BOTTLED AND CANNED FRUIT: Studies of Processing Requirements and Fuel Consumptions by Domestic Methods

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The rates at which heat penetrates through fruit during preserving by bottling and canning have been studied by six different domestic methods. Determinations have been made of the processing times and temperatures required to give adequate control both of the spoilage micro-organisms at the different pH levels found, and of the oxidase-enzyme activity in the fruits having light-coloured flesh. The quantities of gas or electricity used in preserving 1 lb., 5 lb. and 10 lb. of fruit, in the higher and lower pH ranges, have been recorded for each method, both for the initial and for the subsequent processes.

Introduction

The investigation was undertaken to determine the minimum processes for fruit bottling required to obtain products that would remain free from spoilage micro-organisms while maintaining a good appearance and texture. Since the survival and growth of bacteria depend largely on the pH of the medium, the distribution of the pH values in the different kinds of fruits is of importance.

Most workers accept foods with a pH value below 4·5 as being safe from spoilage by *Clostridium botulinum*, but foods having a pH value above 4·5 require treatments that ensure the destruction of the spores of this organism.

Cameron & Esty[1] classified foods for preserving purposes into the following pH ranges:

Low acid, pH 5 and higher. Members of this group, containing most meat, fish, milk and some vegetables, are subject to spoilage by mesophilic and thermophilic bacteria.

Medium acid, pH 5 to 4·5, contains principally meat and vegetable mixtures, specialities such as spaghetti and soups that are also subject to spoilage by the bacteria in the low-acid group. In this group the thermophilic anaerobes are of greater importance than the flat-sour group of micro-organisms.

Acid, pH 4·5 to 3·7, containing tomatoes, pears, figs, pineapples and nectarines as well as other fruits. These are subject to spoilage by non-sporing acid-tolerant micro-organisms as well as by spore-forming anaerobes allied to *Clostridium pasteurianum* Winogradsky.

High acid, pH 3·7 and below, contains the more acid fruits. These are subject to spoilage by yeasts, moulds and acid-tolerant bacteria, but are immune from spoilage by spore-forming bacteria.

Since this study is confined to fruit-processing, most of the products would fall into the acid or high-acid groups, but estimations of the pH values have shown that a few fruits fall into the medium-acid group, above. Correct processing times are of particular importance in the medium-acid group, to ensure either destruction or inhibition of any pathogenic organisms.

Considerable spoilage in tomato juice by the organism *Bacillus thermoacidurans* has been reported by Stern, Hegarty & Williams,[2] Becker & Pederson[3] and other workers in the U.S.A., but does not appear to have been noted in this country. Spoilage by similar acid-tolerant bacteria has been noted recently in connexion with these processing tests in tomato products, and further work on the survival of these organisms after processing at different pH levels is in progress.

In the authors' experience, fruit, other than tomatoes, processed in a water bath, method (*a*), has been generally free from microbiological spoilage, and the minimum temperatures obtained were taken as those required for the different kinds of fruit when processed by other methods. Processing temperatures found satisfactory for fruits in the high-acid group were a minimum of 157° F, or over 150° F maintained for 20 minutes. Baumgartner[4] considers most of the spoilage organisms in this group to be destroyed by 30 minutes' heating at 149° F. An exception is the mould *Byssochlamys fulva*, first noted by Olliver & Smith[5] and further tested for the heat resistance of its spores by Gillespy.[6] The heating required for the destruction of the spores of this mould was found to over-cook the fruit for culinary requirements, and since this organism does not seem to be a main cause of spoilage in domestic preserving, its presence has not been considered in the evaluation of processing times.

The discoloration of some bottled pears and plums, processed at temperatures considered sufficient to prevent spoilage by micro-organisms, was found by James & Crang[7] and Crang & Kendall[8] to be due to oxidase-enzyme activity. The temperatures necessary to inactivate the enzyme systems completely may vary considerably from one variety to another in the

same kind of fruit. Enzymic discoloration can be prevented either by processing above the maximum temperature of enzyme activity, or by processing for a longer period just below the maximum required for rapid inactivation of the enzyme. When fruit is canned the former method of control usually operates, but the latter method is usually the more satisfactory when fruit is bottled owing to the slow transference of heat through glass in heating and cooling.

