5	84·7	68·0
No. 5. Superfine ..	16·3	92·6	91·0

It is obvious that there is a close agreement between the particle-size frequency, as represented by the "micro value," and the degree of fineness which can be detected and appreciated by the average palate.

As the latter is an indication of the degree of refining which is required to satisfy popular taste, the former may be used to control manufacture accordingly.

In most tasting investigations the object is to obtain information regarding the likes and dislikes of individuals and groups of people, but this investigation is especially interesting because the tasters had to express their opinion on something which can be accurately measured by a scientific method. Many inferences can be drawn from the results, but the psychological aspects of the investigation are outside the scope of this paper.

TECHNICAL APPLICATIONS.—The connection between the "micro value" and the results of tasting tests having been established, the former can be applied in many ways, a few of which will be briefly described:

(*a*) *Standardisation of Refining.*—The microscopical test was applied to 64 samples of proprietary brands of chocolate which were purchased from retail confectioners. The selection of samples includes all qualities and prices of all the best-known brands of chocolate.

In Table IV a summary is given of the number of brands falling within each grade, as defined by the "micro value."

TABLE IV

PROPRIETARY BRANDS. GRADING AND DISTRIBUTION

	Micro value	Number examined
Superfine	Less than 35	10
Fine	,, ,, 70	15
Medium	,, ,, 100	16
Coarse	,, ,, 140	14
Very coarse	Greater ,, 140	9
		64

The limits of the "micro value" for each grade were decided by reference to the tasting results; and they may be regarded as standards for fineness of commercial brands of chocolate.

Comparison of the individual results shows that the more expensive brands of chocolate are usually highly refined, and manufacturers of several qualities of chocolate generally take more care in the refining of their better-quality products than with the cheaper varieties.

(*b*) *The Refining Process.*—Table V gives the results of two series of tests on chocolate, one refined on the usual type of roller mill, and the other in the Bausman disc mill.

TABLE V

THE REFINING PROCESS

Number of "Units" and Micro Value

	Sugar				Cocoa			
	100μ	50μ	25μ	Micro value	100μ	50μ	25μ	Micro value
Steel rollers—								
Millings 1st	1·65	20·0	22·0	452	0·075	0·45	15·4	22·8
,, 2nd	Nil	0·29	72·4	74·4	Nil	0·33	12·3	14·6
,, 3rd	Nil	Nil	48·8	48·8	Nil	0·26	10·4	12·2
Bausman disc mill—								
Millings 1st	0·27	15·1	177	296	0·23	0·69	5·1	22·7
,, 2nd	0·11	8·3	98	145	0·11	1·1	4·6	18·5
,, 3rd	Nil	5·8	81	122	0·10	0·9	3·2	15·1
,, 4th	Nil	3·0	65	86	0·12	0·63	3·5	14·6
,, 5th	Nil	3·9	55	82	0·04	0·75	3·8	11·2

The results are merely suggestive, as the setting of the mills and the time allowed are important factors in the efficiency of the refining process.

The results show that the principal effect of refining is to break down the larger sugar particles, and that the disc type of refiner is efficient for reducing the cocoa particles.

(*c*) *The Maturing Process.*—After chocolate has been refined, it is subjected to a maturing process which consists in continuous agitation of the heated chocolate for one, two or more days in various types of machines. During this process changes in composition, flavour and fluidity of the chocolate occur, and there is

some difference of opinion as to whether there is any further reduction in particle-size.

Definite information on this point is necessary, because it is convenient to apply the fineness test to the chocolate before it is subjected to the maturing process, and, as individual tests gave variable results, it was decided to test a series of chocolates matured in three types of machines before and after treatment for 48 hours. The results are set out in Table VI.

TABLE VI

THE MATURING PROCESS

Change in Micro Value of Sugar Particles. 48 hours.

	Stirring kettles	Rotary conches	Conches
Revolutions per minute	120	300	—
Number of tests	23	35	16
Original micro value (average) ..	50	50	72
Maximum difference	14·4	20·5	17
Minimum ,, ...	2·0	2·7	5
Average ,, ...	8·4	9·6	10·7
Less, correction for fat	5·0	5·0	7·2
Reduction in micro value ..	3·4	4·6	3·5
Reduction, per cent.	7·5	10	5

After allowance had been made for the dilution of the chocolate by the cocoa fat added during the process to regulate the fluidity, it was found that there is a small average reduction in the micro value, but it is by no means uniform. The violence of the agitation of the chocolate is apparently a factor, and it is probably the collisions and friction between the particles which cause their reduction.

This treatment may improve the texture of the chocolate by removing the sharp points and edges, but it is not so efficient in breaking down large particles as the ordinary refining machinery.

Table VII gives the observations, in greater detail, on three batches of chocolate matured in the reciprocal conche, and the results have been corrected for the added cocoa fat.

TABLE VII

CONCHING. TYPICAL RESULTS FOR RECIPROCAL CONCHE

	Time in conche	Sugar "units" 100μ	50μ	25μ	Micro value	Cocoa "units" 100μ	50μ	25μ	Micro value
1.	Nil	Nil	2·0	92·8	107	0·08	0·84	6·0	16·4
	52 hours	,,	1·5	79·6	90	0·06	0·74	7·2	15·9
2.	Nil	Nil	0·37	61·4	64	Nil	0·15	11·7	12·7
	48 hours	,,	0·24	52·6	54	Nil	0·17	11·4	12·6
3.	Nil	Nil	0·12	44·5	45	Nil	0·10	5·3	6·0
	48 hours	,,	0·26	38·5	50	Nil	0·08	4·7	5·3

(*d*) *Cocoa Powder.*—The results of the microscopical test on four well-known brands of cocoa are given in Table VIII.

TABLE VIII

COCOA POWDERS

Brand	Max. particle	"Units" per grm. 100μ	50μ	25μ
A	330μ	1·5	6·0	59·5
B	360μ	2·2	7·8	38·3
C	200μ	2·3	7·6	49·8
D	400μ	5·2	13·0	63·0

The presence of cocoa particles much larger than are usually found in chocolate is due to the absence of sugar crystals, which, by their abrasive action during the refining process, help to break down the cocoa.

An accurate estimation of the fineness of cocoa should be useful in the study of the so-called solubility of cocoa, which must depend, to a very large extent, on the particle-size and distribution.

(*e*) *Other Applications of the Method.*—The lycopodium method has been applied successfully to tooth pastes, metal polishes and emery powders, and to the estimation of shell in cocoa and chocolate.

It is of special use for pastes, fatty materials, and other preparations which cannot conveniently be sieved. In my laboratory it is in constant use for controlling the working of refining mills, for standardising products, and for testing the efficiency of new types of machinery.

I wish to express my thanks to the Directors of Messrs. John Mackintosh & Sons, Ltd., for allowing me to publish this paper, and to Messrs. J. M. Tucker and J. Brear for their valuable assistance in the microscopical work.

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DISCUSSION

Mr. T. E. WALLIS said that he was pleased to find that other workers had confirmed his experience of the remarkable accuracy of the lycopodium method. Using similar methods for the quantitative examination of drugs, he had obtained results agreeing within 2 per cent. He thought that application of the method on lines similar to those described in the paper would prove extremely useful in the examination of some of the standardised drugs mentioned in the new edition of the British Pharmacopoeia. In using the method he had had some trouble from the inclusion of air bubbles in the preparations, and he asked the author if he could suggest any methods for overcoming this difficulty.

Dr. H. W. BYWATERS asked if it was justifiable to assume that particles measuring 100μ, when broken down to 25μ, would produce 64 particles, as a thin plate, such as a cocoa flake, would not behave in this way. He also expressed the opinion that the sharpness of the edges of the crystals, as well as their size, would affect the palate of the taster. He thought that the time required for completing a test was an objection to the method for routine testing, but agreed that the results showed that, instead of following a common practice of estimating the average size of the twelve largest particles, it was necessary to measure many more particles. He would like to have had more detailed particulars of the tasting experiments.

Dr. L. E. CAMPBELL thought that the method would be of great value to those engaged in research work on chocolate and confectionery, as particle-sizes and

distribution were important contributory factors to the quality of chocolate, cocoa and fondant creams. He was interested in the effect of conching on particle-size. The method should also be useful for testing the efficiency of new types of grinding mills, and might be standardised for this purpose.

Mr. S. B. PHILLIPS criticised the microscopical method, as he thought that the time required was longer than was desirable in a busy works laboratory. For controlling manufacture more rapid methods were essential, and he referred to elutriation and sifting methods for estimating the fineness of powders. Cocoa and sugar particles had different effects on the palate, but this point had not been considered in the discussion of the results.

Mr. A. R. TANKARD thought that the results would be useful to those manufacturers who were particular about the quality of their products, and he hoped that it would lead to the abolition of the objectionable practice of adding alkali to cocoa in order to increase its "solubility."

The CHAIRMAN (Mr. John Evans) referred to the eye-strain produced by quantitative microscopy, and suggested that a counting device would be a useful addition to the method.

Mr. MASON, replying to the discussion, thanked the speakers for their interest in the paper, and expressed his indebtedness to Mr. Wallis, the originator of the lycopodium method. Its accuracy had been checked on many occasions, and experienced workers had no difficulty in obtaining duplicate results in the complete test agreeing within 2 per cent. Air bubbles were absent from the suspensions in oil, but were present in the aqueous suspensions in which the cocoa particles were examined. They did not present much difficulty, as the larger cocoa particles were easily distinguished.

The time required was certainly an objection to the test for routine purposes. In his laboratory the complete test was used only for research purposes; a simplified form of the sugar count was used for the routine testing of the factory production, and, when a rapid test was necessary, the oil suspension was prepared quantitatively and examined qualitatively by an experienced assistant.

The "micro value" was merely a crude attempt to combine the sizes and distribution of the particles in a single value which simplified comparisons and standardisation. Other methods of adjustment of particle-sizes were tried, but the one described compared most favourably with the tasting tests. Some of the particles counted as 100μ were very much larger, and, as they varied in size, an exact estimation of the equivalent number of smaller particles was impossible. Eye-strain could be avoided by using a projection apparatus, and large numbers of particles could be counted with ease by means of the ordinary type of counting device supplied for use on wrapping machines.

Methods used in the Analysis of certain Lead Alloys*

By B. S. EVANS, M.C., D.Sc., F.I.C.

This paper deals with some of the methods used in the analysis of a series of somewhat complicated lead alloys. As several of the methods are, to the best of my belief, new, at any rate in their present combination, and as all have been subjected to experimental verification, I thought it worth while to put them on record, in the hope that some of the suggestions put forward may be of use to others faced with similar problems. The alloys fell into three categories:

(*a*) Lead alloyed with a single other metal (Ba, Ce, Tl, Te, Ni).

(*b*) Lead alloyed with antimony and with one other metal.

(*c*) Lead alloyed with antimony and cadmium and with one other metal.

The subsidiary metals present in groups (*b*) and (*c*) were the following:—Tin, bismuth, mercury, zinc, copper, nickel, calcium, magnesium, lithium, tellurium, thallium, sodium; the amounts supposed to be present being 0·5 or 0·05 per cent.

Thallium.—This metal forms two series of salts corresponding to Tl^{I} and Tl^{III}, and it can be titrated like antimony with bromate in acid solution (*cf.* Marshall, *J. Soc. Chem. Ind.*, 1900, **19**, 994); the thallium being completely reduced to the thallous condition by treatment with sulphur dioxide, the latter boiled off and the thallous salt titrated to the thallic condition with potassium bromate, using methyl orange as indicator. Two points require to be noted.

(*a*) The atomic weight of thallium is high (204·0), and, since the oxidation is from Tl^{I} to Tl^{III}, 1 c.c. of the approximately $N/20$ solution of bromate used corresponds with approximately 0·0051 grm. of thallium. The alloy which was being analysed was made up to contain not more than 0·5 per cent.; therefore, in order to get a titration of about 10 c.c., it was necessary to work on a sample weight of 10 grms. The chloride from 10 grms. of lead, however, would form a heavy precipitate in the titration flask, hindering boiling, and carrying down most of the slightly soluble thallous chloride with it. For this reason a separation from lead was required.

(*b*) As thallium behaves in a precisely similar manner to antimony in the bromate titration it was necessary to separate the thallium from antimony also in cases where the latter was present.

An attempt was made to apply Strecker and de la Peña's cobaltinitrite method of separation (*Z. anal. Chem.*, 1925, **67**, 256), but without success. Another method, based on the fact that lead in alkaline citrate solution can be precipitated with carbon dioxide, leaving in solution thallium which can afterwards be precipitated with sodium sulphide, although it gave one or two fair results, was relinquished owing to its being cumbersome and involving the difficulty of knowing when to stop the stream of carbon dioxide, an excess of carbon dioxide re-dissolving the lead carbonate. Incidentally, in the course of this work it was found that a

* Communication from the Research Department, Woolwich

cyanide solution of zinc sulphide appears to dissolve thallium sulphide in somewhat the same way that an alkaline solution of tin sulphide will dissolve cadmium sulphide.

As it was found that lead iodide dissolved readily and completely in ammoniacal ammonium citrate solution, whilst thallium iodide did not, this behaviour was made the basis of a method of separation. The addition of a little silver nitrate, which was precipitated as iodide together with the thallium, seemed to correct the tendency to incomplete precipitation noted by Moser and Brukl (*Monatsh.*, 1926, **47**, 667), and the precipitate filtered readily; it had to be washed with dilute ammonia containing potassium iodide, otherwise loss occurred. The complete method is as follows:

A convenient quantity (say, 10 grms.) of the sample is dissolved in 120 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) and 50 c.c. of nitric acid (sp.gr. 1·2); the solution is made alkaline with ammonia and completely cooled; 10 c.c. of silver nitrate solution (0·5 per cent.) are added, followed by 20 c.c. of potassium iodide solution (4 per cent.), and the liquid is allowed to stand overnight. The precipitate is filtered off and washed 4 times with 2 per cent. ammonia containing 0·10 per cent. of potassium iodide, and then 6 times more with the same wash liquor to which has been added saturated potassium cyanide solution (treated beforehand with bromine water to remove sulphides; *cf.* ANALYST, 1929, **54**, 396) in the proportion of 10 c.c. to 500 c.c. of wash liquor. The precipitate is dissolved on the filter in to a clean flask by repeated treatment with hydrochloric acid alternating with hot water, and the pulp is well washed with hot water; the resulting filtrate is made fairly strongly alkaline with sodium hydroxide, and the thallium is precipitated with sodium sulphide. The thallium sulphide is collected on a pulp filter and lightly washed with hot water, and then dissolved off the filter into a clean flask by treatment with 10 c.c. of a saturated solution of bromine in hydrochloric acid. This is followed by a wash with hot water, then with 40 c.c. of hydrochloric acid, and finally with hot water so as to give a total volume of about 300 c.c. Lastly, the thallium is reduced by passing a rapid stream of sulphur dioxide for two or three minutes, the solution is boiled for 40 minutes, and a bromate titration is carried out at 55° C. By this process antimony, as well as lead, is separated from thallium. As in all bromate titrations, there is a "blank," due to the reducing power of the indicator, and also probably to non-volatile reducing agents carried over with the sulphur dioxide used, which must be determined and deducted; in the case of the following results, obtained on a series of synthetic mixtures, the "blank" was 0·25 c.c.:

Lead taken Grms.	Antimony taken Grm.	Cadmium taken Grm.	Thallium added Grm.	Titration $KBrO_3$ solution c.c.	Thallium found Grm.	Percentage of thallium	
						added	found
10·0	Nil	Nil	0·0100	2·15−0·25=1·90	0·0100	0·100	0·100
10·0	0·20	0·10	0·0500	9·85−0·25=9·60	0·0504	0·500	0·504
10·0	0·20	0·10	0·0400	7·85−0·25=7·60	0·0399	0·400	0·399
10·0	0·20	0·10	0·0300	5·95−0·25=5·70	0·0299	0·300	0·299
10·0	0·20	0·10	0·0200	4·05−0·25=3·80	0·0200	0·200	0·200
10·0	0·20	0·10	0·0100	2·15−0·25=1·90	0·0100	0·100	0·100

1·0 c.c. of the potassium bromate solution used = 0·00525 grm. of thallium.

TELLURIUM.—The method of precipitation with sulphur dioxide was tried, but precipitation appeared to be very slow, and there was difficulty in knowing when it was complete. As it was found that, like arsenic, tellurium is precipitated as metal by hypophosphorous acid and that, unlike arsenic, the precipitation will take place in dilute sulphuric acid, which need not be very strong, a method of determination was based on this reaction. Instead of weighing the precipitate obtained, it would manifestly be an advantage if it could be titrated in a similar manner to that of arsenic in like cases; the first work done, therefore, was directed towards establishing this titration.

An attempt to treat the tellurium precipitate in the same way as an arsenic one (Evans, ANALYST, 1932, **57**, 492) gave low results, owing to the fact that the tellurium precipitate is by no means readily soluble in neutral iodine solutions, as is shown by the following figures:

Tellurium taken Grm.	Tellurium found Grm.
0·0020	0·0018
0·0050	0·0032

It was found that an addition of potassium iodide to the solution before precipitating with hypophosphite resulted in a precipitate of different texture which dissolved readily; trials were therefore made, using this modification. The volume of the tellurium solution was about 100 c.c., and contained 0·4 grms. of potassium iodide and 10 c.c. of dilute (1 : 3) sulphuric acid; about 5 grms. of sodium hypophosphite were added, and the flask was allowed to stand on a steam-bath for 2 to 3 hours. This procedure gave high results:

Tellurium taken Grm.	Titration $N/100$ iodine solution c.c.	Tellurium found. Grm.
0·0050	19·5 − 3·0 = 16·5	0·0054
0·0040	19·8 − 5·5 = 14·3	0·0046
0·0030	19·1 − 8·3 = 10·8	0·0034
0·0020	20·3 − 12·3 = 8·0	0·0025
0·0010	19·2 − 15·1 = 4·1	0·0013

It seemed probable that part of the tellurium was being converted into the Te^{VI} instead of the Te^{IV} condition; calculations made on this assumption gave the following figures:

	Grms. of tellurium				
Present	0·0050	0·0040	0·0030	0·0020	0·0010
Titration calculated on $Te \rightarrow Te^{IV}$ assumption	0·0054	0·0046	0·0034	0·0025	0·0013
Titration calculated on $Te \rightarrow Te^{VI}$ assumption	0·0035	0·0030	0·0023	0·0017	0·0009
*Percentage of Te converted into Te^{VI}	11	28	30	56	62

The comparative regularity with which the apparent Te^{VI} increased with an increasing excess of iodine lent support to this view.

* Calculated from formula $0{\cdot}319a - 0{\cdot}0682b = 106x$, where a = weight of Te present, b = number of c.c. of $N/100$ iodine consumed, x = weight of Te converted into Te^{IV}.

An attempt to get all the Te converted into Te^{VI} by dissolving it in a good excess of iodine, in presence of a little sodium bicarbonate, and allowing it to stand for 10 minutes, gave a low result:

Tellurium taken Grm.	Titration c.c.	Tellurium found (calc. on $Te \rightarrow Te^{VI}$ assumption) Grm.
0·0050	29·3—10·5=18·8	0·0040

From these results it was evident that steps must be taken to prevent the oxidation of the Te beyond the Te^{IV} state. This was achieved by adding 0·5 grm. of potassium iodide and a few drops of dilute sulphuric acid to the beaker containing the filter and precipitate before adding the iodine; after solution small quantities of sodium bicarbonate were added until carbon dioxide ceased to be evolved; the titration was then carried out exactly as described for arsenic (Evans, ANALYST, 1932, **57**, 492). In this manner, reasonably accurate results were obtained:

Tellurium taken Grm.	Titration $N/100$ iodine solution c.c.	Tellurium found Grm.
0·0050	23·9— 8·6=15·3	0·0049
0·0040	20·5— 7·8=12·7	0·0041
0·0030	20·3—11·2= 9·1	0·0029
0·0020	19·9—13·9= 6·0	0·0019
0·0010	20·0—16·7= 3·3	0·0011

SEPARATION FROM LEAD AND LEAD-ANTIMONY-CADMIUM ALLOYS.—On account of the fact that the hypophosphite precipitation is carried out in sulphuric acid solution it was necessary to separate the lead; this was achieved by precipitating the lead as acid tartrate. The complete method evolved was as follows:

The sample (10 grms.) is dissolved in 60 c.c. of dilute nitric acid (sp.gr. 1·2) and 50 c.c. of tartaric acid solution (100 grms. dissolved in 200 c.c. water). The solution is cooled, and ammonia is added until the liquid smells fairly strongly of it. The precipitate first formed should now re-dissolve; this is apt to take time, and the beaker is allowed to stand, with occasional shaking, until a clear solution is obtained; if necessary, more ammonia may be added, but it is desirable to avoid too great excess, owing to the large precipitate of ammonium bitartrate subsequently obtained; in any case, however, the solution must be clear. The liquid is now made strongly acid to litmus with tartaric acid; it is again cooled, filtered, and the lead tartrate is washed with cold water; 10 c.c. of potassium iodide solution (4 per cent.) and 40 c.c. of dilute (1:3) sulphuric acid are added to the filtrate, and it is allowed to stand for 15 minutes. The precipitate formed is filtered off and washed 2 or 3 times with cold water; 20 c.c. of ammonium chloride solution (20 per cent.) and 2 or 3 grms. of sodium hypophosphite are added to the filtrate, and it is warmed till the iodine colour is discharged; a further 5 grms. of hypophosphite are then added, and the liquid is boiled for half an hour, allowed to stand on the steam-bath for half an hour, and filtered while hot, and the precipitate is washed with hot 5 per cent. ammonium chloride solution. The tellurium precipitate is dissolved by treating the filter in a beaker with a mixture of 10 c.c. of a saturated solution of bromine in hydrochloric acid, 20 c.c. of hydrochloric acid and 30 c.c. of

water; the paper pulp is then filtered off and washed with hot water, filtrate and washings, to give a total volume of about 300 c.c. Ten c.c. of potassium iodide solution (4 per cent.) are added to the filtrate, which is then decolorised with sodium hypophosphite, and the tellurium is precipitated exactly as before, the only difference being that the pulp used for filtering off the second tellurium precipitate is prepared beforehand by treatment with bromine and hydrochloric acid, as described for arsenic (Evans, ANALYST, 1932, **57**, 493). The tellurium precipitate is washed with hot 5 per cent. ammonium chloride solution, and the filter is transferred to a beaker, 2 or 3 c.c. of dilute sulphuric acid (1:3), and 10 c.c. of potassium iodide solution (4 per cent.) are added, followed by a good excess of $N/100$ iodine solution (run in from a burette) and about 50 c.c. of water, and the beaker is allowed to stand for two or three minutes after its contents have been thoroughly stirred. Sodium bicarbonate solution is added in small quantities until further addition ceases to result in a violent evolution of carbon dioxide; this is followed by 5 c.c. of benzene, and the beaker is gently shaken and its contents immediately titrated with $N/100$ arsenious oxide solution until the benzene is decolorised, 2 or 3 drops being added in excess; 3 to 4 grms. of sodium bicarbonate are then added, followed by about 30 c.c. of water and a little starch solution, and the titration is finished by addition of $N/100$ iodine solution until the coloration (brown or blue) of the starch is obtained. The number of c.c. of $N/100$ arsenic solution used is deducted from the total volume of $N/100$ iodine solution added, and the result is the number of c.c. of $N/100$ iodine solution used to convert the tellurium present into the Te^{IV} conditions.