In the work described in this paper, the methods of bottling which had been recommended for some years in publications issued by the Ministry of Agriculture were the first to be tested, and modifications were made as required either to improve the colour or texture, or to lessen the risk of spoilage by micro-organisms.

The quantities of gas and electricity used in processing by the different methods were measured, since no information was available on the relative amounts of fuel used in the domestic bottling methods.

Experimental

Methods of testing the pH value

The pH values were tested on freshly pulped fruit at 20° C by means of a glass electrode. Most of the results were obtained during the seasons 1950–1952.

Microbiological tests

The following kinds of fruit, selected to cover the different pH ranges, were preserved during the 1950 season: blackcurrants, cherries (Frogmore Prolific and morello), damsons, gooseberries, pears, strawberries and tomatoes (whole in brine and 'solid pack'). Twenty to thirty jars or cans were prepared of each kind of fruit. One sample of each process was inoculated with spores of *Byssochlamys fulva*. The samples were stored at 64–77° F for 2–2½ years before examination. The jars or cans were opened under sterile conditions in an inoculation cabinet. All were examined for visible spoilage; in addition a sample of the gooseberries, damsons, pears and tomatoes from each container was inoculated in triplicate on the following media: (i) liver broth, (ii) tomato broth, (iii) glucose/malt/yeast-extract broth, (iv) nutrient broth and (v) potato agar. The inoculated plates and tubes were incubated at 22°, 37° and 57° C, one replicate at each temperature, in order to isolate organisms having different optimum temperatures of growth. Smears (Gram-stained) were prepared from each sample of the bottled and canned fruit and from any sub-cultures that were positive.

Enzyme activity

Two tests for oxidase activity were used: (1) the formation of a red colour on the addition of 1% alcoholic solution of guaiacol to pears, (2) the formation of a blue-black colour on the addition of 1% alcoholic solution of benzidine to plums or apples.

Methods of testing rate of heat-penetration

Throughout the experiments thermocouples of enamelled copper–Eureka wire (22-S.W.G) were used with an extra protection of plastic sheathing. The exposed tips were sprayed with a thin film of Araldite wax and subsequently stoved for 5 hours at 150° C. A Doran thermocouple potentiometer was used with either distilled-water ice kept in a vacuum flask or a Sunvic cold-junction thermostat. Periodic standardizations have been made against standard thermometers.

Glass preserving jars of the screw-band type (1-lb., 2-lb. or 4-lb. sizes), or lacquered cans (1-lb. or A2½ sizes) have been used throughout. The lids were bored to take the thermocouples, held tightly in place with a split rubber bung. The length of the wires was adjusted so that the thermocouple tips penetrated the tissue of the fruit in the coolest part of the container. Fagerson & Esselen[9] showed that the cold spot for convection packs in American 1-lb. glass jars was at the apex of a cone, ¾ in. from the base of the jar. The jars used in the present work were taller than the American ones and the comparable position was found to be 1 in. from the base.

The thermocouple wires were led into the pressure pan through a ¼-in. hole drilled in the lid. A tightly fitting rubber bung, through which the leads were threaded, was held firmly in the hole by a specially designed metal cap. The temperature in the cooker was taken about 1 in. from the top. The oven temperatures were taken by a thermocouple placed about 1 in. from the jar to be tested, with the tip on a level with that inside the jar. A simple key enabled the use of a threefold unit connected to one cold junction.

Processing methods

Fresh, good-quality fruit was prepared in the usual way for preserving. For most packs, 11 oz. of fruit was used per 1-lb. jar and fruits that could be packed more tightly were tested separately. Apple slices were covered with 15°-Brix syrup, and whole tomatoes with 1% brine, but 30°-Brix syrup was used with all other fruits. The solid-pack apples and tomatoes were scalded before packing into jars. Details of preparation and processing may be found elsewhere.[10, 11]

The processing times in methods (*b*), (*c*), (*d*) and (*e*) were varied considerably during the course of the tests in order to find processing values comparable with methods (*a*) or (*f*). The final times that proved satisfactory were as follows:

(*a*) *Bottling: slow water-bath method.*—The jars were filled with fruit and cold syrup, placed on a rack in a pan with cold water just to cover them. The water was raised to 165°, 180° or 190° F in 1½ hours and maintained at these temperatures for 10, 15, 30 or 40 minutes according to the kind of fruit being processed.