1·0 c.c. of $N/100$ iodine ≡ 0·000319 grm. of tellurium.

The following are the results obtained with synthetic mixtures:

Lead taken Grms.	Antimony taken Grm.	Cadmium taken Grm.	Tellurium added Grm.	Titration c.c.	Tellurium found Grm.	Tellurium added Per Cent.	Tellurium found Per Cent.
10·0	0·20	0·10	0·0050	26·7—11·1=15·6	0·00498	0·050	0·050
10·0	0·20	0·10	0·0040	20·8— 8·1=12·7	0·00405	0·040	0·040
10·0	0·20	0·10	0·0030	21·8—12·3= 9·5	0·00303	0·030	0·030
10·0	0·20	0·10	0·0020	15·7— 9·7= 6·0	0·00191	0·020	0·019
10·0	0·20	0·10	0·0010	10·5— 7·2= 3·3	0·00105	0·010	0·010

CERIUM.—The alloys in question here contained only lead and cerium, and, therefore, the problem was narrowed down to a separation of cerium from a vastly greater mass of lead; it so happens that cerium is a difficult element to separate from a large amount of lead. Cerium forms, of course, two series of salts, cerous and ceric, of which the ceric salts are strong oxidising agents and can be titrated with reducing agents; the method of oxidation with persulphate, using a silver catalyst, was tried, in the hope that lead would not interfere; it was at once obvious that, under the conditions laid down, lead peroxide was precipitated, and either dragged down cerium with it, or else prevented the cerium from being fully oxidised. An attempt to oxidise the cerium by boiling with lead dioxide, which was filtered off before titration, gave low results; another attempt to separate the lead first as sulphate yielded only little more than half the cerium, which is not surprising in

view of the ready hydrolysis of cerous salts. It was found that the most reliable oxidation of cerous salts was obtained by boiling the sulphuric acid solution with sodium bismuthate, any undissolved excess of the latter being filtered off through asbestos before titration; a number of variants of this oxidation, using nitric acid, were tried, but yielded low results; hence, separation of the lead was still necessary.

The somewhat curious behaviour of cerium and lead, when treated in alkaline citrate solution with hydrogen peroxide, was investigated; an attempt to base a colorimetric method on it proved a failure, but the following facts emerged:

(*a*) If hydrogen peroxide is added to an ammoniacal citrate solution of the metal, cerium gives a permanent yellow coloration, with occasionally a tendency to precipitation, lead turns first brown, then colourless, and manganese a permanent brown.

(*b*) If sodium hydroxide is used instead of ammonia, cerium gives an orange precipitate, lead is also precipitated but slowly redissolves, manganese gives a brown colour in the cold, and precipitates on boiling.

These reactions proved unmanageable from a quantitative point of view, but, on trying them in very feebly acid instead of alkaline solution, it was found that hydrogen peroxide stabilised with phosphoric acid would give a precipitate with cerium, whilst that stabilised with sulphuric acid would not; further investigation showed that sodium perborate, added to a slightly acid solution, acted as an excellent precipitant for cerium in presence of either lead or manganese. The precipitate tends to be reduced and to go into solution at the boiling temperature; also, if allowed to stand, hot, for any length of time; the filtration must, therefore, be carried out as rapidly as possible, the flask containing the part of the liquid which will not go at once on the filter being meanwhile cooled.

The following process was worked out for lead-cerium alloys:—A 10-grm. sample of the alloy is dissolved in 50 c.c. of dilute nitric acid (sp.gr. 1·2) diluted with 50 c.c. of water. The solution is made alkaline with ammonia and just acid to litmus with acetic acid, three or four drops being added in excess. The solution is brought to 90° C., and about 2 grms. of sodium perborate added; it is shaken for a few seconds and then filtered immediately in the manner described above. The precipitate is washed with hot water and dissolved into the original flask by treatment on the filter with hot dilute nitric acid (sp.gr. 1·2); the filter is washed with hot water, and the filtrate is made alkaline with ammonia, then just acid with acetic acid, and the cerium is precipitated as before, immediately cooled, and filtered off. The cerium precipitate, after being filtered and washed with hot water, is dissolved into the original flask by treatment on the pulp with 50 c.c. of dilute (1:3) sulphuric acid, followed by washing with hot water up to about 150 c.c.; about 0·5 grm. of sodium bismuthate is added, and the liquid is boiled for 5 minutes and cooled. The solution, which now contains the cerium in the ceric condition, is filtered through asbestos, and the filter is washed with 2 per cent. sulphuric acid; a measured excess of dilute ferrous ammonium sulphate solution is added, followed by 1 c.c. of a solution of disulphine blue (0·1 per cent. in water), and the excess of ferrous sulphate is titrated back with $N/100$ potassium permanganate solution; the difference between this titration and that required by the amount of

ferrous ammonium sulphate added, multiplied by 0·0014, gives the weight in grms. of the cerium present. The function of the disulphine blue is simply to give a sharp end-point (*cf.* J. Knop and O. Kubelkova, *Z. anal. Chem.*, 1931, **85**, 401); the red end-point colour takes one or two seconds to develop, and fades on standing. Tests of the process made on 10-grm. quantities of lead, to which varying amounts of cerium had been added, gave the following results:

Lead taken Grms.	Cerium added Grm.	Titration, *N*/100 potassium permanganate c.c.	Cerium found Grms.	Cerium	
				added Per Cent.	found Per Cent.
10·00	0·0200	36·10—21·80=14·30	0·0200	0·200	0·200
10·00	0·0100	9·65— 2·30= 7·35	0·0103	0·100	0·103
10·00	0·0080	9·50— 3·45= 6·05	0·0085	0·080	0·085
10·00	0·0060	9·50— 5·30= 4·20	0·0059	0·060	0·059
10·00	0·0040	9·50— 6·45= 3·05	0·0043	0·040	0·043
10·00	0·0020	9·65— 8·05= 1·60	0·0022	0·020	0·022
10·00	0·0010	9·50— 8·60= 0·90	0·0013	0·010	0·013

The method given for lead will separate cerium equally well from manganese.

ANTIMONY.—In most of the alloys of this series the antimony could be determined direct by bromate titration after solution in perchloric acid, as described in a recent paper (Evans, ANALYST, 1932, **57**, 557). Complications occurred in the alloys containing thallium and tellurium, the former because it behaves like antimony in the bromate titration, the latter because it is precipitated by the sulphur dioxide used for reduction of the antimony. Tellurium was eliminated by passing the sulphur dioxide for a considerable time until all tellurium was precipitated, filtering off the tellurium precipitate and washing it with 5 per cent. hydrochloric acid, and finally boiling down and titrating with bromate as usual; carried out thus, 1·98 per cent. of antimony was found in an alloy considered to contain: Antimony 2·00, cadmium 1·00, tellurium 0·05, lead 96·95 per cent. In the case of the thallium alloys the samples were dissolved, as usual, by the perchloric acid method; the solution, after the hydrochloric acid treatment was cooled and filtered, the lead chloride precipitate washed with 5 per cent. hydrochloric acid, and the antimony separated from the filtrate by Järvinen's method (*Z. anal. Chem.*, 1923, **62**, 184), carried out in the following way:—One grm. of electrolytic iron was added to the filtrate, which was boiled for one hour and filtered hot, and the precipitated antimony was washed with hot water; the filter was placed in a beaker, the antimony, etc., dissolved by treatment with 25 c.c. of dilute (1 : 1) hydrochloric acid to which bromine had been added, and the filter pulp was filtered off and washed with 5 per cent. hydrochloric acid. The filtrate was diluted to 300 c.c., the bromine reduced with sulphur dioxide, the excess of the latter boiled off, and the antimony thrown down as sulphide with hydrogen sulphide; after being filtered off this was washed with 5 per cent. ammonium chloride solution, dissolved by treatment with a mixture of 100 c.c. of water, 25 c.c. of hydrochloric acid and 5 c.c. of a saturated solution of bromine in hydrochloric acid, and, after adjustment to the correct acid strength and volume (50 c.c. of concentrated hydrochloric acid in 300 c.c.), the antimony was titrated with bromate in the usual way.

A trial carried out on these lines with a mixture of 0·04 grm. of antimony, 2·0 grms. of lead and 0·01 grm. of thallium gave 0·039 grm. of antimony recovered. A weak point of the method probably lies in the washing of the precipitated metallic antimony with water; during some other work with a totally different object I had occasion to try a number of washing liquids on antimony precipitated with sodium hydrosulphite, with a view to washing the antimony free from hydrosulphite; I experienced great difficulty, and found that the following solutions all yielded bright filtrates which contained considerable quantities of antimony:—

Ammonium	chloride,	sodium	chloride,	potassium acid sulphate.
,,	sulphate,	,,	sulphate,	hypophosphorous acid.
,,	phosphate,	,,	phosphate,	10 per cent. glycerin.
,,	acetate,	,,	hypophosphite,	10 per cent. acetic acid.
,,	citrate,	,,	hydroxide.	

Water washed the antimony through the filter, and potassium cyanide solution gave a bright filtrate which contained only a trace of dissolved antimony, but its action appeared to be somewhat uncertain. The only solution tried which satisfied the requirements of a bright filtrate containing no antimony was potassium dichromate (approximately $N/50$). In view of these results it would probably be desirable to substitute dilute potassium dichromate solution for the hot water used for washing the metallic antimony precipitated by iron in the above process.

In order to be sure that the mercury in the lead-antimony-cadmium-mercury alloy was without effect on the bromate titration of the alloy, two portions of an antimony solution, each containing 0·050 grm. of antimony, were taken, and 0·027 grm. of mercuric chloride was added to one of them; the acid conditions were adjusted and bromate titrations carried out. Each solution required 16·35 c.c. of bromate solution, showing that mercury has no influence.

COPPER.—The ordinary methods could be applied without difficulty, but the following new method was found to be as accurate and much quicker:—A 10-grm. sample of the alloy was dissolved in 40 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) and 100 c.c. of dilute nitric acid (sp.gr. 1·2); the solution was made ammoniacal, 10 c.c. of saturated potassium cyanide solution were added, followed by about 10 grms. of sodium hydrosulphite, and the liquid was boiled for one minute and allowed to stand for 15 minutes; the dense precipitate of lead and antimony was filtered off and washed as described in a former paper (Evans, ANALYST, 1929, **54**, 396). The cadmium was removed by treatment with excess of sodium sulphide, boiling and filtering, and the copper was precipitated as sulphide by acidifying with acetic acid and boiling. The copper sulphide was finally dissolved in nitric acid and determined colorimetrically as usual. The results agreed exactly with those obtained by the longer method.

NICKEL.—This metal, like copper, is immiscible with lead, except in very small proportions; the alloys to be analysed were supposed to contain 0·05 per cent. It was found that, if 20 grms. of the alloy were dissolved in a mixture of citric and nitric acids and made slightly alkaline with ammonia, the nickel could be precipitated direct with glyoxime. The precipitate formed very slowly, and the

flask had to be allowed to stand for a day or two; the nickel glyoxime was then filtered off, and the nickel determined, as usual, by cyanide titration. As, however, no other metals were present which give colours with glyoxime, it seemed worth while to attempt a direct colorimetric determination of the nickel, using a modification of Rollet's method (*Compt. rend.*, 1926, **183**, 212). This proved successful, and the following process, which seems sufficiently delicate to be used for determining nickel in "chemical" lead, was worked out:

A sample weight of 20 grms. (a large amount is used to allow for the inevitable segregation of the nickel) is dissolved in a diluted mixture of 40 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) and 200 c.c. of dilute nitric acid (sp.gr. 1·2). The solution is cooled and diluted to 500 c.c., and 25 c.c. of this solution (≡1·0 grm. of sample) are placed in a Nessler tube, 10 c.c. of the citric acid solution are added, and ammonia (1 : 1) is run in until the precipitate just re-dissolves, 5 c.c. being then added in excess; 2 c.c. of a saturated solution of dimethylglyoxime in acetone is next added, followed by 20 c.c. of bromine water, and the contents of the tube are made up to the mark and stirred. The standard tube contains 10 c.c. of the citric acid solution which has been neutralised with ammonia and cooled; 5 c.c. excess of ammonia (1 : 1) are added, followed by 2 c.c. of the glyoxime solution and 20 c.c. of bromine water. The contents of the standard tube are then titrated with a standard nickel solution (1 c.c.=0·00005 grm. of nickel) until the brown colours match. The colour forms slowly, and the titration must be made cautiously, the tubes being allowed to stand after each addition. Trial was made of this process in the following manner: 19·4 grms. of lead, 0·4 grm. of antimony and 0·2 grm. of cadmium were dissolved in 200 c.c. of dilute nitric acid (sp.gr. 1·2), 40 c.c. of the citric acid solution and about 100 c.c. of water. The solution was cooled and made up to 500 c.c., varying amounts of nickel were added to 25-c.c. portions of this solution, and the nickel was then determined as described above. The following results were obtained:

Lead taken Grm.	Antimony taken Grm.	Cadmium taken Grm.	Nickel taken Grm.	Titration c.c.	Nickel found Grm.	Nickel added Per Cent.	Nickel found Per Cent.
0·97	0·02	0·01	0·00010	2·00	0·000100	0·0100	0·0100
0·97	0·02	0·01	0·00008	1·60	0·000080	0·0080	0·0080
0·97	0·02	0·01	0·00007	1·50	0·000075	0·0070	0·0075
0·97	0·02	0·01	0·00006	1·25	0·000062	0·0060	0·0062
0·97	0·02	0·01	0·00004	0·85	0·000042	0·0040	0·0042
0·97	0·02	0·01	0·00002	0·45	0·000022	0·0020	0·0022

The process is, of course, only applicable in this form if other metals capable of giving colours with glyoxime in ammoniacal solution (notably copper) are absent. If traces of copper are present, allowance could be made for them by adding to the standard tube the same amount present in the sample; the colour given by copper is very much weaker than that given by the same weight of nickel.

CALCIUM.—The method used in this laboratory for lead calcium alloys is as follows (Koenig, *Chem. Ztg.*, 1919, **43**, 135):—The sample is dissolved in dilute nitric acid and evaporated to dryness, the residue is then taken up with water,

and the bulk of the lead is precipitated with hydrochloric acid. The lead chloride is filtered off on a Buchner funnel and washed with dilute (1 : 2) hydrochloric acid. The filtrate is again evaporated to dryness and taken up with 80 c.c. of water and 20 c.c. of hydrochloric acid; it is then boiled, cooled and filtered off from the further precipitate of lead chloride, which is washed with 5 per cent. hydrochloric acid. The filtrate is neutralised with ammonia, then made slightly acid with hydrochloric acid, and any carbon dioxide present is boiled off; an excess of bromine is added, followed by an excess of ammonia, which causes the remaining lead to precipitate. The liquid, containing the precipitate, is made up to a known volume, and an aliquot part is filtered off, in which the calcium is precipitated as oxalate, the final determination being made by titration of the oxalate radicle with permanganate. This method was inapplicable to the alloys under discussion, because antimony forms "metantimonic acid" when attacked with nitric acid, and cadmium gives an oxalate precipitate with ammonium oxalate; on the other hand, it was inadmissible to add citric acid to keep the antimony in solution, as in that case the lead did not precipitate with ammonia. Attempts were made to precipitate the calcium direct with oxalate in ammoniacal solution after dissolving the alloy in the nitric-citric mixture. These were completely unsuccessful; only a very small precipitate was formed, and this did not appear to contain calcium. The large sample required (20 grms.) precluded resort to perchloric acid as a solvent. I was obliged to fall back upon the method of solution described in a former paper (Evans, ANALYST, 1927, **52**, 568). This, though somewhat tedious, and requiring a rather complicated apparatus, had the great merit, so far as calcium determination was concerned, of giving a solution containing only bromine and hydrochloric acid, in addition to the metals contained in the alloy, and the bulk of the lead was automatically removed as bromide. In the absence of cadmium the resulting solution was merely boiled with a coil of lead strip for an hour to remove the antimony, and the ordinary process for lead-calcium alloys, described above, was carried out on the solution. In the presence of cadmium the solution was concentrated and filtered, to remove as much of the lead as possible as chloride, the filtrate was neutralised with ammonia and again made slightly acid with hydrochloric acid, and the cadmium, antimony, and most of the remaining lead were precipitated with hydrogen sulphide; this precipitate was filtered off and washed with 5 per cent. ammonium chloride solution, and the calcium in the filtrate, after concentration by boiling and treatment with ammonia and bromine, was determined as described for lead-calcium alloys. Time did not allow of a synthetic alloy being taken through the whole process, but a solution of 0·4 grm. of antimony, 0·2 grm. of cadmium, and 0·0102 grm. of calcium was added to the lead bromide residue remaining from the solution, by this method, of 20 grms. of one of the alloys; 300 c.c. of 20 per cent. hydrochloric acid were then added, and the whole boiled, cooled and filtered, and the process last described was carried out on the filtrate. The titration of the resulting calcium oxalate required 5·30 c.c. $N/10$ potassium permanganate solution $\equiv$ 0·0106 grm. of calcium. There still remains, however, the possibility that the prolonged heating of the sample with strong hydrochloric acid and bromine will result in a small amount of calcium being extracted from the glass of the apparatus.

MERCURY.—This element was determined exactly as described in a former paper (Evans and Clarke, ANALYST, 1926, **51**, 224), except that the sample was dissolved in a mixture of nitric and citric acids to keep the antimony in solution, and the acidity was adjusted before percolation.

TIN.—Tin was determined direct according to the method I have given in a recent paper (Evans, ANALYST, 1932, **57**, 555).

BARIUM.—In this case, as the samples were plain lead-barium alloys, the question of separation from antimony and cadmium did not arise. The following method was worked out by Mr. K. F. Allen, of the Research Department, Woolwich: —The sample is dissolved in dilute nitric acid, and the procedure given above for calcium was followed up to the point where the last traces of lead have been removed by precipitation with bromine and ammonia (care must be taken not to allow this precipitate to settle for long, owing to the danger of precipitation of barium carbonate). An aliquot part of the filtrate is boiled down to half its bulk, and, after the addition of 10 c.c. of 30 per cent. ammonium acetate solution, it is heated to boiling and, while boiling, 5 c.c. of 20 per cent. ammonium bichromate solution are added. The liquid is allowed to stand overnight, the barium chromate is then filtered off through asbestos, washed with 0·5 per cent. ammonium acetate solution and dissolved into a clean flask by treatment on the filter with hot dilute nitric acid (sp.gr. 1·2), the filter being washed with 5 per cent. nitric acid. A known excess of ferrous ammonium sulphate solution is added to the cooled filtrate, and the excess of ferrous iron is titrated with $N/10$ permanganate solution; the difference between this figure and the titration value of the ferrous ammonium sulphate added, multiplied by 0·00458, gives the weight of barium present.

The method was tested, with the following results:

Lead taken Grms.	Barium added Grm.	Titration $N/10$ potassium permanganate solution c.c.	Barium found Grm.	Barium added Per Cent.	Barium found Per Cent.
10·0	0·0050	14·35—13·50=0·85	0·0049	0·050	0·049
10·0	0·0100	14·35—12·60=1·75	0·0100	0·100	0·100
10·0	0·0200	14·35—11·00=3·35	0·0192	0·200	0·192
10·0	0·0500	14·35— 5·80=8·55	0·0490	0·500	0·490

Dr. S. G. Clarke, of the Research Department, Woolwich, working independently, arrived at an almost identical method for determining barium and calcium when present together alloyed with lead. He removed the lead by Koenig's method and precipitated the barium as above, except that he faintly acidified the filtrate from the lead precipitate with acetic acid before boiling down; this probably constitutes an improvement, in that it eliminates any chance of precipitation of barium carbonate during the boiling. He found that calcium could be quantitatively precipitated as oxalate in the filtrate from the barium chromate. Having satisfied himself that Koenig's method gave a complete separation from lead, he tested the remainder of the process on synthetic mixtures of barium and calcium, with the following results:

Barium taken Grm.	Barium found Grm.	Calcium taken Grm.	Calcium found Grm.
0·0571	0·0579	0·0201	0·0196
0·0228	0·0232	0·0201	0·0205
0·0057	0·0056	0·0101	0·0102

Both barium and calcium in this case were determined gravimetrically.

The methods used for determining the remaining metals mentioned at the beginning of this paper were modifications of well-known methods, and do not call for any comment.

The Separation and Determination of Traces of Lead in the Presence of Small Amounts of Bismuth

By J. HUBERT HAMENCE, M.Sc., A.I.C.

In the colorimetric determination of small amounts of lead by the sulphide method, bismuth, if present, will also yield a dark coloration on the addition of the sulphide to the ammoniacal solution, and will thus be determined as lead. The colour given by 0·1 mgrm. of lead is nearly the same as that produced by 0·1 mgrm. of bismuth.

No rapid colorimetric method for the determination of traces of lead in the presence of traces of bismuth is as yet known.

The extraction method of Allport and Skrimshire (Analyst, 1932, **57**, 440), based upon the solubility in chloroform of the lead diphenylthiocarbazone complex, unfortunately does not separate lead and bismuth. Also, in the thiocyanate method for the separation of iron and lead (Hamence, Analyst, 1932, **57**, 622), bismuth, if present, is not satisfactorily extracted with the iron as thiocyanate by the ether and amyl alcohol solvent. In this process the percentage of bismuth extracted was found to depend very largely upon the concentration of acid and ammonium thiocyanate present in the solution. It was found that a maximum extraction was obtained when 5 c.c. of 10 per cent. w/w nitric acid and 2 c.c. of saturated ammonium thiocyanate solution were added to 20 c.c. of solution (containing 0·10 mgrm. Bi), and the mixture extracted with 15 c.c. of ether and 15 c.c. of amyl alcohol; under these conditions an eighty per cent. separation was obtained. Unfortunately, the presence of salts was found to prevent the formation of bismuth thiocyanate, and thus render the method useless.

Attempts were made with many other solvents to extract the bismuth thiocyanate quantitatively, but without success.