(*b*) *Bottling: quick water-bath method.*—The jars were warmed, filled with fruit and with hot syrup (140° F), and placed in a pan as in (*a*) but with warm water (100° F) to cover. The temperature of the water was raised to 190° F in 25 to 30 minutes and maintained for 2, 10, 20, 40 or 50 minutes according to the fruit being processed.

(*c*) *Bottling: pressure-pan method.*—Warmed jars were filled with fruit and with boiling syrup. Domestic pressure pans, large enough to hold 2-lb. preserving jars, had 1 pint to 2 quarts of water added, according to the size of pan, a low trivet put in and the water brought to the boil. The jars were placed on the trivet, the lid fitted on with the exhaust valve open, the pan heated, and the exhaust valve closed when steam began to escape. The heat was regulated to obtain 5 lb. pressure per sq. in. in 5 to 10 minutes from the time of placing the jars in the pan. Pressure was maintained at 5 lb. for 1, 3, 5 or 15 minutes according to the fruit processed. The pan was cooled 10 minutes at room temperature before it was opened to remove the jars.

(*d*) *Bottling: slow-oven method.*—The jars of fruit were placed 2 in. apart on an asbestos mat in the central part of an oven thermostatically controlled to give a temperature of 250° F, after preheating for 15 minutes. The jars were processed for 45 up to 125 minutes, depending on the kind and quantity of fruit, then removed from the oven and immediately filled with boiling syrup.

(*e*) *Bottling: moderate-oven method.*—Warm jars, filled with fruit and with boiling syrup to within 1 in. of the top, were placed 2 in. apart on a baking sheet lined with newspaper. This was placed in the central part of an oven controlled to give a temperature of 300° F, after preheating for 15 minutes, and the jars of fruit were processed for times varying from 30 to 100 minutes, depending on the kind and quantity.

(*f*) *Canning.*—The cans were filled with fruit and with boiling syrup to within ⅜ in. from the top. The lids were sealed on and the cans processed in boiling water for 3 to 45 minutes, depending on the kind of fruit, size of can and time taken for the water to re-boil (see publications[10, 11] for processing times).

Gas and electricity measurements

The gas and electricity used in processing by each method was noted on meters fitted for the purpose. In order to facilitate comparisons, the quantities of fuel needed when processing 1 × 1-lb., 5 × 1-lb. and 5 × 2-lb. containers were recorded, and expressed as the quantity needed per 1-lb. jar or can. Several different pans, ovens and cookers were used for each test but the figures given are those for the equipment that proved to be the most economical for the quantity of fruit processed.

Since a considerable amount of fuel was used in preheating the water or ovens in methods (*b*) to (*f*), this has been deducted in calculating fuel requirements for the subsequent processes (Table V).

Results

Range of pH values

The range and distribution of pH values found in fresh fruit are given in Table I.

It will be seen that figs and pears were the only fruits found to have pH values above 4·5, but most of the tomatoes and some of the sweet cherries and plums had pH values in the 4·0–4·4 range.

Since it is realized that comparatively few fruits were tested, a comparison with the