Pyridine Thiocyanate Separation.—On adding pyridine and ammonium thiocyanate to a slightly acid solution of lead and bismuth salts, and extracting with a mixture of equal volumes of ether and amyl alcohol, it was found that the

bismuth was extracted by the ethereal solvent, probably as a pyridine thiocyanate, while the lead remained behind in the aqueous solution. Here, again, it was found that definite concentrations of the reagents were necessary for the complete extraction of the bismuth.

The best conditions, and those finally adopted, are as follows:—To 25 c.c. of the solution are added 0·5 c.c. of concentrated nitric acid, 2 c.c. of saturated ammonium thiocyanate solution and 1 c.c. of pyridine, and this mixture is extracted with a mixture of 15 c.c. of ether and 15 c.c. of amyl alcohol.

The following results were obtained for mixtures of lead and bismuth nitrates under the conditions indicated above:

Lead added Mgrm.	Bismuth added Mgrm.	Lead found Mgrm.	Number of extractions
—	0·25	0·01	1
—	0·50	0·01	2
0·10	—	0·10	1
0·50	—	0·50	1
0·20	0·40	0·18	2

These results show a satisfactory separation of lead and bismuth. It was found to be very important that the concentration of acid and thiocyanate indicated above should be maintained; in neutral solutions some lead is liable to be extracted with the bismuth, and in solutions which are too acid the bismuth will not be completely extracted.

This method of separation was then applied to various pharmaceutical chemicals which are tested for lead. The presence of large amounts of salts was found to render the separation of the bismuth unsatisfactory, probably by inhibiting the formation of bismuth pyridine thiocyanate. It was thus found to be necessary to remove the lead and the bismuth from the solution prior to their separation. This removal was achieved by adsorbing the metallic hydroxides on ferric hydroxide, by precipitating ferric hydroxide in the solution containing the lead and the bismuth and filtering off the precipitate. This precipitate was then dissolved in nitric acid, and the lead and bismuth in the resulting solution, which was free from large quantities of salts, were separated by the pyridine thiocyanate process.

Procedure for Alkali and Alkaline Earth Salts.—Five grms. of the salt are dissolved in about 20 c.c. of water and 1 c.c. of a 0·5 per cent. w/v solution of ferric chloride is added. The solution is then heated and, when near the boiling point, excess of ammonia is added; after being boiled for several minutes the solution is filtered through the smallest workable filter and washed twice with hot water. The filter paper, containing the precipitate, is then boiled for 5 minutes with about 12 c.c. of water and 0·5 c.c. of concentrated nitric acid. This solution is then poured into a separating funnel, and the filter paper left in the beaker is washed with two small quantities of hot water. The volume of the liquid in the separating funnel should amount to 25 c.c. Two c.c. of saturated ammonium thiocyanate solution and 1 c.c. of pyridine are added, followed by 15 c.c. of amyl alcohol and 15 c.c. of ether, and the separator is then vigorously shaken.

When clear, the aqueous solution is filtered into a Nessler tube and the filter washed twice with water. This filtration serves the purpose of removing small pieces of filter fibre which become detached during the boiling, and also of removing traces of an insoluble bismuth compound, which are sometimes produced and which are not extracted by the ethereal solvent. The lead is then determined by the sulphide process.

Potassium cyanide should be added to the solution while it is still acid and the liquid then made ammoniacal; this procedure prevents the formation of a very slight yellow tint, which is sometimes developed in the final solution.

The efficacy of the process was tested by adding known amounts of lead nitrate and bismuth nitrate to 5-grm. portions of salts free from lead and bismuth.

Compound	Lead added Mgrm.	Bismuth added Mgrm.	Lead found Mgrm.	Number of extractions
Ammonium nitrate ..	0·25	0·20	0·26	1
Ammonium sulphate ..	0·10	0·20	0·11	1
Potassium chloride ..	0·40	0·40	0·38	2
Calcium chloride ..	0·10	0·70	0·10	2
Ammonium nitrate ..	0·00	0·20	0·01	1
Magnesium sulphate ..	0·20	0·50	0·20	2
Magnesium sulphate ..	0·40	0·20	0·36	2
Sodium carbonate ..	0·05	0·50	0·06	1
Sodium chloride ..	0·20	0·00	0·18	2
Sodium chloride ..	0·18	0·45	0·18	2

Carbonates and oxides should be dissolved in the minimum quantity of dilute nitric acid before the addition of the ferric chloride solution and precipitation with ammonia.

With alkaline earth salts it was found to be advisable to add 2 grms. of lead-free ammonium chloride, which helps to keep the alkaline earth hydroxide in solution.

Zinc salts may be examined by precipitating with a relatively large excess of ammonia, which will dissolve the zinc hydroxide, and washing with a little dilute ammonia.

NUMBER OF EXTRACTIONS.—The number of extractions necessary to extract all the bismuth is determined best by a rapid preliminary lead test on 5 grms. of the compound. If the dark colour obtained is less than 0·25 mgrm. of lead, one extraction with the mixed amyl alcohol and ether solvent will suffice, but, if a coloration greater than this is obtained, two extractions will be necessary. When, however, the bismuth present exceeds 0·8 mgrm. it is advisable to work on a smaller quantity of the compound.

A blank test should always be made on the reagents, and the result deducted from the lead found.

EXTRACTION OF IRON.—The iron added as a ferric salt to adsorb the bismuth and lead is extracted by the amyl alcohol and ether solvent, and thus does not interfere with the final lead test. This applies equally to traces of iron which may be present as impurity in the compound that is being tested.

ADSORPTION OF BISMUTH AND LEAD BY FERRIC HYDROXIDE.—One of the essential stages in the process is the adsorption of the metallic hydroxides on ferric hydroxide prior to their separation. As shown in a previous paper (*loc. cit.*), 3 mgrms. of ferric hydroxide will adsorb at least 1 mgrm. of lead completely from an ammoniacal solution. The adsorption of bismuth is even greater with this amount of ferric hydroxide, as is shown in the following results:

Bismuth added Mgrms.	Bismuth not adsorbed by 3 mgrms. of ferric hydroxide
1·00	Nil
10·00	Nil

During this investigation all the filtrates left after the removal of the ferric hydroxide precipitate were tested for lead and bismuth, and in no instance was any sulphide coloration obtained; this indicated the complete adsorption of these metals on the ferric hydroxide.

The method, as it stands, is not as yet applicable to citrates and tartrates, in the presence of which it is not possible to precipitate ferric hydroxide by ammonia. A slightly modified procedure has been devised for these compounds which will, it is hoped, be described in a subsequent paper.

I wish to thank Dr. A. M. Ward for his continued help and interest during this investigation.

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The Volumetric Determination of Hydrogen Peroxide and Caro's Acid in the Presence of Perdisulphuric Acid

BY A. J. BERRY, M.A.

SINCE the fundamental investigations by Baeyer and Villiger (*Ber.*, 1900, **33**, 2488; 1901, **34**, 853) many researches have been published on the analyses of mixtures of hydrogen peroxide, Caro's acid, and perdisulphuric acid. It is well known that Caro's acid is a much more powerful oxidising agent than perdisulphuric acid, and much ingenuity has been expended in devising volumetric methods which depend upon the differential oxidising action of these compounds; when hydrogen peroxide is also present, the difficulty of the problem is considerably increased.

It was recognised by Baeyer and Villiger (*loc. cit.*) that, although potassium permanganate is without action upon either Caro's acid or perdisulphuric acid, yet when attempts are made to determine hydrogen peroxide in the presence of these acids by titration with potassium permanganate, irregular results are almost invariably obtained. Price (*J. Chem. Soc.*, 1903, **83**, 543) and Friend (*ibid.*, 1904, **85**, 597, 1533) have published detailed experiments on this subject. It is generally agreed that hydrogen peroxide and Caro's acid do not react together to an appreciable extent in dilute solution, but when potassium permanaganate is added, it induces a reaction involving oxidation of some of the hydrogen peroxide at the

expense of the Caro's acid. Accordingly the determination of the hydrogen peroxide, as calculated from the permanganate titration, gives rise to low results. In a more recent investigation, Wolffenstein and Makow (*Ber.*, 1923, **56**, 1768) have claimed that correct results can be obtained in the titration of hydrogen peroxide in presence of Caro's acid by potassium permanganate, if careful attention is paid to the working conditions, of which special importance was attached to the addition of manganous sulphate, considerable dilution, and rapidity of titration. The conditions are, however, somewhat artificial.

Most modern investigators are agreed that the determination of Caro's acid by its oxidising action upon hydriodic acid, followed by immediate titration of the iodine by sodium thiosulphate, is by no means accurate. Wolffenstein and Makow (*loc. cit.*) adapted a method due to Palme (*Z. anorg. Chem.*, 1920, **112**, 97), which consisted in employing sulphurous acid as a reducing agent. This compound is at once oxidised by Caro's acid, but is unaffected by perdisulphuric acid. After titration of the hydrogen peroxide in the solution with potassium permanganate, sodium acetate was added to diminish the hydrogen ion concentration of the solution. The Caro's acid was next titrated with a standard solution of sodium sulphite, a trace of iodine being added to the liquid as an indicator. Finally, the perdisulphuric acid was determined by adding a measured excess of ferrous sulphate and titrating the unoxidised ferrous salt with potassium permanganate. The figures published by these investigators are doubtless convincing, but the method is open to criticism on two grounds, *viz.* the necessity for employing artificial conditions for the determination of the hydrogen peroxide, and the use of such a readily oxidisable substance as sodium sulphite. The authors, however, have pointed out that the stability of sodium sulphite is much increased by the addition of about 2 per cent. of alcohol.

In a recent paper, Gleu (*Z. anorg. Chem.*, 1931, **195**, 61) has abandoned the use of iodimetric methods for determining Caro's acid, and has employed hydrobromic acid for the purpose. The bromine which is liberated corresponds strictly with Caro's acid. Gleu's method is briefly as follows:—First, the Caro's acid is determined by adding excess of potassium bromide and a measured quantity of a standard solution of sodium arsenite, the excess of arsenite being determined by titration with potassium bromate. Secondly, the hydrogen peroxide is determined by titration with potassium permanganate. Lastly, excess of sodium arsenite is added to the solution, the liquid boiled for some time, and the sodium arsenite remaining is determined by titration with potassium bromate. In this way the concentration of the perdisulphuric acid was determined. The method, so far as it is concerned with the determination of Caro's acid with hydrobromic acid, was carefully checked, and the results obtained indicate its reliability.

EXPERIMENTAL.—In view of the difficulties connected with the titration of hydrogen peroxide in the presence of Caro's acid by potassium permanganate, this method was abandoned. It was, however, found that accurate results could be obtained by substituting ceric sulphate for potassium permanganate. At the ordinary temperature, titrations of hydrogen peroxide with ceric sulphate in the presence of Caro's acid are subject to irregularities similar to, though appreciably smaller than those encountered when potassium permanganate is used. When,

however, the titrations are carried out at 0° C. by placing a few fragments of ice in the titration flasks, accurate results are obtained. The best results were obtained by placing a little ice in the flask, adding about 1 c.c. less than the volume of ceric sulphate required to oxidise the hydrogen peroxide in the mixture (as found by a previous direct experiment), then adding the measured volume of the liquid taken for analysis, and finally completing the titration. No indicator was added. The presence of the slightest excess of ceric sulphate was clearly visible if the titrations were carried out in good daylight. In this connection it may be noted that triphenylmethane dyestuffs, such as brilliant green, were found to be very valuable as indicators for standardising solutions of ceric sulphate against ferrous ammonium sulphate, but were useless for the present purpose, as they invariably were bleached during the titrations.

For the determination of Caro's acid it was found that a solution of vanadyl sulphate was an admirable reducing agent. At the ordinary temperature Caro's acid oxidises vanadyl sulphate quantitatively to vanadic acid, whereas perdisulphuric acid is without appreciable action. Even after an interval of 24 hours the amount of oxidation at the ordinary temperature is very small. The solution of vanadyl sulphate was prepared by dissolving 10 grms. of ammonium vanadate in 400 c.c. of dilute (1 : 3 by volume) sulphuric acid, and diluting the resulting solution to 1 litre. It was then reduced to the quadrivalent condition by adding a slight excess of solid sodium sulphite, and boiling thoroughly to expel sulphur dioxide. When cool, the dark blue solution was ready for use. The reaction with Caro's acid is as follows:

$$H_2SO_5 + V_2O_4 = H_2SO_4 + V_2O_5.$$

It was found that a solution of vanadyl sulphate could be oxidised completely by potassium permanganate at the ordinary temperature, if a little patience is exercised in realising the end-point. The determination of Caro's acid was effected as follows:—First, the hydrogen peroxide, if present, was determined by direct titration with ceric sulphate in ice-cold solution. The liquid was then allowed to attain the ordinary temperature, and a measured excess of vanadyl sulphate was added. The vanadyl sulphate remaining unoxidised was then titrated with a standard solution of potassium permanganate. In some experiments the perdisulphuric acid was determined by again adding a measured excess of vanadyl sulphate, boiling the solution thoroughly, and titrating the excess with potassium permanganate. It was, however, usually found more convenient to determine the Caro's acid and perdisulphuric acid together at this stage by the well-known ferrous sulphate and permanganate method.

A large number of experiments were made, and particular care was taken to verify the reliability of the ceric sulphate method for estimating hydrogen peroxide, and also the vanadyl sulphate method for estimating Caro's acid. The solutions of Caro's acid were prepared by triturating potassium persulphate with about double the weight of concentrated sulphuric acid, keeping the mixture cold. After about three-quarters of an hour the liquid was poured on to crushed ice, and diluted to the desired volume. Careful qualitative tests with titanic sulphate showed the absence of hydrogen peroxide from these solutions. The solutions of hydrogen peroxide were prepared directly from sodium perborate, in order to avoid the use

of a substance containing any oxidisable organic preservatives. The solutions required for the analytical experiments were then prepared by mixing the Caro's acid solutions and the sodium perborate solutions in the desired proportions. It was found that the titration value of hydrogen peroxide by ceric sulphate in the presence of Caro's acid was occasionally about 1 per cent. below that observed when the solutions of sodium perborate were titrated directly. Comparison of the results for Caro's acid, as determined by the vanadyl sulphate method, with those obtained by allowing the acid to liberate bromine from potassium bromide, and titrating with sodium arsenite, with methyl orange as indicator, showed similar slight differences, the results obtained by the vanadyl sulphate method usually appearing appreciably lower. The following results may be quoted by way of illustration:

A solution of Caro's acid was prepared, as already described, from 16 grms. of potassium persulphate and 20 c.c. of concentrated sulphuric acid. After quenching with ice, the liquid was diluted to one litre. A solution of 10 grms. of sodium perborate was also prepared, and equal volumes of the two solutions were mixed together.

Ten c.c. of the original sodium perborate solution required 28·5 c.c. of a solution of ceric sulphate (approximately $N/20$).

Twenty-five c.c. of the Caro-perborate mixed solution required 35·1 c.c. of ceric sulphate. The "estimated" titration should have been 35·6 c.c.

Fifty c.c. of vanadyl sulphate were now added, and the resulting solution required 35·0 c.c. of potassium permanganate solution (3·108 grms. per litre).

Fifty c.c. of vanadyl sulphate alone required 44·8 c.c. of permanganate. From this the available oxygen corresponding with the Caro's acid is 0·308 grm. per litre.

Determinations of the Caro's acid in the undiluted solution by the vanadyl sulphate method gave values, expressed in terms of available oxygen, of 0·604 grm. per litre. When the potassium bromide method was employed, the value was found to be 0·616 grm. per litre.

When the solutions were mixed in the ratio of 2/5 of sodium perborate to 3/5 of Caro's acid, closer agreement was observed. The Caro's acid, expressed in terms of available oxygen, was found to be 0·35 grm. per litre by the vanadyl sulphate method, and 0·345 grm. per litre by the potassium bromide method.

In some special experiments which were made in order to determine the influence of perdisulphuric acid upon vanadyl sulphate at the ordinary temperature, it was found that 20 c.c. of a solution of acidified potassium persulphate (20 grms. per litre), when left in contact with 50 c.c. of a solution of vanadyl sulphate for 24 hours, resulted in the oxidation of a quantity of the vanadyl sulphate corresponding with about 1·5 c.c. of $N/10$ potassium permanganate solution. The error involved in determinations of Caro's acid, by leaving the vanadyl sulphate for 24 hours in contact with the Caro's acid before titration with potassium permanganate, amounted to about 2 per cent.

In conclusion, it may be added that many similar experiments in the hands of others have confirmed the reliability of these new methods.

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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.

METHODS OF TESTING MINUTE QUANTITIES OF MATERIAL FROM PICTURES AND WORKS OF ART

THE problem of testing minute samples is quite different from that of examining large quantities of material for traces of impurities, and is largely a question of methods of manipulation. I had recently to examine some small samples of plaster, covered with gold leaf, from Egypt, the problem being to try to decide the medium with which the gold had been attached. Tests for wax and resins can be applied by repeatedly wetting a sample under the microscope with a drop of a suitable volatile solvent and allowing it to evaporate. A surrounding circle of any soluble material is soon obtained. The particles in question were found to be free from beeswax, and, on moistening with water and with dilute acid and evaporating, no ring of glue or gum appeared. A test for nitrogen was made on the substance mixed with soda-lime in a very small crucible, pushed through a hole in a sheet of asbestos board and heated from below with a small spirit-lamp flame. A microscope cover-glass was laid on the top with a fragment of wet neutral litmus paper sticking to it, to test for ammonia. The presence of ammonia was confirmed by repeating the experiment with another cover-glass moistened with a drop of platinum chloride. The crystals of the ammonium salt were clearly visible under the microscope. In testing for phosphorus the material was oxidised on a quartz slide with a mixture of strong sulphuric and strong nitric acid. Another method used was to fuse the material on the quartz slide with potassium nitrate. The fused mass was dissolved in nitric acid, a drop of ammonium molybdate solution was placed on the slide, and the two drops brought into contact. Phosphates were absent. Testing for sulphur proved a difficult matter. The method finally adopted was to moisten a minute platinum spatula with a strong solution of sodium hydroxide prepared from sodium, to press the wet spatula on to the powder to be examined, gently dry, put on a drop of the strong caustic soda solution, and heat the mixture in a small spirit-lamp flame until the mass ceased to bubble. It was then scraped off on to a clean silver plate, dissolved in a drop of water, a drop of dilute hydrochloric acid placed near the drop of water, and the silver plate tipped so as to allow the drop of acid to flow gently into the drop of water. The drop of acid must not be too large, as the drop of water must only be partly flooded. Under these conditions the reaction is very sensitive. Sulphur was found to be present. The conclusion arrived at was that white-of-egg had been used.

Testing for sulphates by the Hepar test should be carried out as follows:—It must not be done in a gas flame (owing to the sulphur present in the gas). A mixture of sodium and potassium carbonates (in the usual proportions) with a little cream of tartar, is made into a stiff paste. This is placed on a platinum wire loop and pressed on to a minute pinch of the powder to be tested. The mass is heated in the spirit-lamp flame until it just fuses, the bead is then dipped into cream-of-tartar powder, and again heated for a few seconds in the flame. The silver test described above is carried out as before.

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THE REICHERT–MEISSL VALUE OF THE FAT IN GORGONZOLA CHEESE

A VERY low figure having been obtained for the Reichert–Meissl value of the fat in certain samples of Gorgonzola cheese, the question arose whether prolonged keeping of the cheese might affect this figure.

At the end of September, 1932, a large piece of fresh Gorgonzola cheese was bought; it contained, on the average, 27 per cent. of fat, the Reichert–Meissl, Polenske and Kirschner values of which were determined. The remainder of the sample was kept in a large jar covered with a plate of glass. Other determinations were made in November, 1932, January and March, 1933, the sample becoming gradually so over-ripe as to be uneatable.

The average results of the duplicate determinations made at each date were as follows:—

	September	November	January	March
Reichert–Meissl value ..	19·8	17·3	10·0	7·8
Polenske value	1·9	2·2	2·6	2·2
Kirschner value ..	14·2	12·5	6·9	5·7

Parkes (ANALYST, 1911, **36**, 63) refers to the fact that the Reichert–Meissl value of the fat of Gorgonzola cheese is frequently low (about 22), and Kirsten (ANALYST, 1899, **24**, 34) refers to a Neufchatel cheese, the Reichert–Meissl value of the fat of which was lowered from 29 to 26 by a month's ripening.

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A RAPID METHOD FOR THE DETERMINATION OF ARSENATES

WILLIAMSON's method, and other methods in which hydriodic acid is used for the determination of arsenates, have three drawbacks:—(i) A high acid concentration and the use of a large excess of potassium iodide. (ii) The possibility of back-reaction between free iodine and arsenious acid. (iii) A lengthy period of time to ensure reduction.

In the method detailed below, which is applicable to most arsenates, it is possible to employ a very small quantity of iodine to secure the reduction of the arsenate. The iodine is automatically reduced by the phosphorus as rapidly as it is formed from the oxidation of hydriodic acid. The time taken to secure complete reduction is never more than three minutes at boiling point, and the acid concentration used throughout is comparatively low.

From 0·25 to 0·5 grm. (representing about 0·15 grm. of arsenious oxide) of the arsenate is weighed and transferred to a beaker. Twenty c.c. of water and 5 c.c. of concentrated sulphuric acid (sp.gr. 1·84) are added, and then 2 c.c. of $N/10$ iodine solution and 0·2 grm. of amorphous phosphorus, so fine that the whole of it will pass through a 100-mesh sieve.

The contents of the beaker are heated to boiling point and maintained at this temperature until reduction is complete (approximately 3 minutes)—*i.e.* until the yellow colour (due to free iodine) has disappeared and the solution is colourless, with the exception, of course, of particles of red phosphorus in suspension. The mixture is filtered warm through a Gooch crucible with asbestos pad, and the residue is washed with three successive portions of 10 c.c. of water. The filtrate is rendered nearly neutral with 5 N sodium hydroxide solution and titrated with $N/10$ iodine solution after the addition of excess of sodium bicarbonate.

The following results were obtained in test determinations:—A standard ($N/10$) solution of arsenic oxide was prepared by oxidising 2·475 grms. of arsenious

oxide with nitric acid and making the solution up to 500 ml. with water, after removal of the excess of nitric acid. Fifty ml. of this solution, reduced as described, after the addition of 10 ml. of concentrated sulphuric acid to preserve the degree of concentration necessary for reduction, required 49·95 ml. of $N/10$ iodine solution previously standardised against $N/10$ arsenious oxide solution.

Lead arsenate (0·5 grm.), treated exactly as described, required 28·4 ml. of $N/10$ iodine solution, as against 28·25 ml. by Mohr's sulphur dioxide reduction method, and 28·50 ml. by the method of K. and W. Bottger, described in Mitchell and Ward's *Quantitative Chemical Analysis*, 1932, p. 34.

M. FITZGIBBON

LUNEVALE PRODUCTS LTD.
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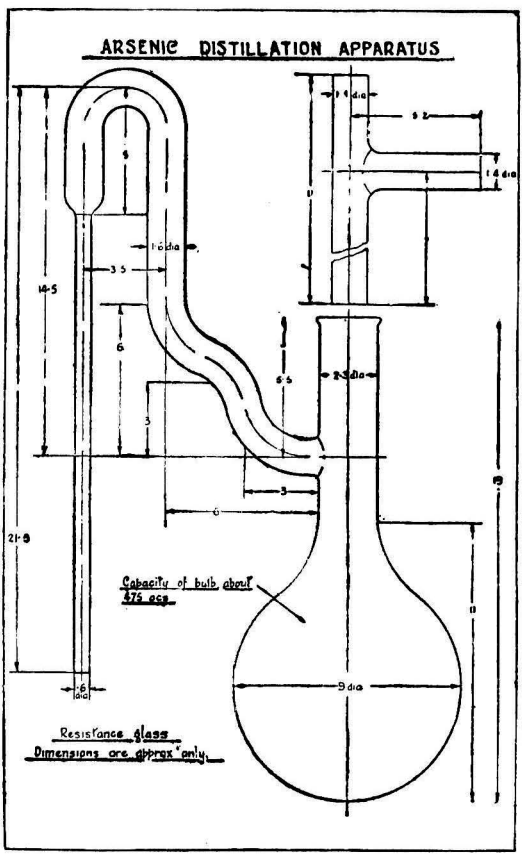
ARSENIC-DISTILLATION APPARATUS WITHOUT GROUND-GLASS CONNECTIONS*

THE apparatus consists of a modified Wurtz flask and a T-piece, as shown in the diagram. The T-piece is held in position in the neck of the flask by an ordinary



bored cork, through which the end of the T-piece just projects, the position of the T-piece being that shown in the diagram lowered by about 1-inch. The upper

* Communication from the Research Department, Woolwich

end of the T-piece is closed by a cork carrying a thermometer, and the side arm is connected with a supply of compressed air. The leading tube is attached to a Liebig condenser by means of a bored cork, the position of the latter being at the top of the narrow portion, so that the open end of the leading tube is well down in the cooled part of the condenser. During distillation a slow stream of air is passed through the apparatus, and, with a suitable rate of flow, it will be found that a cushion of air prevents the acid from attacking the cork, the acid fumes being visibly "patted" down when they get slightly above the level of the side tube. As the free end of the leading tube is well down in the cooling system, the acid fumes at this end are condensed and prevented from attacking the condenser cork.

B. S. EVANS

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.

CITY OF LEEDS

ANNUAL REPORT OF THE CITY ANALYST FOR 1932

THE total number of samples examined in 1932 was 3710, of which 1993 were food and drugs; 207 of these were adulterated.

FORMALIN IN MILK.—Of the 1295 samples of milk examined, 181 failed to comply with the Sale of Milk Regulations, 1901. For the first time during the past five years samples (3) contained formalin and annatto (5).

COMPOUND BISMUTH LOZENGES.—Two of 9 samples failed to conform to the B.P. standard (bismuth oxycarbonate, 0·15 grm.; magnesium carbonate, 0·15 grm.; calcium carbonate, 0·3 grm.). One was deficient in bismuth oxycarbonate, magnesium carbonate and calcium carbonate to the extent of 33·3 per cent., 33·3 per cent.; and 13·3 per cent., respectively, whilst the other contained 13·3 per cent. too little bismuth oxycarbonate, and 20 per cent. too little calcium carbonate. The manufacturers explained the deficiency by stating that excess of sugar had been used in the preparation of the lozenges. This explanation did not account for the fact that the percentages of all three constituents had not been equally lowered. A subsequent sample was satisfactory.

ANALYSES OF LEEDS DUST.—At a recent conference in Newcastle Dr. J. T. Dunn said that he had found appreciable amounts of arsenic and lead in Newcastle dust. It was therefore decided to examine samples of dust from six different parts of Leeds, and the accompanying table summarises the results obtained.

		Arsenic (oxide) Per Cent.	Lead Per Cent.	Copper Per Cent.
No. 1.	Clock Chamber, Leeds Town Hall	0·013	0·05	0·06
2.	Turret Floor, Market Buildings	0·035	0·46	0·15
3.	Bell Tower Floor, Christ Church, Meadow Lane	0·012	1·50	0·72
4.	Disused Office, Sth. Accom. Rd.	0·018	0·44	0·05
5.	Tower Floor, Harehills Congregational Church	0·020	0·02	0·03
6.	Belfry, Whitkirk Church	0·004	0·004	0·01

It is evident that the amounts of arsenic, lead, and copper which can occur in and near the centre of an industrial city are quite appreciable. As was expected,

the smallest amounts of all three were found on the extreme outskirts, as represented by Whitkirk. Again, at Harehills, about 2 miles out, the amounts of lead and copper were less than those in and about the centre of the city, the sieved floor dust from the bell tower of Christ Church, Meadow Lane, being the most highly contaminated. On the other hand, the arsenic-content of the latter was actually less than that at Harehills. It may be that the lighter particles of white arsenic are carried much further by the wind than the heavier lead and copper. The arsenic is derived both from the combustion of coal and coke and from smelting operations.

The lead and copper are likely to be disseminated into the air as a result of various industrial processes which are accompanied by the production of the dust of these metals. They may also find their way into the air from the combustion of low-grade coals. (*Cf.* Dunn and Bloxam, p. 500.)

C. H. MANLEY

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

THE scope of the work undertaken in the Government Laboratories at Singapore and Penang, under the direction of the Government Analyst (Mr. J. C. Cowap) has been similar to that described in the Report for the previous year (ANALYST, 1932, **57**, 653), and has been largely concerned with the protection of revenue.

The number of samples of toddy examined has shown an increase from 2248 to 3453. Regular analyses, together with the results of the investigation into the analytical characteristics of coconut toddy (ANALYST, 1932, **57**, 627), and stricter control by the Monopolies Department of the sources and sale of toddy, have had the result that a much purer and very much less harmful beverage is supplied than was available to the consumer a few years ago.

A Committee was appointed by the Governments of the Colony and Federated Malay States to inquire into the Regulations under the Sale of Food and Drugs Ordinance regarding milk and ghee. Recommendations were made that condensed milks should be of a standard minimum quality, and that alterations in the labelling regulations should be made.

Definition of Ghee.—Hitherto "ghee" has been a generic term for almost any kind of edible oil or fat, but it was recommended by the Committee of the two Governments that the name should be confined exclusively to fat prepared from the milk of the cow, buffalo or goat.

POLICE DEPARTMENT.—*Toxicology.*—Thirty-nine exhibits associated with poisoning cases were examined. The poisons found included opium, phenols, tuba, alkalis, acids, potassium cyanide, strychnine, brucine, datura and powdered glass. In one case of attempted poisoning the contents of a small sack, which had been discovered suspended in a well, were found to be a mixture of pounded tuba root, datura seeds and gadong (a wild yam)—three well-known poisons.

In addition to the foregoing, ten other specimens in cases of the unauthorised use or sale of poisons were examined. One of these consisted of a large number of St. Ignatius beans (containing strychnine and brucine) which were being sold as a remedy for stomach ache.

Counterfeit Coins.—Exhibits were received in nineteen cases connected with counterfeit coins. Coins made by local counterfeiters are generally manufactured from an easily fusible alloy, are cast in plaster of paris moulds and

are then silvered. Several complete outfits for making coins by this method were examined. Other counterfeit coins made from harder alloys, such as brass or a copper-silver alloy, are, in general, believed to be imported, but this year the police seized a full equipment for making coins of this kind. It consisted of furnaces, crucibles, metals, a rolling mill, stamps, dies, etc. The total number of coins received was 2,019.

General.—Sixty-two specimens of fireworks were examined. Of these, forty contained prohibited ingredients. Investigations were made in two cases of bomb explosions, and, in each, the material from which the bombs had been made was discovered. Twelve suspected persons were examined in connection with coining and sedition charges. In two cases violet and green writing dyes belonging, respectively, to the suspected persons, were identified with those used in the writing of seditious documents. Other inquiries conducted for the police called for the examination of documents, inks, exhibits in cases of arson, cheating, theft, throwing of corrosives, shooting, etc.

Memorandum on British Trade Mark Law

THE Joint Committee appointed by the Board of Trade to consider the British Trade Mark Law, from the point of view of chemistry, pure and applied, comprised representatives of the following bodies, arranged in alphabetical order:—The Association of British Chemical Manufacturers, The Institute of Chemistry, The Institution of Chemical Engineers, The International Society of Leather Trades Chemists, The Society of Chemical Industry, The Society of Glass Technology, and The Society of Public Analysts and Other Analytical Chemists.*

The following bodies have, by request, been kept informed of the work of the Committee, and have had an opportunity of examining the final memorandum and of expressing their views on it:—The Biochemical Society, The Faraday Society, The Institution of Gas Engineers, The National Federation of Associated Paint, Colour and Varnish Manufacturers, and The Society of Dyers and Colourists.

The Chairman was Mr. C. A. Hill, and the Secretary, Mr. A. J. Holden.

The observations in the Committee's Memorandum (dated June 26th, 1933) are arranged in the order of the Trades Marks Acts to which they refer. Very briefly summarised, they are as follows:

DESCRIPTIVE MARKS (*Trade Marks Act*, 1905, *Sec.* 9).—It is suggested that some guidance might, with advantage, be given to the Registrar in the matter of "descriptiveness."

TRADE MARK APPEALS (*Trade Marks Act*, 1905, *Secs.* 12, 14, 20, 23, 32, 34, etc.; *Trade Marks Act*, 1919, *Secs.* 8, 9, 11).—It is suggested that, in many cases, an Appeal Tribunal, identical with, or constituted similarly to, the Patents Appeal Tribunal, might be substituted for the Board of Trade or the High Court.

ASSIGNMENT OF TRADE MARKS (*Trade Marks Act*, 1905, *Sec.* 22).—It is recommended that suitable amendments should be made in the existing law so as to provide for the following points:

(i) That a Registered Trade Mark which has not been associated, or is no longer associated with goods, should be freely assignable without reference to goodwill other than that intrinsic value which it may possess and which may be the basis for a future goodwill; provided always that such assignment, in the case of a mark which has been associated with goods, is not calculated to deceive the public.

* Represented by Dr. L. H. Lampitt

(ii) That a Registered Trade Mark should be assignable with the goodwill in the particular goods upon which it has been used, even when the goodwill in goods of the same class distinguished by a different trade mark is not assigned.

(iii) That a parent company and its subsidiaries should be allowed to use in common a mark (*e.g.* a house mark) registered by the parent company.

(iv) That a parent company should be allowed to use any mark registered by its subsidiary companies.

CHANGE IN NATURE OF CONNECTION BETWEEN GOODS AND OWNER (*Trade Marks Act*, 1905, *Sec.* 35).—Deception will only occur if the public has come to recognise the mark as indicating manufacture only, but usually the mark merely means the connection between the owner and the goods defined in Section 3. It is recommended that it should be made clear in the Act that so long as the relation between the goods and the owner of the mark remains within the definition, no change in that relation will endanger the mark.

PIRATING OF TRADE MARKS (*Trade Marks Act*, 1905, *Sec.* 39).—It is suggested that the existing law be amended in such a way that (i) it is clearly defined that the use by one trader of the Registered Mark of another in any manner shall constitute an infringement; (ii) that a fine recoverable summarily should be imposed as a penalty for such offence, in addition to any other remedy already existing.

UNAUTHORISED USE OF TRADE MARKS (*Trade Marks Act*, 1905, *Sec.* 39).—It is suggested that the rights obtained by registration of a trade mark should include the right to prevent the use of the mark in relation to the goods by any other person, without the expressed consent of the registered owner.

TRADE MARK AS ONLY CONVENIENT NAME FOR GOODS (*Trade Marks Act*, 1919, *Sec.* 6).—In view of differences of opinion on this point, the Committee are unable to put forward any suggestion.

CLASSIFICATION OF MARKS (*Trade Mark Rules*, 1920, *Rule* 5).—To prevent conflict between goods in different classes, it is suggested that there should be a grouping of classes in accordance with trade distribution, any trade mark registered in one class of a group being citable against an application in any class in the same group.

BRITISH EMPIRE TRADES MARKS CONVENTION.—The suggestion is made that there should be a British Empire Trades Marks Convention, formed on lines similar to the Berne Arrangement, under which subjects of the Empire would be assured of the protection of their marks throughout the Empire. A suggested scheme for this purpose is discussed in the Appendix to the Memorandum.

COSTS.—It is strongly urged that the question of costs awarded by the Registrar or the proposed Appeal Tribunal should be revised, to bring the scale into line with the Patents side of the Office.

GENERAL.—The Committee support, in general, the proposals of the Trades Marks, Patents and Designs Federation, especially in regard to the following matters of particular chemical interest: Revision of Classification; Refused List; Standardisation Marks; Unassailable Marks.

The Determination of Small Amounts of Bismuth in Copper

THE following communication has been received from the Fiscal Policy Technical Sub-Committee of the Brass and Copper Industries, with a request for its publication:

"In view of various developments which have recently taken place in the metallurgy of copper and brass, the effect of small proportions of bismuth upon the mechanical and other properties of these materials has assumed greater importance than ever before. Simultaneously, the development of various sources of copper which may contain more or less bismuth has rendered it supremely important for the manufacturer to be able to know with certainty the bismuth-content of the metal he is employing.

"Since the proportions of bismuth which have to be determined are very small, the actual estimation is an operation which presents considerable difficulties, and a careful examination of the whole position by the Technical Sub-Committee of the Fiscal Policy Committee of the Brass and Copper Industries has shown that there is generally a good deal of uncertainty in the assays which are made. Since the bismuth-content affects the buying and selling of many thousands of tons of copper per annum, it is obviously essential that entirely sound and reliable results shall be obtained when analysing for this element, and in an endeavour to arrive at such a position the above-mentioned Technical Committee has thoroughly investigated the matter.

"As a result of this examination, a set of principles has been enunciated by the Committee which they consider will, in the hands of competent analysts, produce reliable and reproducible figures. In making a statement of these principles, the Committee does not wish it to be believed that it is excluding other possible methods, but wishes to affirm that, in laying down certain rules, it has produced a means whereby sound analytical results can be obtained.

"In view of the exceedingly great importance of securing the most complete reliability in analysing for bismuth, the Committee would be grateful if you would arrange to give publication to the document enclosed and also to this letter, which explains how it came into existence. It is hoped that by these means, all those who are interested in this problem will have an opportunity of seeing and criticising these proposals with a view to the eventual perfection of this particular determination, and the Committee will be glad to receive from interested parties any comments or suggestions tending towards this result. These should be addressed to the Secretary (Mr. Lester Smith, c/o Squiers & Co., King's Court, 115, Colmore Row, Birmingham, England)."

(*Signed*) A. J. G. SMOUT (*Chairman*)
J. LESTER SMITH (*Secretary*)

THE DETERMINATION OF SMALL PROPORTIONS OF BISMUTH IN COPPER (Up to 0·020 per cent.)

"In dealing with this matter, it has been considered desirable to enunciate those analytical principles which should be observed in making an analysis for bismuth, rather than to lay down details of chemical procedure. The intention is to provide a set of rules which, in the hands of competent analysts, will produce reliable results. Within the principles enunciated, there is ample scope for variation in accordance with individual preference. It is not claimed necessarily that the methods which would follow from the given rules are the only ones which may give reliable results, but it is claimed that the principles set out below, if faithfully observed, will always yield reliable and reproducible values.

(1) The proportions of bismuth in question are too small to allow of satisfactory determination by gravimetric means. If a gravimetric estimation is attempted, it is necessary to use a very large quantity of material and, as a result, the operations involved in the separation of the bismuth become too clumsy for the requisite accuracy to be obtained. Furthermore, the handling of the final precipitate presents marked difficulties in view of the small quantity which is present.

(2) The most satisfactory method of determining the bismuth is by colorimetric means, and a suitable reaction for this purpose is that between bismuth sulphate and potassium iodide. This reaction releases bismuth tri-iodide, which dissolves in an excess of potassium iodide, producing a yellow solution.

(3) In opening out the copper, solution should be effected by nitric acid. Ten c.c. of nitric acid (sp.gr. 1·20) per grm. of copper is a suitable allowance. In the event of an insoluble residue being obtained this should be filtered off, ignited and fused with potassium bisulphate, the fusion dissolved in dilute sulphuric acid and added to the original filtrate.

(4) In order to ensure that the whole of the bismuth is precipitated during separation, it is necessary to have present a sufficient quantity of another element to act as a collector. Of the various elements which might be employed, iron is the most satisfactory. In impure coppers there may be sufficient iron present to act as a collector, but in view of the uncertainty of this iron content, it is preferable to make a specific addition of iron to the dissolved sample. (0·25 grm. of ferrous ammonium sulphate per 10 grms. of sample is a satisfactory proportion.)

(5) In precipitating the bismuth, the caustic alkalis should be definitely avoided, and an entirely satisfactory precipitant is ammonia.

(6) Re-precipitation of the mixed hydroxides of bismuth and iron is essential in order to avoid contamination of the bismuth solution finally obtained, with copper.

(7) The complete precipitation of the bismuth requires some considerable time, and it is necessary to allow the solution both for the initial precipitation and the re-precipitation of the bismuth to stand in a warm place for at least six hours.

(8) When the final precipitate of the mixed hydroxides of iron and bismuth, from which the copper has been completely removed, is re-dissolved, solution should be effected in sulphuric acid. The resulting solution should be neutralised, then brought to a condition of slight acidity, after which all the iron must be reduced to the ferrous condition. The reduction can be effected most conveniently by means of sulphurous acid.

(9) The final solution is matched against a blank solution which has been prepared by carrying through all the analytical operations as applied to the sample under assay, but to which no sample has been added. Into this resulting solution, the standard bismuth solution (containing 0·0001 grm. of bismuth per c.c.) is added until the colours match. The bismuth solution is best prepared by dissolving 1 grm. of metallic bismuth in 20 c.c. of concentrated sulphuric acid and making up to a litre.

(10) In the final solutions the acidity should be approximately 2 per cent. by volume, and the amount of potassium iodide added should be adequate but not excessive. A suitable proportion being about 10 c.c. of a 2 per cent. solution. The aliquot proportion taken of the solution under assay should be such that not more than 4 c.c. of the standard bismuth solution should be required."

"For proportions of less than 0·002 per cent. of bismuth the methods based on the above principles may not be trustworthy. Methods for the determination of these very small proportions are at present under investigation."

Ministry of Agriculture and Fisheries

STATUTORY RULES AND ORDERS

1933, No. 538

[CANNED FRUITS]

*The Agricultural Produce (Grading and Marking) (Canned Fruits) Regulations, 1933, dated May 23, 1933, made by the Minister of Agriculture and Fisheries as to Grade Designations and Grade Designation Marks for Canned Fruits.**

In exercise of the powers conferred upon him by the Agricultural (Grading and Marking) Acts, 1928, and 1931, the Minister of Agriculture and Fisheries, has prescribed grade designations to indicate the quality of apples, blackberries, cherries, gooseberries, loganberries, plums, raspberries, redcurrants, and strawberries, produced and canned in England and Wales, and the

* H.M. Stationery Office, Kingsway, London, W.C. Price 2d. net

quality indicated by such grade designations shall be deemed to be as described in column 2 of the First Schedule (*infra*).

The Grade Designation Mark is to be associated with a silhouette map of England and Wales, on which is a circle surrounding the Union Jack and inscribed with the words: "Produce of England and Wales," and associated with the words "Empire Buying Begins at Home."

These Regulations came into force on May 23, 1933.

SCHEDULE I

FRUIT PRODUCED AND CANNED IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS OF QUALITY

Grade Designation 1	Definition of Quality 2
Select Apples.	The fruit shall be of minimum diameter of 2¼ inches, cored and peeled; free from blemishes and extraneous matter, and packed solid in slices of uniform size and colour; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present.
Select Apples (in syrup).	The fruit shall be of diameters between 2¼ inches and 2¾ inches, cored and peeled; free from blemishes and extraneous matter, and packed in quarters of reasonably uniform size and colour; the fruit shall be canned in a syrup containing not less than 40 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. The syrup shall be reasonably clear.
Select Cultivated Blackberries. Select Blackcurrants. Select Dessert Gooseberries. Select Loganberries. Select Redcurrants. Select Strawberries.	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and reasonably uniform in size; the fruit shall be canned in a syrup containing not less than 45 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be firm and unbroken and the syrup shall be clear.
Select Raspberries.	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and reasonably uniform in size; the fruit shall be canned in a syrup containing not less than 45 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be reasonably firm and unbroken and the syrup shall be clear.
Select Dessert Cherries.	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and reasonably uniform in size; each fruit shall measure not less than 11/16 inch in diameter; the fruit shall be canned in a syrup containing not less than 35 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be firm and unbroken and the syrup shall be clear.

Grade Designation 1	Definition of Quality 2
Select Morello (Morella) Cherries.	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and reasonably uniform in size; each fruit shall measure not less than $\frac{11}{16}$ inch in diameter; the fruit shall be canned in a syrup containing not less than 45 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be firm and unbroken and the syrup shall be clear.
Select Dessert Golden Plums. Select Dessert Purple Plums. Select Dessert Red Plums. Select Dessert Victoria Plums. (or Select Dessert Plums.) Select Dessert Damsons. Select Dessert Greengages.	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and reasonably uniform in size; the fruit shall be canned in a syrup containing not less than 40 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be firm and unbroken and the syrup shall be clear.
Select Dessert Victoria Plums (Halves).	The fruit shall be firm-ripe, free from blemishes, stalks, leaves, and other extraneous matter, and shall be cut longitudinally in halves, reasonably uniform in size; the stones shall be removed but a proportion of kernels may be added; the fruit shall be canned in a syrup containing not less than 40 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruit shall be firm and unbroken and the syrup shall be clear.
Select Raspberries and Redcurrants.	The fruits shall be firm-ripe, reasonably uniform in size for each kind, free from blemishes, stalks, leaves and other extraneous matter; the proportions of each fruit shall be approximately equal by weight; the fruits shall be canned in a syrup containing not less than 45 per cent. by weight of sugar (saccharine and glucose free) when packed; no preservatives and/or artificial colouring agents prohibited under the Public Health (Preservatives, etc., in Food) Regulations in force for the time being shall be present. After processing the fruits shall be reasonably firm and unbroken and the syrup shall be clear.