Table I

Range and distribution of pH values in fresh fruit

Fruit	No. of samples	Range	No. of samples in each pH range				
			Below 3·0	3·0 to 3·4	3·5 to 3·9	4·0 to 4·4	4·5 and above
Apples	51	2·9–3·8	4	40	7		
Blackberries (cultivated)	6	2·8–3·1	5	1			
Blackcurrants	25	2·7–3·3	15	10			
Cherries (acid)	3	2·9–3·6	2		1		
,, (sweet)	10	3·7–4·3			3	7	
Damsons	2	3·1–3·4		2			
Figs	2	4·5–5·3					2
Gooseberries	9	2·9–3·2	1	8			
Greengages and 'Gage' plums	20	3·0–4·2		16	3	1	
Loganberries	1	2·9	1				
Medlars	2	3·4–3·7		1	1		
Peaches	1	3·7			1		
Pears	15	3·7–4·6			4	8	3
Pineapple	1	3·4		1			
Plums (red or purple)	22	2·9–4·3	4	13	1	4	
,, (Victoria type)	14	2·9–3·6	1	11	2		
,, (yellow)	8	2·8–3·5	2	5	1		
Quince	1	3·2		1			
Raspberries	3	3·0–3·1		3			
Redcurrants	1	3·0		1			
Rhubarb	14	3·0–3·6		11	3		
Strawberries	10	3·1–3·6		9	1		
Tomatoes*	219	3·9–4·4			14	205	

* Tomato figures obtained from Miss M. E. Kieser (private communication)

pH ranges in fruit found by other workers would be of value. Goldmann[12] reported a range of pH values found in fruit juices in the U.S.A. The results were generally similar for the fruits mentioned in Table I although she reported the range for apples (30 samples) to be 3·00–5·00 and oranges (18 samples) to be 3·55–4·90, but pears (12 samples) only 3·2–3·90. Figures for tomatoes were not included. The high figures for apples and oranges are not likely to be found in fruit used for preserving in this country.

The distribution of pH values in canned fruit reported by Adam[13] is also similar for most fruits given in Table I, with figs having a pH range 4·4 to 5·2, pears 3·9 to 4·7, and sweet cherries 3·7 to 4·4. The chief differences were in the plums and tomatoes, the highest pH values reported by Adam for canned plums and greengages being 3·3 and 3·5 respectively, and the range for canned tomatoes being from 4·1 to 4·7. The pH of the plums can easily be accounted for, as those with the higher pH values listed in Table I were in varieties not recommended for commercial canning. The higher tomato figures may be due to growth in warmer climatic conditions, since the figures supplied in Table I were all on different tomato varieties grown under glass and outdoors at Long Ashton Research Station, whereas canned tomatoes are often from imported fruit.

Microbiological spoilage

The results of examination of the containers after storage are given in Table II. As will be seen, no microbiological spoilage occurred in the blackcurrants, cherries or damsons. The mould *Byssochlamys fulva* was recovered from one of the inoculated jars of gooseberries, and from three of the jars of strawberries.

Anaerobic organisms were isolated from four bottles of pears, but had apparently remained dormant in the fruit itself. The processes for the solid-pack tomatoes, by methods (*c*) and (*d*), were inadequate. The times of processing this pack by methods (*a*) to (*e*) were subsequently increased to give minimum temperatures comparable with those found in canning.

Enzyme inactivation

The maximum temperatures at which oxidase-enzyme activity was found in the fruits tested were as follows: apples 150–165° F, plums 150–185° F and pears 180–195° F. In these tests the pulp was heated and cooled rapidly. Since enzyme inactivation bears a time–temperature relationship, oxidase activity ceased at several degrees below these figures when the slower heating–cooling curves normally used in fruit bottling were followed.