1933, No. 592

[WHEAT FLOUR]

The Agricultural Produce (Grading and Marking) (Wheat Flour) Regulations, 1933, dated June 12, 1933, made by the Minister of Agriculture and Fisheries as to Grade Designations and Grade Designation Marks for Wheat Flour.*

The Minister has prescribed the following grade designations to indicate the quality of meal and flour produced from wheat grown in England and Wales:

ALL-ENGLISH (WHOLEMEAL) OR NATIONAL MARK WHOLEMEAL.
ALL-ENGLISH (STRAIGHTS) OR NATIONAL MARK STRAIGHTS.
ALL-ENGLISH (PATENTS) OR NATIONAL MARK PATENTS.
ALL-ENGLISH SECONDS.
ALL-ENGLISH (SELF-RAISING) OR NATIONAL MARK SELF-RAISING.

* H.M. Stationery Office. Price 1d. net. [In the previous Order, S.R.O., No. 753, 1929; ANALYST, 1930, **55**, 45) there was a specified ash-content of 0·55 per cent. for all flours, but no criteria for fibre or moisture.—EDITOR.]

And the quality indicated by such grade designations shall be deemed to be as described in the First Schedule (*infra*).

The grade designation mark shall be one of the grade designations specified, associated with the design and words described and illustrated in the Second Schedule.

SCHEDULE I

Definitions of Quality

In all cases the Meal or Flour shall be sound, free from taint or objectionable flavour, of good keeping quality, and unbleached by artificial means, made exclusively from sound, well-cleaned wheat grown in England and Wales and in addition the articles specified in the first column hereunder shall have the qualities or characteristics specified opposite these respectively in the second and third columns hereunder

Grade Designation 1	Type 2	Special Characteristics 3
All-English (Wholemeal) or *Alternatively* *National Mark Wholemeal.	The Wholemeal shall comprise at least 95 per cent. of the ground products of the wheat. No bran may be added to or flour extracted therefrom.	*The Ash-Content*, as ascertained in a muffle furnace, shall exceed 1·25 per cent., but shall not exceed 1·70 per cent. of the total weight of the meal calculated on the basis of 15 per cent. moisture-content, and on the same basis the *Fibre*-content shall exceed 1·25 per cent. but shall not exceed 2·0 per cent.
All-English (Straights) or *Alternatively* *National Mark Straights.	The flour shall comprise all the flours obtainable from the wheat.	*The Ash-content*, as ascertained in a muffle furnace, shall not exceed 0·52 per cent. of the total weight of flour calculated on the basis of 15 per cent. moisture-content.
All-English (Patents) or *Alternatively* *National Mark Patents.	The flour shall be as produced at the head end of the mill from "purified" stock.	*The Ash-content*, as ascertained in a muffle furnace, shall not exceed 0·45 per cent. of the total weight of flour calculated on the basis of 15 per cent. moisture-content.
All-English (Seconds).	The flour shall comprise the residue of the flours not otherwise separated as Patents.	*The Ash-content*, as ascertained in a muffle furnace, shall not exceed 0·62 per cent. of the total weight of flour calculated on the basis of 15 per cent. moisture-content.
All-English (Self-Raising) or *Alternatively* *National Mark Self-Raising.	The flour shall comprise National Mark Straights and/or National Mark Patents along with the addition of suitable raising ingredients.	The flour shall contain such ingredients or mixture of ingredients in such quantities and proportions as are properly required to make the flour self-raising.

Where the meal or flour is made exclusively from wheat of "Yeoman" varieties grown in England and Wales, the word "Yeoman" may be included as part of any of the grade designations as set out in Column 1, *e.g.* All-English (Yeoman) Wholemeal, etc.

* The alternative words "National Mark" may only be used in connection with meal or flour to which the Grade Designation Mark as set out in Schedule II has been lawfully applied in accordance with the Agricultural Produce (Grading and Marking) (General) Regulations, 1928.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Composition of Whites, Yolks and Whole Broken Eggs from Commercial Egg-Breaking Establishments. L. C. Mitchell, S. Alfend and F. J. McNall. (*J. Assoc. Off. Agric. Chem.*, 1933, **16**, 247–255.)—In the table below, percentage values are given for 74 samples (3 to 16 days old) of separated whites (A) and yolks (B), and for "broken-out" whole eggs (C) treated on the commercial scale. The methods used were those of L. C. Mitchell (ANALYST, 1932, **57**, 522), and the results should be compared with those obtained on the laboratory scale (*loc. cit.*).

		Solids	Fat	P_2O_5	Total nitrogen	Water-soluble nitrogen
A.	Average ..	12·34	—	—	1·74	1·63
	Maximum ..	12·91	—	—	1·85	1·71
	Minimum ..	11·69	—	—	1·64	1·53
B.	Average ..	45·87	28·04	1·24	2·51	0·60
	Maximum ..	48·06	29·54	1·30	2·58	0·67
	Minimum ..	43·44	26·10	1·14	2·40	0·53
C.	Average ..	26·80	12·15	0·56	2·08	1·16
	Maximum ..	28·33	13·57	0·63	2·18	1·23
	Minimum ..	25·97	11·30	0·51	1·99	1·08

J. G.

Determination of the Egg-Content of Pastry. B. Alberti. (*Chem.-Ztg.*, 1933, **57**, 454–456.)—Juckenack's method (*Z. Unters. Nahr. Genussm.*, 1900, **3**, 1) is based on a determination of the lecithin phosphoric acid soluble in alcohol, but is not regarded as trustworthy for old samples (*cf.* Tillmans, Riffart and Kühn, ANALYST, 1931, **56**, 118); the results may also be influenced by the method of preparation and the nature of the ingredients used. Experiments with ether as extracting agent have shown that the extract (mean value) obtained after 4 hours fell from 2·77 per cent. with an air-dried sample to 2·63 per cent., when the material had been dried for 3 hours at 105° C., and to 2·23 per cent. after it had been dried for 3 hours at 120° C. The ethereal extract from a fresh air-dried sample, containing 9·0 to 12·3 per cent. of water, was 5 to 15 per cent. less than that obtained after mixing 10 grms. of the air-dried sample with 2 c.c. of water, whilst for old samples this difference amounted to 120 per cent. Corresponding differences were also obtained for the alcohol extractions (which were always considerably greater individually than the corresponding ethereal extractions), and determinations of the egg-content (0·8 to 3·4 per 500 grms.) from the lecithin phosphoric acid value, gave results 20 to 100 per cent. higher for the moistened material. Possible changes in the nature of the lecithin which may occur on ageing are discussed, and it is suggested that the above results support the view of Cohn (*Chem.-Ztg.*, 1913, 581), who attributed the lower results obtained with old material to a physico-chemical adsorption of the lecithin by the proteins present (*cf.* ANALYST, 1913, **38**, 205).

J. G.

Iodised Eggs. A. D'Ambrosio. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 231–233.)—The minimum daily dose of iodine necessary to man is usually taken as about 50γ (γ = 0·001 mgrm.), although it varies appreciably with sex, age, climate, altitude, etc. The amount of iodine present in the ordinary hen's egg ranges, in different countries, from about 0·5γ to about 2·5γ, but may be increased enormously by supplying the hens with iodised feed. In Germany the use of "Rukota," consisting of straw, husks, fishmeal, iodides, thiocyanates, cadmium salts, and an oxidising agent capable of displacing iodine from iodides in an acid medium, has led to the production of eggs containing 60γ or more of iodine. In Hungary the iodine-content has been raised in this way to 2500γ, and in Italy eggs containing as much as 260,000γ have been obtained. Iodo-brominated eggs, with about 700γ of iodine and 50,000γ of bromine, are also marketed.

In eggs with an iodine-content not exceeding about 10,000γ, about 90 per cent. of the iodine occurs in the yolk, but with hyper-iodised eggs containing about 260,000γ of iodine this element is found in about equal amounts in white and yolk. It seems that the iodine first saturates the double linkings of the unsaturated fatty acids of the lecithin; any excess then passes to the white of the egg being partly adsorbed and partly converted into iodotyrosine or iodoglobulin. About an hour after a hyper-iodised egg is eaten, iodine is detectable in the urine by means of sodium nitrite; after 48 hours, only traces are present, but on the third day an appreciable quantity is found if the organic matter of the urine is first destroyed.

In order to obtain results comparable with those already published, the iodine in the eggs was determined by a slight variation of Fellenberg's modification of Zahoránszky's method (*cf.* Jaschik and Kieselbach, ANALYST, 1932, **57**, 105; Andrew, ANALYST, 1930, **55**, 269). It is found, however, that this method involves considerable loss of iodine, particularly from the white. For instance, two egg-whites, weighing, respectively, 31 and 32 grms., showed 11,430 and 12,340γ of iodine by Fellenberg's method, whilst two similar ones (33 and 32 grms.) gave 128,905 and 124,600γ of iodine when the albumin was peptonised either by pepsin or by hydrochloric acid under pressure at 135° to 140° C., and the iodine was displaced from the peptone by means of nitrite. The peptonisation method does not show the whole of the iodine, and the determination, and also the mode of combination of the iodine in the egg, are to be considered later. T. H. P.

New Reactions of Reducing Sugars. H. Wuyts. (*Compt. rend.*, 1933, **196**, 1678–1680.)—The condensation of aldehydes and ketones with aromatic thiohydrazides, in presence of a catalyst, to form aryldihydrothiodiazoles, occurs also with reducing sugars. The compounds now described have been prepared from α-phenyl-β-thiobenzoylhydrazide, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}C_6H_5$. Two grms. of the powdered hydrazide, 2 grms. of the powdered sugar, and 2 c.c. of a 5 per cent. solution of hydrochloric acid in alcohol are thoroughly mixed in a stout tube, which is then plunged for a few moments into a boiling water-bath. The mixture reddens, liquefies, and rapidly solidifies. The mass is freed from excess of the sugar by washing with water. Treatment of the residue with sodium carbonate solution, followed by acidification of this solution, shows that the hydrazide is

completely, or almost completely, utilised. The condensation products, which are obtained in high yield and moderately pure, may be purified by crystallisation from boiling ethyl or methyl alcohol, dilute for dextrose or galactose, concentrated for mannose. The arabinose compound is only slightly soluble in alcohols, but crystallises well from a mixture of pyridine and water. The condensation products are optically active and are characterised by their melting-points, which are: Dextrose, 147 to 148° C.; galactose, 178° to 179° C.; mannose, 198° C.; and arabinose, 222° C. Laevulose does not yield a definite compound, and lactose gives a product which has not yet been obtained crystalline. T. H. P.

Determination of Inactive Malic Acid in Fruits and Fruit Products. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agric. Chem.*, 1933, **16**, 277–285.)—Inactive malic acid (prepared by the catalytic oxidation of benzene to maleic acid, which is then heated with water under pressure) is a white crystalline compound with an empyreumatic odour, and is now frequently added to fruit products. The method here described depends upon the determination of the total malic acid, and of the *l*-malic acid, the difference giving the inactive malic acid. The procedure must, therefore, be carried out in duplicate. The 200 c.c. of sample solution of fruit product (jam or jelly) taken for the determination should not contain more than 20 grms. of solids, and the acidity (*A* c.c. as *N* malic acid) should not exceed 150 mgrms. It is first evaporated to 35 c.c., washed into a 250-c.c. flask with 10 c.c. of warm water, and made up to the mark with 95 per cent. alcohol. The mixture is then shaken well and filtered, care being taken to avoid evaporation of alcohol, and 225 c.c. of the filtrate are transferred to a centrifuge bottle. If esters are present they should first be saponified by treating 35 c.c. of the sample at 60° C. with 3 c.c. of *N* potassium hydroxide solution in excess of the quantity required for neutralisation; the next day the solution is neutralised with *N* sulphuric acid and is treated as described above. The filtrate is shaken for 2 minutes with 25 mgrms. of citric acid and *A* (or *A* + 3 if saponification was necessary) c.c. of a 40 per cent. solution of lead acetate in 0·5 per cent. acetic acid, and the mixture is then centrifuged at 900 r.p.m. for 15 minutes; more lead acetate should be added if precipitation is still incomplete. The centrifuge process is repeated after decantation and addition to the residue of 250 c.c. of 80 per cent. alcohol, after which the lead salts are shaken with 150 c.c. of water and the solution is saturated with hydrogen sulphide. The mixture is diluted to 250 c.c. and filtered, 225 c.c. of the filtrate being then evaporated to 100 c.c. to expel the gas, again treated (in a volume of 200 c.c.) with 5 c.c. of a 10 per cent. solution of acetic acid, and *A* (or *A* + 3) c.c. of lead acetate solution, shaken, made up to the mark, and filtered. The new filtrate (which must be quite clear) is diluted to 250 c.c., saturated with hydrogen sulphide, and filtered, and 225 c.c. of the filtrate are evaporated with 75 mgrms. of tartaric acid to 50 c.c., and neutralised to phenolphthalein with *N* potassium hydroxide solution, 5 drops being added in excess, followed by 2 c.c. of glacial acetic acid. The solution is diluted to 250 c.c. with 95 per cent. alcohol, cooled to 15° C., shaken for 10 minutes with some glass beads, and placed in the refrigerator for 30 minutes. It is again shaken for 10 minutes, and then filtered, and 225 c.c.

of filtrate (at 20° C.) are centrifuged with A (or $A + 3$) c.c. of lead acetate solution, decanted and drained and the residue is shaken with 250 c.c. of 80 per cent. alcohol centrifuged, decanted and drained. The lead salts are then boiled with 175 c.c. of water and 3 c.c. of N sulphuric acid, and 1 c.c. of 5 per cent. acetic acid is then added, together with a sufficient quantity of a freshly-prepared 2·5 per cent. solution of tribasic lead acetate to neutralise (to methyl red) 3 c.c. of N sulphuric acid in 200 c.c. of water, plus 2 c.c. in excess of that quantity.* The mixture is boiled for 5 minutes, diluted to 250 c.c., and filtered after being shaken for 5 minutes, left for 30 minutes in the refrigerator, and again shaken for 5 minutes. The clear filtrates are treated with hydrogen sulphide, shaken and filtered, and the two halves of the resulting filtrate are treated as follows:—(1) The solution (225 c.c.) is evaporated to 10 c.c. and neutralised with N potassium hydroxide solution (phenolphthalein as indicator). It is then slightly acidified with acetic acid, and, after evaporation to 5 c.c., is diluted to 27·5 c.c. (in a "Giles flask"), and shaken with glass beads and 4 grms. of uranium acetate for 10 minutes in the dark. The optical rotation of the filtrate in a 200-mm. tube at 20° C., using white light, is read after 30 minutes, and the value (in °V.) × 10·2 gives mgrms. of l-malic acid (L) in the aliquot portion.† (2) The alcohol is removed from 225 c.c. of the duplicate determination by evaporation to 10 c.c., the solution being then diluted to 120 c.c. and heated for 30 minutes in boiling water with 10 c.c. of 30 per cent. sodium hydroxide solution and 25 c.c. of a solution of potassium permanganate, equivalent to, and standardised against, a solution of 28·7556 grms. of oxalic acid per litre. The mixture is heated to about 75° C., and placed for 30 minutes in a boiling water-bath, after which 25 c.c. of the oxalic acid solution and 10 c.c. of sulphuric acid (1:1) are added, and the titration is finished at 80° C. The volume of permanganate used, multiplied by 5, gives the total oxidisable material as malic acid (T mgrms.). Then the inactive malic acid = $4(T - 5 - L)$, where 4 is the factor for converting the amount of i-malic acid in the aliquot portion into that present in the quantity of sample originally taken, and 5 is the amount of material other than malic acid in the aliquot portion, calculated as mgrms. of malic acid. The last factor is an average of figures obtained experimentally for 9 varied fruit products by subtracting the l-malic acid-content (determined polarimetrically, *cf. id.*, 1932, **15**, 645) from the total oxidisable material calculated as malic acid; the two other factors used were determined similarly. As the method is empirical, the details must be strictly observed, and the results must be corrected by subtraction of 0·01 per cent.; this figure represents the maximum error obtained for 29 varied samples (syrups and jams) containing 0 to 2·21 per cent. of added i-malic acid. The amounts of inactive malic acid in various pure fruit juices and fruits, as thus determined, ranged from −0·02 to +0·02 per cent. J. G.

* This reagent is prepared by mixing at 60° C. solutions containing 82 grms. of lead acetate in 170 c.c. of water and 5·8 grms. of ammonia (as NH_3, titrated to methyl red) in 100 c.c.; the next day the precipitate is removed by filtration, and is washed once with water, twice with 95 per cent. alcohol, and once with ether, and allowed to dry in air.

† The uranium-malic complex is sensitive to light, and the flask should, therefore, be wrapped in a cloth during the filtration and polarisation.

General Features Common to Most "Fruit Coat" Fats. T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1933, **52**, 169–171T.)—There are certain general resemblances between "fruit coat" fats of plants belonging to different families, and there are marked contrasts between the "fruit coat" fat and the seed fat from the same fruit. The "fruit coat" fats of the palm nut and olive have been the most thoroughly investigated, but data for a sufficient number are available to make a general survey possible. These fats have, as main component acids, only palmitic, oleic and linolic acids, and the proportions in which they are present determine the consistence and general properties of each fat. The same acids comprise the main part of the fats of seeds in the case of many botanical families, but, in other families, one or more other fatty acids may be a major component, and then these specific seed fat acids, as a rule, determine the characteristic features of the fats. Generally, there is no definite relation between the general nature of the component fatty acids of the "fruit coat" fats and seed fats, although, occasionally, the two are almost identical, as in olive and piquia. The glyceride structure of the two types of fats is frequently essentially different, the glycerides in seed fats being combined with glycerol in such a way that there is a pronounced tendency to evenness of structure, any single glyceride molecule probably containing two or three different acyl radicals. Several "fruit coat" fats, *e.g.* palm, olive, and laurel, contain definite amounts of fully-saturated glycerides. Although the data available for leaf or bark fats of the growing plant are only scanty, it is concluded with some confidence that, substantially, only oleic (with the related linolic and linolenic) and palmitic acids are produced in a plant during growth, but that seed or depôt fats may differ materially from one family to another, both in the kinds of fatty acids present and in their glyceride structure. D. G. H.

Composition of Commercial Palm Oils. III. H. K. Dean and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1933, **52**, 165–169T; *cf.* ANALYST, 1930, **55**, 701; 1931, **56**, 463). The ester fractionation method of analysis has been applied to a further 13 native West African palm oils of known origin, and to five plantation oils from the Belgian Congo, Malaya and Sumatra, and the data obtained (6 tables are included) are considered in relation to the whole series examined. In the districts east of longitude 4–6° W. (Gold Coast, Nigeria) the mixed fatty acids have a "titre" of 44°–45° C., and contain about 40 to 42 per cent. of palmitic, 40 to 42 per cent. of oleic, and 9 to 11 per cent. of linolic acid, the last-named forming 18 to 20 per cent. of the unsaturated acids. With oils from the Ivory Coast and Liberia the titre is lower (40°–42° C.), and the oils contain less palmitic (32 to 35 per cent.) and more oleic acid (49 to 52 per cent.), whilst there is about 8 per cent. linolic acid, forming only 13 to 14 per cent. of the unsaturated acids. In Sierra Leone, the extreme west of the palm oil area, there is again a tendency for the oil to contain more palmitic and less oleic acid. The differences are ascribed to the botanical varieties of the palms, and external conditions, such as rainfall, altitude and soil, appear to be unimportant. Moreover, the differences are closely parallel with the variations of thin-shelled (Liscombé variety) *Elaeis guineensis* (with high oil-content) in the eastern areas and of hard-shelled varieties (with lower oil-content) of Liberia and Sierra Leone. Plantation oils from Sumatra, Malaya and

Belgian Congo were, in all cases, closely similar to those of the Gold Coast, and especially of Lagos, and it is assumed that cultivated palms yield oils of composition similar to the original variety, and that this composition is independent of external factors. D. G. H.

Certain Azelao-Glycerides obtained during the Oxidation of some Simple Synthetic and Natural Glycerides. T. P. Hilditch and S. A. Saletore. (*J. Soc. Chem. Ind.*, 1933, **52**, 101–105T.)—A re-examination of the azelao-glycerides, concurrently produced during the permanganate and acetone oxidation from glycerides containing 1, 2 or 3 oleic or linolic acid radicals, and a study of the properties of a number of simple azelao-glycerides prepared by oxidation of the corresponding oleo-glycerides, have led to the conclusion that the separation and determination of triazelain, or of diazelao-mono-saturated glycerides is not practicable as an analytical aid in the determination of tri-unsaturated or of di-unsaturated-mono-saturated glycerides, but monoazelao-di-saturated glycerides can often be isolated in a fairly pure condition if the corresponding mono-oleo-disaturated glycerides form a substantial proportion (60 per cent. at least) of the whole of the original fat. Any estimate of the four divisions of mixed glycerides (tri-saturated, di-saturated—mono-unsaturated, mono-saturated—di-unsaturated and tri-unsaturated), based only on the permanganate oxidation process, should only state the proportion of completely saturated glycerides, and the limits between which the proportions of the mixed saturated and unsaturated and tri-unsaturated glycerides must lie. In the course of the investigation it was found that the oleodistearin of *Allanblackia* seed fat and some other seed fats is almost entirely the β-oleo-$\alpha\alpha'$ distearin, so that the configuration of a natural glyceride may be extremely selective. The results of the investigation are given under the headings (*a*) triazelain, (*b*) diazelao-glycerides (α-palmito and α-stearo-$\beta\alpha'$-diazelains), and (*c*) monoazelao-glycerides. Really pure specimens of *a* and *b* could not be obtained. D. G. H.

Caffeine-Content of Coffee during Ripening and Drying. E. Herndlhofer. (*Z. Unters. Lebensm.*, 1933, **65**, 561–566.)—Determination of the caffeine in coffee was made by the following modification of Fendler and Stüber's method (*ibid.*, 1914, **28**, 9): 3 grms. of the dry, powdered material are moistened with 3 c.c. of water, left for 30 minutes, and then extracted for at least 3 hours with chloroform in a Soxhlet apparatus. The extract is distilled to remove the solvent, and the residue is transferred, by means of chloroform, to a porcelain dish. After expulsion of the solvent on a water-bath, the residue is treated with hot water for about 10 minutes, and then allowed to cool. It is next treated with 10 c.c. of 1 per cent. potassium permanganate solution for 10 minutes, and then with 1 per cent. hydrogen peroxide solution (containing 1 c.c. of acetic acid per 100 c.c.) to separate the manganese as the dioxide. The peroxide solution is added first only in sufficient amount to destroy the red colour of the permanganate, a further addition being made dropwise until the liquid clears and the manganese dioxide separates in black flocks. No more hydrogen peroxide than is necessary for this should be added, since otherwise part of the caffeine would be destroyed. The liquid is left for 10 minutes on a boiling water-bath and, after being allowed to cool,

filtered into a separating funnel, into which also the washing water of the precipitate is permitted to fall. The filtrate is shaken with five separate quantities of chloroform, and the solvent is distilled from the combined extracts. The residual caffeine is washed into a Kjeldahl flask by means of chloroform, and its nitrogen-content determined as usual after evaporation of the solvent ($N \times 3{\cdot}464 \equiv$caffeine).