Table II

Microbiological results of different processes

Fruit, variety and pH of fresh fruit	Method of processing *	Number of samples	Maximum temperature in coolest part of container, ° F	Results after storage for 2–2½ years
Blackcurrants: Seabrook, pH 2·97	(*a*) Water bath: 180° F in 1½ h., held 15 min.	5†	169° Over 160° for 22 min.	No spoilage apparent
	*(*c*) Pressure: 5 lb. for 4 min.	6	185° ,, ,, ,, 46 ,,	,, ,, ,,
	*(*d*) Oven: 250° F for 1 h.	4†	156°	,, ,, ,,
	(*f*) Canning: 10 min. to re-boil, held 18 min.	7†	195° ,, ,, ,, 22 ,,	No microbiological spoilage but 3 cans developed hydrogen swells
Cherries: Frogmore Prolific, pH 4·08 and morello, pH 3·55	*(*a*) Water bath: 165° F in 1½ h., held 10 min.	7†	156°	No spoilage apparent in either variety
	(*a*) 180° F in 1½ h., held 15 min.	12†	171° Over 160° for 32 min.	
	*(*c*) Pressure: 5 lb. for 4 min.	9	167° ,, ,, ,, 20 ,,	
	*(*c*) ,, 5 lb. for 7 min.	3†		
	*(*d*) Oven: 250° F for 100 min.	10†	181° ,, ,, ,, 34 ,,	
	(*f*) Canning: 5 min. to re-boil, held 15 min.	12†	208° ,, ,, ,, 18 ,,	No microbiological spoilage but all cans developed hydrogen swells
Damsons: Shropshire Prune, pH 3·35	*(*a*) Water bath: 165° F in 1½ h., held 10 min.	4	156° Over 150° for 20 min.	Smears negative; no growth in liver broth, tomato broth, glucose/malt/yeast-extract broth, nutrient broth or potato agar
	*(*c*) Pressure: 5 lb. for 4 min.	6†		
	*(*d*) Oven: 250° F for 45 min.	6†	160° ,, ,, ,, 22 ,,	
	(*f*) Canning: 6 min. to re-boil, held 10 min.	5†	202° ,, ,, ,, 20 ,,	
Gooseberries: Keepsake, pH 3·12	(*a*) Water bath: 165° F in 1½ h., held 10 min.	5†	160° Over 150° for 25 min.	*Byssochlamys fulva* recovered from inoculated jars in potato agar but no apparent breakdown of fruit; all other cultures and smears negative
	*(*d*) Oven: 250° F for 45 min.	5†	163° ,, ,, ,, 36 ,,	All cultures and smears negative
	*(*c*) Pressure: 5 lb. for 2½ min.	6†	173° ,, ,, ,, 46 ,,	
	(*f*) Canning: 3 min. to re-boil, held 16 min.	5	204° ,, ,, ,, 23 ,,	
Pears: Bristol Cross, pH 4·47	(*a*) Water bath: 190° F in 1½ h., held 30 min.	5†	187° Over 180° for 34 min.	*Byssochlamys fulva* recovered in potato agar from 1 inoculated jar; anaerobes isolated in liver broth from 1 jar; other cultures negative
	(*c*) Pressure: 5 lb. for 5 min.	6†	204° ,, ,, ,, 32 ,,	All cultures and smears negative
	*(*d*) Oven: 250° F for 1½ h.	5†	188° ,, ,, ,, 16 ,,	Anaerobes isolated in liver broth from 3 jars; other cultures negative
	(*f*) Canning: 6 min. to re-boil, held 15 min.	5†	196° ,, ,, ,, 11 ,,	All cultures and smears negative
Strawberries: Royal Sovereign, pH 3·38	(*a*) Water bath: 165° F in 1½ h., held 10 min.	7†	154° Over 150° for 10 min.	Slight breakdown due to *Byssochlamys fulva* in inoculated jar; no other apparent spoilage
	*(*c*) Pressure: 5 lb. for 3 min.	6†	— —	No apparent spoilage
	*(*d*) Oven: 250° F for 45 min.	5†	140° —	2 jars (1 inoculated) showed breakdown due to *Byssochlamys fulva*; no other apparent spoilage
	(*f*) Canning: 3 min. to re-boil, held 16 min.	7†	— —	No apparent spoilage

* Processes subsequently altered (see Table IV)
† One sample inoculated with spores of *Byssochlamys fulva*

Table II (*contd.*)