Determinations have been made of the total nitrogen, caffeine nitrogen, and, in some cases, protein nitrogen in Brazilian coffees of various degrees of ripeness, and after drying for different periods and under different conditions. The results obtained indicate that the method of drying coffee usually practised in Brazil leads to an increase in the caffeine-content, largely at the expense of the nitrogen-free constituents. Small-scale experiments, in which fully ripened seeds of *Coffea arabica var. nacional* were dried under varying conditions, reveal the possibility of an increase of the caffeine-content (on the dry matter) without appreciable change in the content of total nitrogen. T. H. P.

Identification of Salvarsan. M. Wagenaar. (*Pharm. Weekblad*, **1933, 70**, 597–606.)—If the vapours obtained by warming a mixture of furfural and pyridine are brought into contact (*e.g.* in a micro gas-chamber) with granules of salvarsan, these are converted into dark blue droplets. Neo-salvarsan remains colourless, but, according to Labot, when treated with 0·5 c.c. of hydrogen peroxide, 0·5 c.c. of ammonia and 1 drop of a 4 per cent. solution of copper sulphate, it gives a blue-green colour which turns violet on addition of hydrochloric acid. The first reaction, which is only given by sodium salvarsan after evaporation with hydrochloric acid, is attributed to the presence of an amino-hydrochloride group and a quinquevalent nitrogen atom, whereas, in neo-salvarsan, the nitrogen in the amino group is in the tervalent condition. The test may be used to detect salvarsan in mixtures of drugs. J. G.

Determination of Inorganic Iodine in Desiccated Thyroid Gland. W. Lawson. (*Biochem. J.*, 1933, **27**, 112–115.)—A method was required for the determination of the proportion of the total iodine in the thyroid gland present as inorganic iodide. A survey of the literature gave no indication of the existence of iodine in the gland in any forms other than inorganic iodide, protein-iodine, and a small trace combined with fat and soluble in petroleum spirit, which could be disregarded. It is shown that extraction of desiccated thyroid glands with water dissolves iodine compounds other than inorganic iodides in amounts which depend on the degree of denaturation of the gland. Aqueous extraction is, therefore, not suitable as a method of determination of inorganic iodine. Exhaustive extraction with alcohol removes only dialysable iodine, together with a trace of iodine combined with fat. Glands were minced and dried to constant weight in a vacuum desiccator with phosphorus pentoxide; a weighed amount of the fine powder was extracted with ethyl alcohol for 12 to 16 hours in a Soxhlet apparatus, and the iodine in the extract was determined. The alcohol dissolved from normal glands an average amount of 1·5 per cent. of the total iodine. From pathological glands (glands removed from patients with exophthalmic goitre after a pre-operative course of treatment with Lugol's iodine solution) varying amounts up to 65 per cent. were dissolved. Shaking with cold ethyl alcohol for 2 to 3 hours dissolves out

smaller amounts of the total iodine than extraction in the Soxhlet apparatus, but shaking with cold methyl alcohol removes approximately the same amount as that dissolved by extraction for 16 hours. A rapid method is therefore described whereby inorganic iodides can be determined in desiccated thyroid glands, regardless of the method by which the glands are dried. A weighed portion of powdered gland (0·2 to 0·3 grm.) is introduced into a stoppered tube and shaken for 2½ hours with 20 c.c. of cold methyl alcohol. The contents of the tube are filtered and the tube and powder washed with a little methyl alcohol. The extract is evaporated and its iodine-content determined. It was found that 94 to 99 per cent. of the iodine in the methyl alcoholic extracts was dialysable. Iodine determinations were made by von Fellenberg's method, as described by Lunde, Closs and Böe (*Mikrochem., Pregl-Festschrift*, 1929, 272).

P. H. P.

Occurrence of Nicotine in Cigarette Smoke. III. C. Pyriki. (*Z. Unters. Lebensm.*, 1933, **65**, 566–571; *cf.* ANALYST, 1931, **56**, 753; 1932, **57**, 727.)—When the procedure previously described for the determination of nicotine in tobacco-smoke (*loc. cit.*, 1932) is followed, the filtrate from the picric acid precipitate always contains small amounts of nicotine. To recover these, the following modification is suggested:—The acid adsorbent solution containing the nicotine is extracted with chloroform and, after removal of this solvent, is rendered alkaline and steam-distilled. The distillate is collected in 20 c.c. of 0·1 *N* sulphuric acid, and the solution is concentrated, neutralised, and treated with picric acid.

Pfyl and Schmitt's method (ANALYST, 1927, **52**, 728) gives low results, although, with smoke from tobaccos of high nicotine-content, the errors are not serious. With cigarettes containing only 0·14 per cent. of nicotine, however, the iodeosin number indicated 0·004 per cent. of nicotine in the smoke, whilst the treatment described above, when applied to the discarded filtrate, indicated 0·034 per cent. of nicotine.

Results are given of experiments on cigarettes prepared from 40 raw tobaccos and on 15 brands of commercial cigarettes. The former show wide variation in the ease with which they burn, this depending, not merely on the bulkiness, but also on the composition. With the commercial brands, the differences in this direction are far smaller. In agreement with previous findings, the commercial cigarettes, prepared from mixed tobaccos, show approximate proportionality between their nicotine-contents and those of the resulting smoke. Although, in general, this is also the case with the cigarettes made from the raw tobaccos, the divergences from such proportionality are much more marked, the ratio between the nicotine-contents of smoke and tobacco ranging from 17·8 to 25·3 per cent.

T. H. P.

Biochemical

Determination of Vitamin *A* in Oils by a Spectrophotometric Method. A. Chevallier and P. Chabre. (*Biochem. J.*, 1933, **27**, 298–302.)—The authors have applied a spectrophotometric method, which permits of very accurate measurement of the ultra-violet absorption given by a substance, to the measurement of the intensity of absorption at 3280 Å of different samples of cod-liver oil.

A continuous ultra-violet radiation, emitted by a hydrogen tube, is dispersed by a quartz monochromator. At the end of the monochromator is placed a potassium photo-electric cell covered with a fluorescent substance. The photoelectric current, generated by the light of the fluorescence, is amplified and measured by a galvanometer. There is a constant ratio between the ultra-violet radiation, the intensity of the fluorescence, and the photoelectric current. Direct readings on the galvanometer give, with consistent accuracy, the value of the absorption of a substance placed in the radiation between 4000 and 1800 Å. Pure hexane was used as the solvent for the oils, and the value of the absorption log. I_0/I was always expressed in concentrations of 1/100 studied in a thickness of 1 cm. The examination of a great number of oils of different origins showed that, besides the presence of vitamin *A*, the free acidity of the oil and, in certain cases, its pigment (if very concentrated) must be taken into account in consideration of the absorption in the neighbourhood of 3280 Å; if necessary, the pigment and free acid must first be extracted with alcohol. The physical tests for vitamin *A* were compared with biological tests on rats; when the free acid-content of the oil is low, the results agree fairly well, the differences not exceeding the usual experimental errors inherent in biological methods. The spectrophotometric method is interesting, not only because it is more convenient and more rapid than the biological method, but also because it enables a direct assay to be made of products which might contain a large quantity of vitamin. P. H. P.

Crystalline Preparations of Vitamin B_1 from Baker's Yeast. H. W. Kinnersley, J. R. O'Brien and R. A. Peters. (*Biochem. J.*, 1933, **27**, 232–239.)—Methods of making crystalline preparations of high vitamin B_1 activity are described in detail, based upon the principle of separation by sodium phosphotungstate at p_H 4·0 to 5·0, followed by treatment with gold chloride and crystallisation of the gold compound from alcohol. Comparatively few stages are needed to concentrate the preparation from the activated charcoal stage. Sodium phosphotungstate is used at two stages, no benzoylation is needed, and hydrogen sulphide can be avoided, if desired, down to an activity of 0·005 to 0·01 mgrm. Use is made of the solubility of vitamin B_1 in alcohol at p_H 3·0, and insolubility of the gold salt in aqueous solution at p_H 2·5. The description applies to aqueous hydrogen chloride extracts of the "active" charcoals prepared from yeast. Approximately 500 mgrms. of crystals have been made from 2000 kilos. of baker's yeast. The crystals vary in activity, the highest potency being $1{\cdot}6\gamma \pm 0{\cdot}4$ for a day dose, orally administered to pigeons. This is greater than the activity of other crystalline preparations previously described. The authors believe that the claim, that vitamin B_1 itself has been prepared, requires re-examination. The conclusion is reached that the crystals made by the methods described are more potent than, and different from, those of others. Three possibilities remain, and are now receiving attention: (1) All crystals hitherto made are a mixture of active and inactive vitamin B_1. This is hard to reconcile with the conflicting position of the ultra-violet bands, presuming these to represent part of the vitamin molecule. (2) The crystals contain vitamin B_1, as impurity. In this case the activity of the true vitamin could be at least $0{\cdot}1\gamma$. (3) More than one compound can function as

vitamin B_1. In this case there might be either a base able to exist free or in combination with other substances, or different bases with identical biological functions.
P. H. P.

The Chemical Nature of Vitamin *C*. J. L. Svirbely and A. Szent-Györgyi. (*Biochem. J.*, 1933, **27**, 279–285.)—The object of this investigation was to show that the antiscorbutic activity of the "hexuronic acid" (*ascorbic acid*) preparations of the authors is due to the acid itself, and not to contamination by some more potent substance. It is shown that paprika contains ascorbic acid in relatively large quantities, and under conditions which make its isolation fairly simple. The method of preparation is described. The yield from 10 litres of juice is 6·5 grms. of crystals. In animal experiments 0·5 mgrm. of the substance, given daily, protects guinea-pigs against scurvy in a 65-day test period. About 450 grms. of recrystallised ascorbic acid have been prepared, and the monoacetone derivative of the acid was also prepared. It is shown that the latter substance is moderately active as an antiscorbutic agent. However, the ascorbic acid recovered from the monoacetone derivative is fully active. This is regarded as definite evidence concerning the identity of ascorbic acid and vitamin *C*. It is shown that ascorbic acid (from adrenal glands), when recrystallised five times, retains its activity. Ascorbic acid readily disappears from the adrenal glands of animals on a diet free from vitamin *C*. The results suggest that there is a wide limit between health and scurvy, and that animals fed on restricted amounts of the vitamin, though not showing signs of scurvy, are greatly depleted of their vitamin store. No ascorbic acid is formed on the treatment of glucose with alkali at high temperatures, although strongly reducing substances are obtained. P. H. P.

Specificity of Hexuronic (Ascorbic) Acid as Antiscorbutic Factor. L. J. Harris and S. N. Ray. (*Biochem. J.*, 1933, **27**, 580–589.)—In order to determine whether antiscorbutic activity is inherent in hexuronic acid or due to associated impurity, a series of experiments was carried out. The antiscorbutic activity of a given amount of hexuronic acid was found to be invariably the same, whatever the source of the acid, and acids from over 30 natural sources (*e.g.* suprarenal cortex, paprika), in relative amounts ranging from 1 to 300, were examined. The statement also applies to specimens of acid recovered from various sources, to preparations purified by chemical means and repeatedly recrystallised, to its disappearance and synthesis in the animal and plant organisms, and to its destruction by chemical means. Full antiscorbutic activity was found for specimens of hexuronic acid, the purity of which was 99 per cent., as judged by titration-curve results (Birch and Harris, *Biochem. J.*, 1933, **27**, 595), by iodine titration, or by elementary analysis. The rate of destruction of the acid under varying conditions of aeration, heat, and alkali was similar to that of antiscorbutic activity, and in the guinea-pig the antiscorbutic activity of the suprarenal cortex or liver was lost, and scurvy developed, and at the same time hexuronic acid disappeared, whereas in animals (rats, dogs) which synthesise their own vitamin when none is provided, both the antiscorbutic activity and the hexuronic acid were unaffected. Similarly, the acid is synthesised concurrently with

antiscorbutic activity by the plant on germination. The considered conclusion is that hexuronic acid is itself the vitamin. Antiscorbutic activity was determined by alternative methods, curative, tooth structure and preventive, and the amount of hexuronic acid, equivalent to 1·0 c.c. of orange juice, was found to be greater than 0·33 mgrm. and less than (or equal to) 0·66 mgrm.; best value is 0·6 mgrm.; or "minimum protective dose" per guinea-pig per day, 0·9 mgrm. Its adoption as an international standard is recommended. D. G. H.

Micro-Chemical Method for Determining the Hexuronic Acid (Vitamin C) Content of Food Stuffs, etc. T. W. Birch, L. J. Harris and S. N. Ray. (*Biochem. J.*, 1933, **27**, 590–594.)—A small amount of the foodstuff is weighed, ground with sand and sufficient trichloroacetic acid (20 per cent. solution) added to give a final concentration of about 5 per cent., and the extract is made up to suitable volume (a suitable dilution for potent substances, such as orange and lemon juice, is 1 in 10). The filtered extract is placed in a micro-burette graduated to 0·01 c.c. A measured volume of, say, 0·05 c.c. of a recently prepared and standardised solution of 2 : 6-dichlorophenolindophenol is placed at the bottom of a small pointed tube and the trichloroacetic acid is run in until the red colour is discharged, the titration being completed within 2 to 3 minutes. As the indicator is standardised in terms of hexuronic acid, the acid-content of the foodstuff can be calculated, and thus its antiscorbutic value, which can be expressed either in terms of guinea-pig dosage, or compared with the potency of a standard material. The indicator is standardised by titrating the same amount as was used in the estimation, under the same acid conditions, against a solution of hexuronic acid, and the amount of pure acid in this solution is, in turn, checked by iodine titration.

Cysteine was the only naturally occurring reducing agent which appreciably reduced the indicator under the conditions described, so that, if working with stale or autolysed tissues, a control test for cysteine should be made. The sensitivity of the method is far greater than that obtained biologically. The hexuronic acid content as mgrm. per grm. for some 30 foodstuffs was determined; these included: cabbage, 1·0, 0·61; orange juice, 0·48, 0·59, 0·75; grape fruit juice, 0·59, 0·65; potato, 0·15; carrots, 0·028; horseradish, 1·6; apples (cortex and peel): Bramley's seedling, 0·16, 0·77; Newtown Wonder, 0·053, 0·24; Blenheim Orange, 0·031, 0·33; Edward VII, 0·017, 0·12; Cox's Orange Pippin, 0·016, 0·09; suprarenal cortex (ox), 1·85; liver (ox), 0·68; cows' milk, variable, 0·025 to 0·019; egg-yolk, 0·00.

D. G. H.

Water Analysis

The "Stability Test" of Sewage and its Relation to Enzyme Activity. W. R. Wooldridge. (*Biochem. J.*, 1933, **27**, 193–201.)—An enquiry has been made into the so-called "stability test" (*Standard Methods of Water Analysis*, 1925) of sewage. In this test 150 c.c. of the sewage to be examined are incubated at 22° C. in a 150-c.c. bottle, closed with a water seal, together with 0·4 c.c. of a 1/2000 methylene blue (zinc salt) solution, and its "stability" assessed from the time required, in days, for the complete decolorisation of the dye. In this form the test presents certain possibilities of error; first, the time taken for the methylene

blue reduction to take place will depend, to some extent, on the amount of oxygen already dissolved in the sewage, and, secondly, the concentration of methylene blue is so low that any error produced as a result of this variability in the amount of oxygen dissolved will be very significant, especially as the reducing system is generally such a weak one. These sources of error can be avoided by the use of the Thunberg technique, the addition of a larger concentration of methylene blue, and the shortening of the time required for reduction by incubation at a higher temperature. From the results of the experiments the reducing power of crude sewage towards methylene blue is shown to depend largely upon the enzymic activity of suspended matter in the sewage. The sludge (*i.e.* the suspended matter of 1 litre of crude sewage, washed and suspended in 100 c.c. of distilled water), besides possessing a marked reducing power of its own, also activates substances present in solution as hydrogen donators. Both reducing effects are destroyed when sludge is heated to 100° C. for 15 minutes. Sulphydryl compounds are rarely, if ever, found in sewage, unless this has been kept anaerobically for some time. Strong sewages contain potential hydrogen donators, and good effluents contain potential hydrogen acceptors, of which nitrate is usually one. In addition to its dehydrogenase activity some other enzymic properties of the sludge have been examined. A modified "stability test" is described. The period is shortened by incubation at 45° C., and by the addition of washed sludge and a hydrogen donator, such as formate. The sewage is incubated in vacuum tubes, together with 1 c.c. of 1/5000 methylene blue solution, formate and washed sewage sludge, and the time required for complete reduction of the dye is compared with that in a control tube not containing the sewage. Variations of this test are given. It is concluded that the modified test, whereby a sewage-sludge-formate-methylene blue system is incubated anaerobically at 45° C., can be used with advantage whenever the "stability test" is of value. It may also prove of use for following sewage research, although its general application will always remain limited; it is not so satisfactory as the ordinary Biochemical Oxygen Demand (B.O.D.) method, if the actual strength of a sewage is required. P. H. P.

Organic Analysis

Potentiometric Titration of Sodium and Calcium Cyanamides. H. Sinozaki. (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 145B–146B.)—The alkaline cyanamide solution is titrated with silver nitrate, giving a yellow precipitate which coagulates well. The potentiometric titration curve shows a well-defined end-point. The method is stated to be simpler and more accurate for the analysis of commercial cyanamide than Kjeldahl's or Devarda's process, but a correction for silver consumed by the sulphide present must be applied. W. R. S.

Thionylaniline as a Reagent in Organic Chemistry and its Use for the Identification of Acids by the Formation of Anilides. P. Carré and D. Liebermann. (*Bull. Soc. Chim.*, 1933, **53**, 293–295.)—Thionylaniline ($C_6H_5N:S:O$) is easily prepared by the action of thionyl chloride on a suspension of aniline hydrochloride in benzene (*cf.* Michaelis and Herz., *Ber.*, 1891, **24**, 746). Unlike phenylisocyanate, it will not form addition compounds with alcohols,

even in the presence of pyridine, but usually dehydrates them with the production of hydrocarbons; it will not react with phenol even at 185° C. Acids, however, form addition compounds of the type $R.CO.NH.C_6H_5$ in the cold, or on warming at 110° to 180° C., the yields being lowest for the aromatic acids (particularly those in which the carboxyl group is attached to the nucleus), since green, blue or violet compounds containing sulphur are also formed. If an unsaturated linkage is present, but is not too near the carboxyl group (*e.g.* in the undecylenic acids), the reaction is unaffected, but otherwise resinic substances are produced which cannot be separated from the anilide. Most dibasic acids react, but the method is not recommended for acids of the malonic series. J. G.

Application of the Orcinol Reaction to the Determination of the Nature and Amount of Carbohydrate Groups in Proteins. M. Sórensen and G. Haugaard. (*Compt. rend. Lab. Carlsberg*, 1933, **19**, 1–45.)—The methods previously employed for the identification or determination of the carbohydrate constituents of proteins are discussed. The orcinol method (*cf.* Tillmans and Philippi, *Biochem. Z.*, 1929, **215**, 36) is chosen as the best for these purposes, and experiments have been made to ascertain the effects of temperature, concentrations of the orcinol and sulphuric acid, and time of heating on the course of the reaction. The most suitable conditions, *i.e.* those under which different carbohydrates give the most different results, are as follows: 1 c.c. of the solution to be investigated is pipetted into each of a number of 150-c.c. conical flasks, and 2 c.c. of 2 per cent. orcinol solution (made by dissolving 2 grms. of orcinol in 50 c.c. of water and adding a cooled mixture of 20 c.c. of concentrated sulphuric acid with 30 c.c. of water) and 15 c.c. of dilute sulphuric acid (6 vols. of concentrated acid plus 4 vols. of water) are added. The mixtures are then heated at 80° C. for 5, 10, 15, 20, 25 or 30 minutes, after which they are at once transferred to ice-water in the dark. With mixtures heated for only a short time, the measurement of the colour developed must be made as soon as possible, but those which have been heated for 15 minutes or longer remain unchanged for hours in the dark. Instead of comparing the colours of the mixtures with those of glucose solutions, similarly treated, in an ordinary colorimeter, the authors prefer to use a Pulfrich step-photometer, in which the colour is measured by determining the extinction coefficient of the liquid with a suitable colour filter, a blank mixture (without orcinol) being used as compensating liquid. From the results obtained with the various mixtures a curve showing the relation of depth of colour formed to the time of heating is drawn.

Measurements made in this way with aldohexoses, ketohexoses and pentoses show that the various monosaccharides may be characterised by the varying form and position of the time-curves. Tests made with lactose, raffinose, glycogen, and inulin show that the reaction of these complex carbohydrates with orcinol and sulphuric acid is an additive process, the shade and intensity of the colour produced being the sum of those produced with the separate components. The method has been applied, with satisfactory results, to the determination of the glucose-content of amygdalin and salicin. For salicin, the comparison time-curve must be constructed from results obtained with a mixture of glucose and salicyl alcohol in the

proportions formed on hydrolysis of the salicin, since salicyl alcohol (or, perhaps, the anhydride, saliretin) gives a yellow colour with orcinol.

To determine the quantity of carbohydrate which forms an integral part of the protein molecule, it is first necessary to ascertain, if possible, which carbohydrate is present. For this purpose, the protein solution is diluted until, after heating 1 c.c. of the solution for 20 minutes with 2 c.c. of 2 per cent. orcinol solution and 15 c.c. of sulphuric acid, an extinction between 0·4 and 0·8 is obtained on measuring in a 30-mm. cell with filter S53. This solution is then used to obtain a complete set of time-curves under the standard conditions, using both filter S53 and S43. The course of these curves and the relations between them will, in all probability, show which carbohydrate is present. A solution of this carbohydrate is prepared of such concentration that identical extinctions are obtained from the protein solution and the carbohydrate solution, after heating for 20 minutes and measuring with filter S53. If the correct carbohydrate has been chosen for comparison, the time-curves for carbohydrate solution and protein solution, obtained simultaneously and under identical conditions, should coincide. Usually, however, a certain time elapses before the protein is completely hydrolysed by the acid, so that the values of the extinction, after heating for 5 or 10 or sometimes 15 minutes, are often lower for the protein than for the carbohydrate, whereas the values for longer times of heating agree.