Fruit, variety and pH of fresh fruit	Method of processing *	Number of samples	Maximum temperature in coolest part of container, ° F	Results after storage for 2–2½ years
Tomatoes: whole in brine, pH 4·27	(*a*) Water bath: 190° F in 1½ h., held 30 min.	5†	188° Over 180° for 28 min.	All cultures amd smears negative
	*(*c*) Pressure: 5 lb. for 7 min.	6†	204° ,, ,, ,, 39 ,,	
	*(*d*) Oven: 250° F for 1½ h.	5†	177° —	1 jar unsealed, *Endomyces* sp. isolated
	(*f*) Canning: 5 min. to re-boil, held 27 min.	5†	204° ,, ,, ,, 27 ,,	All cultures and smears negative
Tomatoes: solid-pack, pH 4·26	*(*a*) Water bath: 190° F in 1½ h., held 30 min.	5†	172°	Inoculated jar unsealed and obvious spoilage; cultures and smears from other jars negative
	*(*c*) Pressure: 5 lb. for 7 min.	6†	158°	Obvious spoilage in 5 jars, 4 of which were unsealed and contained mixture of moulds, yeasts, and bacteria, including *Endomyces* sp. and lactobacilli
	*(*d*) Oven: 250° F for 1½ h.	5†	155°	1 jar unsealed, *Endomyces* and yeasts isolated; cultures from other jars negative
	(*f*) Canning: 3 min. to re-boil, held 38 min.	5†	184° Over 180° for 8 min.	All cultures and smears negative

* Processes subsequently altered (see Table IV)
† One sample inoculated with spores of *Byssochlamys fulva*

There is also a considerable reduction of enzyme activity as the temperature approaches the maximum at which it can be demonstrated. In several processes discoloration due to enzyme activity was therefore very slight, even though the fruit was not heated sufficiently to inactivate the oxidase system completely.

The method of heating the fruit in an oven and adding the boiling liquid after processing, method (*d*), is, of course, one that gives no protection against oxidation, and any fruits with light-coloured flesh were very discoloured before the liquid was added. On this account the method cannot be recommended when processing such fruits.

Peroxidase activity remained in pears at temperatures considerably above that required to inactivate the oxidase system, but did not appear to have any adverse effect on the colour of preserved fruit.

Rates of heat-penetration

Typical heating–cooling curves obtained when stone-fruits were processed by the six different methods of bottling or canning studied are given in Figs. 1 and 2. Fig. 2 also shows the effect of the quantity of fruit processed when oven methods are used.

In order to simplify processing, fruits were grouped according to their pH values, density of pack, maximum temperatures permitting oxidase activity and the minimum temperatures of processing required. The tightness of the pack made a considerable difference to the rate of heat-penetration, and different processing times had to be considered for 'average' packs (approximately 11 oz. of fruit and 5 fl. oz. of liquid per 1-lb. jar), and tight packs in which the ratio of fruit to liquid was greater than this.

The time taken for the heat to penetrate to the 'cold spot' in a 2-lb. container was longer than in a 1-lb. jar under the same conditions, but as the larger jar also maintained its heat longer, increases in the processing times were not essential for the water-bath methods. Longer times were required for jars larger than the 2-lb. size.

In addition to satisfactory keeping quality, the texture of the product is of importance. Some fruits are bottled chiefly for pies, and so are re-cooked after they are taken from the jars. Rhubarb (included as a fruit for preserving) and gooseberries, when processed sufficiently for use in pies, were tough when required for immediate use, and alternative processing times are given for pie or for dessert use.

The way in which the fruits were grouped when processing requirements were calculated are given in Table III. The minimum internal process temperature of the fruits had to be sufficient to prevent survival of micro-organisms at the different pH levels, and to control