Tests made on these lines showed that egg albumin, after repeated recrystallisation, contained 1·71 per cent. of mannose. A readily-soluble fraction of serum albumin, recrystallised several times, contained 0·47 per cent. of a mixture in equal parts of mannose and galactose, whilst a sparingly-soluble fraction contained only about 0·02 per cent. of carbohydrate. Horse-serum globulin, several times precipitated, contained 1·82 per cent. of equal proportions of mannose and galactose. Well-purified casein contained 0·31, and well-purified lactalbumin 0·44, per cent. of galactose, with no lactose in either. A sparingly-soluble fraction of wheat gliadin, many times precipitated, contained 0·20 per cent. of mannose. T. H. P.

Constitution of Starch. New Method of Acetylation. W. S. Reich and A. F. Damanski. (*Compt. rend.*, 1933, **196**, 1610–1613.)—All previous methods for acetylating starch have yielded a tri-acetate, the presence of three free hydroxyl groups in each of the dextrose molecules constituting starch being thus indicated. In the method of acetylation now described, use is made of a reagent prepared by mixing 100 c.c. of pure, anhydrous pyridine with 8 c.c. of acetyl chloride, both at −20° C., and leaving the mixture at that temperature for 30 minutes. Three grms. of starch (previously dried over phosphorus pentoxide at 80° C. and under 1 mm. pressure) are then added, the mixture being kept for an hour at −20° C. and for an hour at the ordinary temperature, and afterwards heated, slowly and with frequent shaking, to 70° to 80° C. Under this treatment amylose yields a triacetate, amylopectin a di-acetate, and starch itself a mixture of the two, containing only a small proportion of tri-acetate. This proportion may be increased by heating the starch beforehand in water at 90° C. The conclusions drawn are that amylopectin forms the fundamental substance of the

starch granule, and that amylose is the result of a transformation of amylopectin involving the liberation of a hydroxyl group, either by destruction of a linking between the dextrose molecules or by stereoisomeric change. The small amount of amylose found in starch probably results from slight transformation of the amylopectin during the preparation of the starch. T. H. P.

Determination of Dextrin in the Presence of Glue. J. Alexander. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 200).—To a 0·6-grm. sample of the glue, 10 c.c. of dilute hydrochloric acid (5 per cent.) are added, and the whole is kept overnight at about 60° C. in order to hydrolyse the dextrin. The solution is neutralised and diluted to 50 c.c. Into a 150-c.c. flask are placed 3 grms. of anhydrous sodium carbonate and 25 c.c. of Benedict's solution [(prepared by pouring a solution of 18 grms. of copper sulphate crystals in 100 c.c. of water into a hot solution of 200 grms. of sodium citrate, 200 grms. of sodium carbonate crystals and 125 grms. of potassium thiocyanate diluted to 800 c.c. with water, adding to the mixture 5 c.c. of potassium ferrocyanide solution (5 per cent.), and diluting the whole to 1000 c.c.)]. The solution is kept briskly boiling, and the glue solution is run in slowly until the blue colour is discharged. The volume of glue solution added is, at this point, equivalent to 0·05 grm. of dextrose, and the dextrose figure, multiplied by the factor 0·9, gives a close approximation to the amount of dextrin present. No reduction was found to occur with pure glue, and samples of several commercial dextrins gave concordant results when mixed with this pure glue.
S. G. C.

Determination of Small Quantities of Benzyl Alcohol. J. Callaway and S. Reznek. (*J. Assoc. Off. Agric. Chem.*, 1933, **16**, 285–289.)—The sp.gr. of aqueous solutions of benzyl alcohol vary too slightly for the accurate determination of the composition in this way, but, in conjunction with the immersion refractometer reading (r) at 20° C. an indication may be obtained in the presence of other substances in solution. If only benzyl alcohol is present, then $(r-14{\cdot}40) \times 0{\cdot}193$ gives the grms. of alcohol in 100 c.c. of solution. For the chemical determination of benzyl alcohol in aqueous solutions containing no other volatile substances, a quantity corresponding with 0·5 to 3 grms. of alcohol is diluted to 110 c.c. and distilled in a Reichert–Meissl flask until about 20 c.c. remain, when 50 c.c. of water are added and 50 c.c. removed by distillation. This last process is repeated, and the sp.gr. and immersion refractometer reading of the combined distillates, diluted to 200 c.c., are determined. A mixture of an aliquot portion (containing 0·05 to 0·175 grm. of the alcohol) and 10 c.c. of a saturated solution of potassium permanganate is then diluted to 60 c.c. and shaken occasionally for 1 hour in a stoppered flask in the cold, 5 c.c. of a saturated solution of sodium sulphite, and 1 c.c. of concentrated sulphuric acid being then added. The colourless solution is saturated with salt (an excess being avoided), and is extracted in succession with one 50-c.c. and three 25-c.c. portions of chloroform, the extracts being filtered through cotton-wool and evaporated at 75° C. until about 30 c.c. remain. The remainder of the solvent is removed in a slow current of air at a temperature not exceeding 40° C., and the dry residue is placed in a desiccator

overnight, and is then dissolved in 25 c.c. of alcohol and titrated to phenolphthalein with 0·1 *N* alkali (1 c.c. ≡ 0·0108 grm. of benzyl alcohol). The results vary from 93 to 109 per cent. of the amount of alcohol taken. J. G.

Chemical Changes Induced in Wood by Saturated Steam under Pressure. W. G. Campbell and K. F. Taylor. (*Biochem. J.*, 1933, **27**, 158–164.)—A brief summary is given of recent work by various investigators on the chemical changes which occur in wood under the influence of moderate heat. No attempt has yet been made to explain the mechanism of the thermal reactions described; for instance, it does not appear to be known whether the presence of a certain amount of water vapour is an essential factor. An investigation is now described which was made to determine the effect of saturated steam at various pressures on the chemical composition of both a hardwood and a softwood. The hardwood material consisted of small pieces of beech wood (*Fagus sylvatica*), measuring approximately $2\frac{1}{2} \times \frac{1}{2} \times 10$ inches, and the softwood material, consisting of pieces of the same size, was cut from African pencil cedar (*Juniperus procera*) heartwood. The results show that when wood is heated by means of saturated steam under pressures ranging from 20 to 80 lbs. per square inch, it appears to undergo the same order of chemical change as when heat is applied by other means, but the initial process takes place more rapidly and at temperatures as low as 109° C. The greater part of the residues consists of pentosans in hardwoods and hexosans in softwoods. Depending upon the conditions under which the wood is heated, there is a temperature below which the residues can condense to a product which is insoluble in 72 per cent. sulphuric acid, and above which they are more or less completely hydrolysed to reducing sugars. Part of the reducing sugars may even be decomposed into volatile products. The temperature at which the tendency towards hydrolysis of depolymerised units is greater than the tendency towards condensation to a lignin-like product is lower for hardwoods than for softwoods. On the basis of these considerations, the results recorded can be reconciled both with those of Hawley and Wiertelak (*Ind. Eng. Chem.*, 1931, **23**, 184) and of Slavik (*Chem. Listy.*, 1932, **26**, 211). P. H. P.

Determination of Uronic Acids and Methoxyl in Certain Plants and Plant Materials. M. Phillips, M. J. Goss and C. A. Browne. (*J. Assoc. Off. Agric. Chem.*, 1933, **16**, 289–292.)—The material, partly dried in a current of air at 70° to 90° C., is ground, and drying is completed at 105° C.; materials which darken in colour (*e.g.* melon) are dried in a vacuum over sulphuric acid at 56° C. Uronic acids are determined by a modification of the method of Dickson, Otterson and Link (*J. Amer. Chem. Soc.*, 1930, **52**, 775), 1 to 2 grms. first being heated for 30 minutes at 70° C. with 100 c.c. of 12 per cent. hydrochloric acid to decompose any carbonates. The carbon dioxide is removed in a current of air free from this gas, and the temperature is then maintained at 135° to 140° C. for 5 hours, the carbon dioxide now liberated from the uronic acids being removed in a stream of air and absorbed in a tower containing 0·2 *N* barium hydroxide solution (for apparatus, cf. *loc. cit.*). The unused alkali is titrated with 0·1 *N* hydrochloric acid to phenolphthalein, and if the value obtained in a blank experiment is deducted, the uronic acid = 4 × carbon dioxide evolved. Phillips's method for the

determination of methoxyl (ANALYST, 1932, **57**, 402) was applied after extraction of the material with a mixture of benzene and alcohol. The percentage results for the respective determinations were:—Honey melon, 3·60, 0·15; cantaloupe, 4·00, 0·23; Lima beans, 4·20, 0·86; peas, 4·88, 0·74; peeled cucumbers, 8·32, 0·94, (peel 11·96, 0·85); asparagus stalks, 9·16, 1·48 (tips, 9·88, 1·36); carrots, 10·24, 0·64; spinach, 10·32, 0·96; summer squash, 10·64, 0·89; cabbage leaves, 11·16, 0·97; pea pods, 11·32, 2·06; cauliflower, 12·56, 0·93; radish tops, 12·72, 0·80; egg plant, 13·08, 1·07; apple peel, 13·16, 1·53; kale, 14·04, 0·82; head lettuce leaves, 14·20, 0·76; beet tops, 14·52, 0·66; carrot tops, 16·28, 1·50; celery (leaf and stalk), 16·72, 0·80; orange peel, 17·72, 2·32. J. G.

Electrometric Determinations in Tannin Solutions. H. Schweitzer. (*Coll.*, 1933, **755**, 149; *J. Inter. Soc. Leather Trades Chem.*, 1933, **17**. 376.)—The dissociation constant of the carboxyl group of gallic acid in $N/20$ solution is $4{\cdot}5 \times 10^{-5}$. Neutralisation with sodium hydroxide would be complete at p_H 8·4 if the acidity of the more acid hydroxyl group did not interfere. The author prefers to add successive equal quantities of sodium hydroxide, records the corresponding p_H value by means of the Ehrhardt electrode, and calculates, by comparison with neighbouring points, the exact point of inflection. Using this principle, he has been able to determine the amount of gallic acid in admixture with tannin; also the mono- or di-galloyl groups of the tannin. It is thus possible to determine, in a single titration, the number of galloyl groups in the presence of a given tannin, but without gaining information as to the number of mono- or digalloyl groups. Application of the same principle enables the process of degradation of a given tan to be studied. R. F. I.

Inorganic Analysis

Brucine as an Internal Indicator in Dichromate Titrations. S. Miyagi. (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 146B–147B.)—The author has used brucine instead of diphenylamine in dichromate titrations of ferrous and stannous ions. Brucine is claimed to give a sharper end-point in presence of chromic ion; the acidity should be higher than 3 *N*. The red colour produced is discharged by reduction. Brucine sulphate (1 grm.) is dissolved in 100 c.c. of strong sulphuric acid; 20 drops of the solution are used. W. R. S.

Colorimetric Method for Copper and Manganese. K. Shimada. (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 262B–264B.)—The dilute solution of a copper or manganese salt, treated with piperidine pentamethylenedithiocarbamate, gives a brownish precipitate. As little as 0·1 part of metal per 1,000,000 of solution can be detected and determined colorimetrically. The comparison is made in cylinders holding 100 c.c., 10 c.c. of a 0·1 to 0·5 per cent. solution of the reagent being added. The amount of copper to be determined should not exceed 0·0002 grm. per c.c. W. R. S.

Iodimetric Determination of Copper, Iron, Zinc, and Aluminium in the presence of each other. R. Lang and J. Reifer. (*Z. anal. Chem.*, 1933, **93**, 161–172.)—*Copper.*—The sulphate or nitrate solution, free from chloride,

and containing 3 to 5 c.c. of sulphuric acid, is neutralised with ammonia, diluted to 50 or 60 c.c., cooled, and treated with 2 grms. of potassium bifluoride. When dissolved, the solution is titrated with 0·1 *N* thiosulphate solution after addition of 2 to 3 grms. of potassium iodide and starch solution. *Iron.*—The solution is next treated with 10 to 15 c.c. of 5 *N* sulphuric acid, 3 grms. of crystallised boric acid, and 1 grm. of potassium thiocyanate, and the titration is continued for iron. *Zinc.*—After addition of a little sodium sulphite the liquid is heated to incipient boiling and filtered, and the filter is washed. The filtrate is treated with a strong, warm solution of syrupy phosphoric acid (5 grms. of the acid), followed by bromine water to reoxidise the iron and sulphite, heated just to boiling, and cooled to room temperature, and the blue colour is accurately discharged with the thiosulphate solution. The zinc is then determined by the addition of successive portions of 0·2*M* ferricyanide solution, followed by titration with thiosulphate until the blue colour fails to return after half a minute's standing, the zinc being precipitated as ferrocyanide. *Aluminium.*—The titrated solution is made up to 200 c.c., and an aliquot portion of the filtrate is treated with hydroxyquinoline. The precipitate is determined volumetrically by adding a measured amount of bromide and bromate, the excess of which is ascertained with potassium iodide and thiosulphate. The authors have applied the process to the analysis of aluminium alloys.

W. R. S.

Determination of Small Amounts of Antimony in Copper. B. Park and E. J. Lewis. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 182–183.)—Antimony has been determined in various samples of copper by the spectrographic method of Nitchie (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 1), the antimony being first separated by Blumenthal's process (*Z. anal. Chem.*, 1928, **74**, 33), which involves its precipitation by occlusion on manganese dioxide from the solution of a 500-grm. weight of sample. The antimony-content of the samples, as found by this method, ranged from less than 0·00002 to 0·001 per cent. (*cf.* ANALYST, 1929, **54**, 28).

S. G. C.

Determination of Zirconium in Steels. S. G. Simpson and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 211–212.)—A modification of the author's zirconium selenite method (ANALYST, 1933, 243) has been devised in order to overcome a difficulty with tungsten, which, if present, may precipitate with the zirconium selenite, which then requires purification. The modification involves solution of the selenite precipitate and final precipitation of the zirconium as phosphate. The original method (*q.v.*) is followed up to the stage of obtaining the combined zirconium selenite precipitates. These are dissolved in 50 c.c. of 18 *N* sulphuric acid; the solution is diluted to 200 c.c., warmed to 50° C., and 20 c.c. of hydrogen peroxide (3 per cent.) and 50 c.c. of diammonium phosphate solution (20 per cent.) are added. After keeping for 2 hours, the precipitate of zirconium phosphate is filtered off, washed with ammonium nitrate solution (5 per cent.), ignited, and weighed as ZrP_2O_7. The method gave satisfactory results in tests with solutions of a plain steel (3 grms.) with added solutions of titanium, uranium, vanadium, chromium, and tungsten (20 mgrms. of each element, separately and together).

S. G. C.

Determination of Aluminium in Nitriding Steels by the Use of 8-Hydroxyquinoline. H. A. Bright and R. M. Fowler. (*Bur. of Standards J. Research,* 1933, **10**, 327–335.)—The process consists in (*a*) separating the aluminium from the bulk of the iron by an initial precipitation with sodium bicarbonate, (*b*) separating the nickel, etc., accompanying the aluminium, with sodium hydroxide, (*c*) finally precipitating the aluminium with 8-hydroxyquinoline, the resulting compound being either weighed or determined volumetrically. A 4-grm. sample of the steel is dissolved, as far as possible, in 50 c.c. of dilute sulphuric acid (1+9). The liquid is diluted to 150 c.c., heated to boiling, and sodium bicarbonate solution (8 per cent.) is added from a burette, with constant stirring, until the commencement of the formation of a permanent precipitate (usually 38 c.c. are required), followed by 0·2 c.c. more of the solution for each mgrm. of aluminium anticipated, or 5 c.c., whichever is the greater amount. "For high chromium steels, more sodium bicarbonate will be needed because it is apparently necessary to precipitate a considerable part of the chromium before all the aluminium is precipitated . . . an excess of 0·35 c.c. of bicarbonate solution for each mgrm. of aluminium suffices for high chromium steels." The solution is boiled for 1 minute and filtered, any turbidity of the filtrate, which is due to oxidation of the ferrous bicarbonate, is "of no consequence." The precipitate is dissolved from the filter in 25 c.c. of hot dilute hydrochloric acid (1+2), and the filter is well washed with hot dilute hydrochloric acid (1+9), the filtrates being received in the original vessel. (Any aluminium oxide present in the steel will remain on the filter at this point, and can, if desired, be included in the analysis by igniting the filter paper and residue, fusing with potassium bisulphate, dissolving the melt, and adding it to the main solution). The solution is boiled for two minutes after the addition of 1 c.c. of nitric acid, cooled somewhat, and "nearly neutralised" with sodium hydroxide; the solution is adjusted in volume to 150 to 175 c.c., warmed to 70° C., poured slowly into 150 c.c. of hot sodium hydroxide solution (10 per cent.), with vigorous stirring, and the whole is boiled for 1 minute and cooled. The liquid is diluted to 500 c.c. and filtered, and 250 c.c. of the filtrate are taken and neutralised with hydrochloric acid; 3 to 5 c.c. excess of concentrated hydrochloric acid are added, and 1 grm. of tartaric acid is dissolved in the liquid, which is rendered slightly ammoniacal; 10 to 15 c.c. of hydrogen peroxide (3 per cent.) are then added in order to aid in the separation of aluminium from molybdenum and vanadium (*cf.* ANALYST, 1929, **54**, 770). The solution is heated at 50° to 55° C., and 0·7 c.c. of 8-hydroxyquinoline solution (prepared by dissolving 2·5 grms. of the compound in 5 c.c. of glacial acetic acid, pouring into 100 c.c. of water and filtering) is added for each mgrm. of aluminium expected, together with 5 c.c. in excess. Then 2 c.c. of ammonia (sp.gr. 0·9) are added, and the liquid is stirred mechanically for 12 to 15 minutes. The precipitate is filtered off on a sintered glass filter of fine porosity, and washed with about 60 c.c. of warm dilute ammonia (1+99) at about 50° C. The precipitate may be weighed after drying at 135° C. for 1½ hours (it contains 5·87 per cent. of aluminium), or, for rapid work, titrated. For the titration, the precipitate is dissolved in dilute hydrochloric acid (1+6) at 75° C.; the solution is diluted with water so that the concentration of hydrochloric acid is about 8 per cent. by volume, cooled to room

temperature, and standard 0·35 *N* potassium bromate-bromide solution (9·743 grms. of potassium bromate and 34 grms. of potassium bromide per litre) are added in slight excess (until a test drop added to 1 drop of potassium iodide and starch solution gives a blue colour). The solution is kept for 1 minute, 15 c.c. of potassium iodide solution (25 per cent.) are added, and the liberated iodine is titrated with standard thiosulphate solution, with starch as indicator; 1 c.c. of 0·35 *N* bromate-bromide solution = 0·002248 grm. of aluminium. The separations involved in this method were tested, with satisfactory results. S. G. C.

Separation of Rhenium from Molybdenum. J. H. Müller and W. A. La Laude. (*J. Amer. Chem. Soc.*, 1933, **55**, 2376–2378.)—Rhenium is quantitatively precipitated as sulphide from hydrochloric acid solution by hydrogen sulphide. In ammoniacal rhenium solutions, hydrogen sulphide produces a precipitate after prolonged action, quantitative recovery being achieved after 48 to 72 hours. Ammoniacal solutions containing molybdenum and rhenium were submitted to hydrogen sulphide treatment; the precipitate was ignited in hydrogen, the residue dissolved, and the precipitation with hydrogen sulphide from ammoniacal solution repeated. The rhenium sulphide precipitate thus obtained was washed with ammonium chloride solution containing hydrogen sulphide; washing with water caused loss of rhenium, shown by the violet tint of the filtrate. The combined filtrates from the rhenium sulphide precipitations were acidified with hydrochloric acid containing hydrogen sulphide, the precipitate was dried and ignited in hydrogen at 450° to 550° C., and weighed as MoS_2. The results indicate that a separation of the two elements was achieved. W. R. S.

Determination of Small Amounts of Potassium by the Cobaltinitrite Method. A. H. Lewis and F. B. Marmoy. (*J. Soc. Chem. Ind.*, 1933, **52**, 177T–182T.)—Precipitation by cobaltinitrite and its application in soil and plant analysis were re-investigated. The following details of technique were adopted: separation of the precipitate by the centrifuge, use of 70 per cent. alcohol for washing, colorimetric determination of the cobalt by Tomula's modified thiocyanate method or Jacobs and Hoffman's choline-ferrocyanide method, or determination of the nitrite by Griess's process. Volumetric determination of the nitrite by permanganate (Kramer and Tisdall's procedure) was also applied. The authors give preference to the thiocyanate method. In all cases standardisation was effected by means of potassium sulphate solution put through the entire process. The methods used, which gave very satisfactory results, are fully described in the paper. W. R. S.

Rapid Volumetric Determination of Sulphur in Coal and Coke. E. L. Skau and I. L. Newell. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 180–182.)—A new modification of the benzidine sulphate method has been found by tests on 15 samples of coal and coke to be a satisfactory alternative to the usual and more lengthy methods. A 1-grm. sample of the finely divided coal or coke is burnt in oxygen in a calorimetric bomb in the same manner as for carrying out a determination of calorific value, the temperature measurements being omitted unless this determination is also required. An Emerson bomb with a gold lining and a

silica capsule for holding the sample were used. The bomb is dismantled after firing, and the interior parts are washed out with a saturated solution of benzidine sulphate in water (up to 150 c.c.); 60 c.c. of saturated benzidine hydrochloride solution are added, with stirring; the precipitate formed, which may be filtered off immediately, is washed with saturated benzidine sulphate solution until free from acid. The precipitate and paper are transferred to the precipitation beaker, macerated in 100 c.c. of water, and titrated with 0·0624 *N* sodium hydroxide solution, phenolphthalein being used as indicator. The liquid is heated to boiling just before the end-point of the titration is reached. The number of c.c. of alkali used, divided by 10, gives directly the percentage of sulphur on a 1-grm. sample.