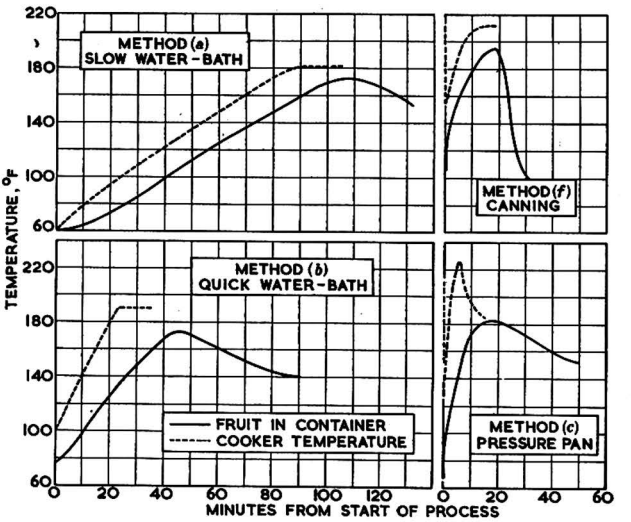

FIG. 1.—*Heating–cooling curves for stone-fruit in* 1*-lb. containers*

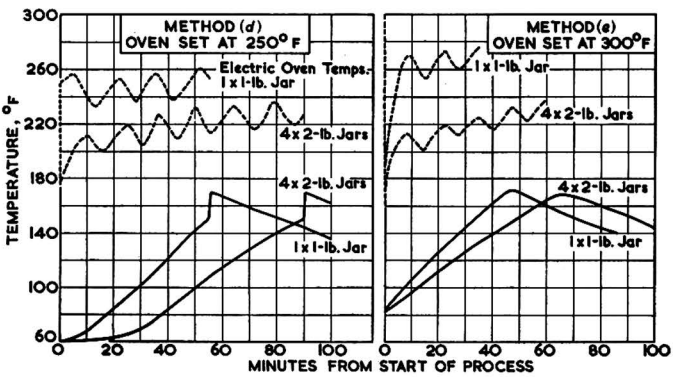

FIG. 2.—*Heating–cooling curves for stone-fruit in jars processed in an oven*

sufficiently the oxidase activity of the light-coloured fruits. The figures given were derived from a study of the microbiological tests together with the temperatures required for inactivation of the enzymes.

It will be seen that the minimum internal temperature was not always sufficient to inactivate the oxidase-enzyme system in all varieties of the fruit, but as this would entail over-processing when other requirements were considered, and as most of the fruit would reach temperatures considerably above that at the ' cold spot ' in the container, the risk of slight discoloration was felt to be justified.

The processing times recommended for the different groups of fruit bottled by the five methods finally adopted are given in Table IV. The canning times have not been included, as they have not been altered from those previously published.

Fuel consumptions

The quantities of gas or electricity used when different loads of fruit in Groups I and IV were processed for the times given in Table IV are shown in Table V. Since there was a great variation depending on the type of equipment used, these figures are the minimum obtained for each process. As would be expected, it is usually more economical to preserve 8–10 lb. of fruit at a time than smaller quantities, but if it necessitates the use of a large container this may not be so, e.g. the large pressure-pans are more wasteful of fuel than the smaller ones.

Table III

Fruit	pH range	Maximum temp. permitting oxidase activity, °F	Minimum internal process temp., °F
Group I	2·7–3·8		
Soft fruit, average packs, including gooseberries and rhubarb for pies		—	157° or maintained over 150° for 20 min.
Apple slices		150–165°	
Group II	2·8–4·3		
Soft fruit, tight packs		—	as Group I
Gooseberries and rhubarb for dessert		—	165° or maintained over 160° for 20 min.
Most whole stone-fruit		163–185°	
Group III	2·8–4·3		
Apples, solid-pack		150–165°	as Group I
Strawberries, soaked		—	
Nectarines		—	165° or maintained over 160° for 20 min.
Peaches		—	
Plums, halved		163–185°	
Group IV	3·7–4·6		
Figs, in acidified syrup		—	183° or maintained over 180° for 15 min.
Pears		181–188°	
Tomatoes, whole in brine		—	
Group V	3·9–4·4		
Tomatoes, solid-pack		—	as Group IV

Table IV

Fruit processing times : method of processing

Fruit group (see Table III)	(a) Slow water-bath	(b) Quick water-bath	(c) Pressure pan
I	Cold to 165° F in 1½ h. Maintain 10 min.	Warm to 190° F. 25–30 min. Maintain 2 min.	5 lb. pressure in 5–10 min. Maintain 1 min.
II	Cold to 180° F in 1½ h. Maintain 15 min.	,, 10 min.	,, 1 min.
III	,, ,, ,,	,, 20 min.	,, 3–4 min.
IV	Cold to 190° F in 1½ h. Maintain 30 min.	,, 40 min.	,, 5 min.
V	,, 40 min.	,, 50 min.	,, 15 min.