S. G. C.

Occurrence and Source of Lead, Copper, Zinc, and Arsenic Compounds in Atmospheric Dusts. J. T. Dunn and H. C. L. Bloxam. (*J. Soc. Chem. Ind.*, 1933, **52**, 189T.)—The compounds of lead, copper, zinc and arsenic found in industrial dusts, domestic soot and dust, and in the atmospheric dust of Newcastle-on-Tyne have been traced to the pyrites present in the coal burnt. The lead compounds found in herbage alongside motor roads are attributed to lead tetraethyl in the petrol. In analyses of pyrites from seventeen Durham coals the lead varied from nil to 461 parts per million; the copper from nil to 140 parts; zinc from nil to 80 parts. Compounds of these metals were also found in gas liquor, gas tar and coke, flue dusts, and domestic soots from mixed Durham and Northumberland coals, flue dusts containing the most (lead 63 to 1060 parts, copper 55 to 650, zinc nil to 12,050 parts per million), and gas liquor the least (lead nil to 1·7, copper nil to 2·8, zinc nil). Various dusts were examined from office bookshelves, portico of a city building, and from the electrical fittings of ceilings. Lead, zinc, copper and arsenic were invariably found in comparatively large proportions. Grass from some of the open spaces in and around Newcastle was found to contain from 58 to 116 parts of lead, and 9 to 22 parts of copper per million. The lead, copper and zinc deposited in the soot and dust of a soot gauge (area=4 sq.ft.) situated in the middle of the city amounted, in the course of 12 months, to 0·2725 grm. of lead, 0·0346 grm. of copper, and 0·1115 grm. of zinc. The rain water collected 0·0639 grm. of lead, 0·0069 grm. of copper, and 0·0352 grm. of zinc. Variations were very great even in the same season of different years. Grasses analysed in cases of cattle poisoning have been found free from lead when growing remote from dwellings, although traces of copper were occasionally found. Dusty grass from the east side of a motor road contained 7 parts of lead and 4 parts of copper, but no zinc, whereas from the west side there was no lead or zinc, and the amount of copper was only 1·2 part per million. Lead and copper have been found in the organs of fowls. As soon as the poisonous dust was removed, the fowls, which had previously been ill, recovered. The cause of the death of a five-year-old child was found to be small amounts of lead, which could only be accounted for by being air-derived.

These results are in concordance with those of Manley, who examined atmospheric dusts from 6 different parts of Leeds and found lead (40 to 15,000), copper (100 to 7200), and arsenic oxide (40 to 350), expressed as parts per million (*cf.* p. 471).

R. F. I.

Microchemical

"Spot" Plate which can be Heated. E. Fränkel. (*Mikrochem.*, 1933, **13**, 179–182.)—An electrically-heated "spot" plate, suitable for temperatures up to 80° C., is described. The plate has a porcelain top, cemented on to the heated portion, through which an electric current passes. The porcelain top contains twelve depressions for ordinary "spot" reactions, and two flattened depressions suitable for heating Feigl's micro-gas-test apparatus (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, Leipzig, 1931, p. 121). Two or four depressions are black for the examination of pale precipitates, and the rest are white. When the "spot" test is carried out on impregnated filter paper, this may also be heated by placing it on the "spot" plate. (The apparatus is made by Paul Haack, 4 Garelligasse, Vienna IX.) J. W. B.

Microchemical Detection of Coumarin. M. Wagenaar. (*Mikrochem.*, 1933, **13**, 140–144.)—Coumarin crystallises in colourless prisms (m.pt. 67° C., b.pt. 291° C.). It is soluble with difficulty in cold water, more readily in hot water, and easily soluble in alcohol, ether, acetone and chloral hydrate. *Sublimation.*—Coumarin sublimes readily without decomposition, the first-formed droplets solidify in a network of crystals; these dissolve in warm dilute alkali and are re-precipitated by acetic acid. *Precipitation.*—Solution in hot water and cooling, or solution in acetone and evaporation give good crystals; or coumarin may be dissolved in a drop of warm dilute alkali, containing a little alcohol, and precipitated with acetic acid, when 0·02 mgrm. in 1 : 500 dilution may be detected. *Crystal formation with iodine solution.*—This is the best identification test. When a crystal of coumarin (or a drop of a solution in chloral hydrate) is placed in a drop of a very dilute iodine solution in potassium iodide, blue-black thread-like crystals are formed. These crystals are soluble in acetone and re-form on evaporation, to give a network of blue crystals. Starch and narceine form crystals of similar colours; the colour is destroyed by thiosulphate. Iodine in zinc iodide solution may also be used as a reagent; 0·01 mgrm. in 1 : 1000 dilution may be detected by this test. *Crystal formation with thallium salts.*—This test is not so sensitive. After three evaporations to dryness of the sodium salt of coumarin with thallium nitrate sulphur-yellow prisms are obtained. *Crystal formation with mercuric chloride.*—The crystals are easily confused with those of coumarin by itself; but when Congo red or chloral hydrate is added to the coumarin solution, the crystallisation of coumarin at the edge of the drop is inhibited; a crystal of powdered mercuric chloride is added, and, if necessary, a drop of water, and the long, needle-shaped crystals are then slowly formed; 0·01 mgrm. in 1 : 1000 dilution may be detected. Two photomicrographs are given. J. W. B.

Reaction of Caffeine with Iodine in Caesium Iodide Solution. M. Wagenaar. (*Mikrochem.*, 1933, **13**, 145–146.)—Although caffeine gives a fine micro-crystalline precipitate with potassium tri-iodide in the presence of dilute hydrochloric or sulphuric acid, the crystals are too small to serve as a good test, but when a few crystals of caesium chloride are added, large, deep brown anisotropic stars are formed with disappearance and subtraction colours in the longitudinal

direction of the crystals. The test is sensitive to 0·002 mgrm. in 1 : 1000 dilution. Theobromine and theophylline do not form such crystals, but only micro-crystalline rosettes. Rubidium gives crystals which are not nearly so well defined. Xanthine and guanine do not react. Two photomicrographs are given. J. W. B.

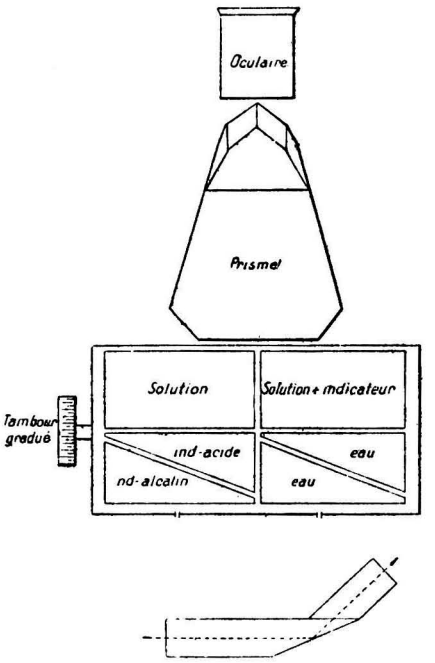
Nephelometric Determination of Caffeine. E. Herndlhofer. (*Mikrochem.*, 1932–33, **12**, 227–230.)—The turbidity formed on adding a concentrated solution of sodium phosphotungstate to a dilute solution of caffeine can be used as a method of determining the caffeine in as little as 0·25 grm. of dried raw material containing about 1 per cent. of caffeine, and the caffeine-content of coffee leaves in different states of development can be compared. A Kleinmann nephelometer is used, and the standard solution for comparison is a 0·005 per cent. solution of caffeine. The concentration of the test solution should lie between 0·005 and 0·002 per cent. *Reagent.*—A 20 per cent. solution of sodium phosphotungstate containing 2 per cent. of hydrochloric acid. *Preparation of material.*—The raw material is dried and ground to a powder, moistened with water in a shaking funnel, and left for 30 minutes. Chloroform (1 grm. of material requires about 150 c.c. of chloroform) is then added, the mixture is shaken for half an hour and filtered, the residue is washed with chloroform, and the chloroform is then distilled from the extract and washings. The residue is taken up in a little chloroform, transferred to a porcelain crucible, and the chloroform is evaporated. The resulting residue is dissolved in hot water, cooled, filtered into a graduated flask, and made up to a known volume. *Nephelometric determination.*—It is important that the temperature of the standard and test solutions should not differ by more than 0·1° C., otherwise large errors occur. The standard solution and reagent are mixed in the proportions of 100 c.c. of standard to 5 c.c. of reagent; a similar amount of reagent is added to the test solution, and the mixture is well shaken. The turbidity remains unchanged for a considerable time; 20 c.c. of solution are required for each measurement in the nephelometer, so that as little as 0·0004 grm. of caffeine can be determined. The error is of the order of ±2 per cent.

J. W. B.

Physical Methods, Apparatus, etc.

New Colorimeter. R. Legendre. (*Compt. rend.*, 1933, **196**, 1875–1877.)—A pedestal on a fixed base supports a platform, at right angles to the rays of light, and moved on a drum actuated by a screw. On this are placed, side by side, two series of three cells, each cell 4 cm. long, one series comprising a rectangular cell filled with the liquid under examination, a "prism" cell containing the acid indicator with, front to back, a similar cell containing the alkaline indicator solution. The second series consists of three similar cells containing, in the first, the liquid and a convenient concentration of indicator solution, and in the other two, water. The whole series is enclosed in a black chamber, and each series receives a ray of light from the same source through a narrow slit, the slits being 4 cm. apart. The light rays travel through the cells to the lateral faces of a Pulfrich prism so arranged that the images of the two luminous fields are reflected at an

angle of 45°, and exactly touch each other, with no black band between. By moving the supporting platform the colour of one field is varied, whilst the other remains fixed, and when the movable field has been matched with the immovable,



the position of the cells in relation to the slits is noted (by means of a scale), and from this the ratio of the thickness of the two colours through which the light has passed is known, and consequently the tone of colour or the p_H value. D. G. H.

Reviews

HANDBUCH DER LEBENSMITTEL-CHEMIE. Vol. I. ALLGEMEINE BESTANDTEILE DER LEBENSMITTEL. Edited by A. BÖMER, A. JUCKENACK and J. TILLMANS. Pp. 1371. Berlin: Julius Springer. 1933. Price 126RM. unbound (129.6 bound).

There are fifteen contributors to this, the first volume of what is perhaps the most comprehensive treatise on the chemistry of food yet written, and it is edited by three of the best-known food chemists in Germany. It is intended to produce the whole series in eight volumes by the end of 1935. Volume I deals with the general constituents of food, and is necessarily largely concerned with theoretical matters, the structure of compounds and their mutual relationship. Volume II is to treat of general methods of investigation; Volume III, milk, eggs and meat; Volume IV, oils and fats; Volume V, starches, sugars, honey, fruit and vegetables; Volume VI, spices and food containing alkaloids; Volume VII, alcoholic beverages;

and Volume VIII will treat of water, air and special foods. It is evident that even the encyclopaedic "König" will be eclipsed, and from an examination of the first volume it is clear that the work has been planned with the most admirable thoroughness, and that the treatment will be comprehensive from all points of view.

The reviewer gladly pays tribute to the excellent lines on which this work is conceived, and the erudition displayed in its execution. Food chemistry is apt sometimes to be regarded as a subsidiary or minor branch of chemical science, but no one could think so after scanning this volume; he would see how the genius of Willstätter and of Robinson in elucidating organic structures, and the work of Harden and others on fermentation, or of the army of those who attack vitamins, all form a part of the complex whole which is beyond the capacity of one man, and still constitutes but the fringe of the chemistry of food. After a section dealing with the importance and extent of the food industry, within and without Germany, there follows the history of the subject from the most ancient times, then a discussion of the chemistry of the fundamental constituents, all considered in detail, from the standpoint of chemical constitution, mutual relationship and dietetic importance. Enzymes occupy about 100 pages; the section on vitamins is almost a treatise in itself, with 200 pages and a host of references. Preservatives, dyes, bleaching, flavouring, polishing and the arts of the food factory receive careful description. Then come 100 pages on poisonous substances which may occur, including metallic impurities (figures are given for the rare as well as the common ones), alkaloids, toxins, saponins, glucosides and ptomaines.

The next section deals with digestive processes, calories, energy requirements and rations; and, lastly, there is a synopsis of all the food laws of all the leading countries.

From what has been said it will be obvious that one reviewer cannot adequately comment upon all parts of so wide a field. The general impression gained on going through the volume is that it is excellent and up-to-date, and the mode of presentation is good. One criticism which may be put forward is made in the hope that the editors will note it for future volumes; the work is of international value, and it is evidently hoped to sell it in the English-speaking countries as well as in Germany, yet there is an inadequate mention of the work of non-German food chemists. For example, who would have thought it possible to write a 30-page history of food chemistry (though it be largely the history of chemistry itself) without mentioning the names of Alfred Allen, Otto Hehner, and others of our famous forebears? The *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel** was founded in 1898, but THE ANALYST was founded 23 years earlier, and out of some thousands of references to original papers we have noticed only one to this journal. A better study of English journals would have prevented certain omissions—though it may be that these will be filled in the subsequent volumes.

The section on food law, other than German, seems the weakest; perhaps it was an impossible task. Who could adequately summarise English food law in less than two pages? It is inadequately done by extracting sections from the Food and Drugs (Adulteration) Act, 1928, and perhaps it is excusable that the author has not been able to comprehend potable spirits at 35° U.P.

* Now *Zeitschrift für Untersuchung der Lebensmittel.*

These few defects can be overlooked, and we welcome this monumental work of reference, congratulate the authors and editors on their achievement so far, wait with expectation and high hope for the succeeding volumes, and with the wish that they may be less expensive.

H. E. Cox

CELLULOSE ACETATE: ITS MANUFACTURE AND APPLICATIONS. By A. G. LIPSCOMB. Pp. xii and 304. London: Benn. 1933. Price 21s. net.

This monograph deals with the chemistry and physics, and their application, of the latest of the cellulose derivatives to attain industrial success in the production of rayon and plastic masses. The reviewer has made day-to-day use of this volume during the past few months, and has found it an excellent guide and reliable reference book. It is probably the only monograph on its subject written by an author who has been actually engaged in the industry, who grew up with it through many of its early problems and difficulties, and who is now free to tell fellow chemists and technologists all about it: that is his unusual and special qualification for his task. There is, then, about this book an air of reality; the methods and processings and patents described and discussed are mainly those either in actual use to-day or those formerly used and now superseded by better ones; and the book is singularly free from the fault, common in monographs on technological topics, of cataloguing methods that have never been worked indiscriminately with those that have, in a more or less academic discussion that leaves the reader with no clear notion of what processing steps the industry really uses, and why.

After a short history of rayon and plastics in general, the particular properties of acetate rayon and plastics are discussed against a background of chemistry and physics based on present-day ideas of the structure of cellulose and dextrose, derived from *X*-ray methods and Haworth's structural formula of dextrose. In a new edition the author should explicitly introduce Haworth's six-member ring, instead of an earlier five-member ring, into his discussion on p. 14, as he has already done, implicitly, on p. 19.

Dispersibility and viscosity relations of primary and secondary acetates are then discussed in connection with the phenomena of ripening, and then the book gets on to the description of raw materials and how they are used industrially for the preparation of cellulose acetate and how the by-products are recovered and re-used. This particular industry owes its present-day success, in spite of exceptional technical difficulties, not a little to the remarkable efficiency of the recovery processes it employs, and this book is especially interesting in its lucid description of much that has hitherto been known in detail only to the few; the description of the Suida process for recovering acetic acid will interest many who have had no first-hand contact with it. The spinning of acetate dope, solvent recovery, and finishing processings are fully described without excessive detail, and a non-specialist can follow the description with ease. The illustrations are well chosen, in the sense that they clearly illustrate just what is discussed in the text, and without conveying the impression that the book is, in part, an illustrated trade catalogue.

Chapter X deals with the dyeing and printing of cellulose acetate, which, in their day, have been among the most difficult problems of their kind that have ever had to be solved. Whether or not this particular chapter would satisfy the requirements of specialists in dyeing and printing is hardly to the point, because the author does not write specially for them; but the non-specialist, including the majority of chemists, will find it interesting and informative. Similarly, plasticisers to-day are really the affair of specialists, and accordingly they are dealt with in this book only in general terms, in Chapter XI, which deals with the use of cellulose acetate in the plastics industry.

Finally, analysts will turn with special attention to Chapter VII, of 42 pages, which deals with "Laboratory Controls and Methods of Analysis," and they will find therein assembled a description of methods, based on lengthy experience, for assaying raw materials, finished products and by-products, which commend themselves.

CHAS. J. J. FOX

QUALITATIVE ANALYSE AUF PRÄPARATIVER GRUNDLAGE. Third Edition. By W. STRECKER. Pp. 203. Berlin: Julius Springer. 1932. Price RM8.

Books on qualitative inorganic analysis appear frequently. Many of them, fortunately, have a short life, as they are written with little appreciation of the complex behaviour of mixtures of compounds when treated with reagents, and their chief purpose is to force the elements into a stereotyped set of groups from which they not unnaturally endeavour to escape, much to the despair of student, and, sometimes of the teacher. The fact that the present work is in its third edition is some indication that it is in an altogether higher class, and reading the book amply supports this. The author has tried, in what appears to be a successful manner, to cater for the needs both of the beginner and the more advanced student. Some space is devoted to describing the preparation of simple compounds which are to be used for subsequent qualitative testing, or which have an analytical significance, *e.g.* tetrammine cupric sulphate. A large section is devoted to a consideration of the reactions of the commoner elements. These reactions appear to be generally well chosen and well described. A detail is, however, open to correction in connection with the Marsh test for arsenic (p. 125); zinc and hydrochloric acid are used in the evolution flask and copper sulphate is added to "activate" the zinc; no doubt, if much arsenic were present, some of it would be evolved as arsine, but this exercise would be a bad preliminary to quantitative work, since the formation of copper arsenide by the Reinsch reaction of arsenic with the deposited copper is overlooked. Incidentally, the very valuable Reinsch reactions of arsenic and antimony are not mentioned.

An attempt has been made to include some of the newer reactions which have been proposed in recent years, but the treatment of these is rather uneven, probably owing to limitations of space, and there is a tendency for British and American work to be neglected in favour of German. One may doubt the wisdom of including in a book of this kind diphenylthiocarbazone (p. 99) and diphenylcarbazide (p. 115) as colour tests for zinc and mercury respectively, as the usefulness of these reagents

for qualitative testing is not fully substantiated, and interference by other metals is likely. The quinalizarine test for magnesium (p. 65), however, would appear to be a valuable inclusion, but there seems little to justify sodium alizarine sulphonate as a reagent for aluminium (p. 69) as the numerous sources of interference are not dealt with, whereas a highly specific reagent for this metal, *viz.* aurintricarboxylic acid, is not mentioned. Uranyl acetate, giving crystals of characteristic form with sodium acetate, is described (p. 13) as a microscope reagent for sodium, but one regrets the absence of the invaluable and unique zinc uranyl acetate precipitation reaction for sodium.

The section on the group separations of the elements shows evidence of much careful thought, and should appeal to students by reason of the useful alternative methods of separation given. It must be emphasised that what criticisms are made above are not to be taken as detracting from the value of the book as a whole, which would appear to be one of the best of its kind available.

S. G. CLARKE

PRINCIPLES OF FRUIT PRESERVATION. By T. N. MORRIS, M.A. Pp. 240. London: Chapman & Hall, Ltd. 1933. Price 15s. net.

This book is one of an excellent series of monographs on Applied Chemistry under the editorship of Dr. E. Howard Tripp, and his choice of an author for it is a happy one. In view of work previously published by Mr. Morris, we should expect to find the present effort of a high order, the more so since the opening sentence of his preface tells of nine years' research and factory experience in the fruit-preserving industry and five years' research on the special problems of canning. Nor are we disappointed, particularly in those chapters dealing with the theoretical side of the subject.

The book is divided into four parts, dealing, respectively, with Jams and Fruit Jellies, Canning of Fruit, Dried Fruits, and Considerations common to all Preserved Fruits. A useful author- and subject-index is given.

The book is well printed, although not quite free from typographical errors. Attention should be called to the statement on page 59 that 5 grains of sulphur dioxide per lb. is the Board of Trade limit for fruit pulp. Actually, the Public Health (Preservatives in Food) Regulations, 1925–7, allow from 10 to 20 grains of sulphur dioxide per lb. On p. 58, in the sentence commencing on line 8, there is an obvious error in the figures given for sulphur dioxide. There is also a slip on p. 139, in example 1, second line, which should read "weight of cans *plus* water, etc."

The author refers to a great number of original papers, and in a very useful bibliography acknowledges his sources of information. We notice, however, that neither here nor in the closing paragraph of his preface does Mr. Morris mention Messrs. Chivers & Sons' Research Laboratories, where much of the subject matter of the book was worked out—for example, the whole of the hitherto unpublished experimental work of Ogg, referred to at length in Chapter II.

Part I—Jams and Fruit Jellies—very rightly gives prominence to pectin, and the literature on this complex subject is reviewed in a lucid way, giving those engaged in a busy industry a very handy epitome. The manufacture of jams and

jellies is dealt with less fully, and is more open to criticism in some of the details given.

We could have wished that the "General Account of the Processes of Canning" (Part II), and, still more so, the chapter on "Fruit Bottling" were more complete. One aspect of canning is treated very exhaustively in a helpful chapter (pp. 110 to 133) on "Spoilage." In Chapter VI, on the examination of canned fruits, we find no mention of quality, condition, texture, flavour, or colour of the fruit—points which should not have been overlooked.

In Part III the author has collated the salient features of a bulky literature on Dried Fruits, and has made a commendable attempt to balance the merits of different processes. Prominence is given to methods for moisture estimation. On page 158, the recent excellent method of Monier-Williams for the determination of sulphur dioxide is dismissed in six lines, in favour of a long description of a process dating back to 1880.

The closing section of the book deals with causes of discoloration in fruit products and with vitamins. In the former chapter we find no mention of the effect of light, and in the latter the author in one case quotes from work published some 25 years ago. Improved modern technique on vitamin work shows the need for caution in accepting the conclusions of some earlier workers.

We hardly think the technical expert (for whom, according to the preface, this book is mainly designed) will use this work as a text-book, as in most cases he has available the knowledge and work of research associations which can usually furnish more recent information than a book such as the one under review. However, despite these points of criticism, we close the book feeling it to be a very useful contribution to the literature of fruit preservation.

THEODORE RENDLE

Publications Received

THE ANALYSIS OF OIL FOR THE PRODUCTION OF LUBRICANTS. By A. A. ASHWORTH. London: Ernest Benn Ltd. 1933. Price 9s. net.

ELEMENTARY QUALITATIVE ANALYSIS. Second Edition. By C. J. ENGELDER. New York: Wiley & Sons, Inc.; London: Chapman & Hall Ltd. 1933. Price 13s. 6d. net.

VITAMINS IN HEALTH AND DISEASE. By BARNETT SURE. London: Baillière, Tindall & Cox. 1933. Price 11s. 6d.

DER CHEMIE-INGENIEUR. Bd. II. 4th Th. Edited by A. EUCKEN. Leipzig: Akad. Verlagsgesell, m.b.H. 1933.

PRACTICAL PHYSIOLOGICAL CHEMISTRY. Ninth Edition. By S. W. COLE. Cambridge: W. Heffer & Sons Ltd. 1933. Price 12s. 6d. net.

CHEMISTRY TRIUMPHANT. By W. J. HALE. London: Baillière, Tindall & Cox. 1933. Price 5s. 6d.

THE METHODS OF CELLULOSE CHEMISTRY. By C. DORÉE. London: Chapman & Hall. 1933. Price 21s. net.