Fruit group (see Table III)	(d) Slow-oven		(e) Moderate-oven	
	Quantity processed		Quantity processed	
	1–4 lb.	5–10 lb.	1–4 lb	5–10 lb.
I	45–55 min.	60–75 min.	30–40 min.	45–60 min.
II	55–70 min.	75–90 min.	40–50 min.	55–70 min.
III	Not recommended		50–60 min.	65–80 min.
IV	80–100 min.	105–125 min.	60–70 min.	75–90 min.
V	Not recommended		70–80 min.	85–100 min.

The quantities of fuel used in heating the jars, lids, syrup, etc. have been included when these have to be applied hot. Since most methods of processing entail preliminary heating of water or an oven before the jars of fruit are put in, there will be saving on fuel if a second batch is processed immediately after the first. The saving will be found when the amounts of fuel used in the initial and subsequent processes in Table V are compared.

The order in which the processes are placed for fuel economy depends partly on the quantity of fruit being preserved. When the three ' loads ' in Table V are averaged, the processes may be placed in the following order:

Single process		*Subsequent processes*	
Electricity	Gas	Electricity	Gas
Slow water-bath	Pressure pan	Canning	Canning
Pressure pan	Slow water-bath	Pressure pan	Pressure pan
Quick water-bath	Slow oven	Slow oven	Slow oven
Slow oven	Quick water-bath	Quick water-bath	Quick water-bath
Canning	Canning	Moderate oven	Slow water-bath
Moderate oven	Moderate oven	Slow water-bath	Moderate oven

It will be seen from Table V that the oven methods (*d*) and (*e*) are more extravagant on fuel than the other processes if only one jar of fruit is being bottled, but this is not necessarily so when larger quantities are processed.

Table V

Electricity and gas consumptions per 1 lb. jar or can of fruit

Method of processing	Load per batch, lb.	Single process				Subsequent processes			
		Group I fruits		Group IV fruits		Group I fruits		Group IV fruits	
		Electricity, kwh.	Gas, cu. ft.	Electricity, kwh.	Gas, cu. ft.	Electricity, kwh.	Gas, cu. ft.	Electricity, kwh.	Gas, cu. ft.
(*a*) Slow water-bath	1	0·57	4·3	0·91	6·2	0·57	4·3	0·91	6·2
(*b*) Quick water-bath	,,	0·83	5·7	1·03	6·8	0·54	4·3	0·73	5·4
(*c*) Pressure pan	,,	0·63	3·6	0·67	4·1	0·43	2·4	0·47	2·9
(*d*) Slow oven	,,	0·98	6·9	1·19	9·3	0·53	4·0	0·74	6·4
(*e*) Moderate oven	,,	1·09	7·4	1·31	10·0	0·44	3·4	0·76	6·0
(*f*) Canning	,,	0·45	3·6	0·52	4·5	0·21	1·9	0·28	2·8
(*a*) Slow water-bath	5	0·15	1·3	0·22	1·8	0·15	1·3	0·22	1·8
(*b*) Quick water-bath	,,	0·19	1·6	0·25	2·1	0·14	1·3	0·18	1·8
(*c*) Pressure pan	,,	0·25	1·2	0·26	1·4	0·19	0·9	0·20	1·1
(*d*) Slow oven	,,	0·26	1·9	0·31	2·6	0·15	1·3	0·22	2·0
(*e*) Moderate oven	,,	0·27	2·4	0·36	3·2	0·16	1·6	0·25	2·4
(*f*) Canning	,,	0·31	3·0	0·34	3·4	0·10	1·1	0·13	1·5
(*a*) Slow water-bath	8 to 10	0·13	1·2	0·19	1·5	0·13	1·2	0·19	1·5
(*b*) Quick water-bath	,,	0·17	1·5	0·21	1·8	0·13	1·1	0·17	1·4
(*c*) Pressure pan	,,	0·17	1·3	0·18	1·6	0·11	0·9	0·12	1·2
(*d*) Slow oven	,,	0·17	1·2	0·21	1·6	0·11	0·9	0·15	1·3
(*e*) Moderate oven	,,	0·20	1·6	0·24	2·0	0·13	1·2	0·17	1·6
(*f*) Canning	,,	0·20	1·7	0·23	2·0	0·09	0·9	0·11	1·2

Discussion

These studies have shown the complexity of giving recommendations for processing fruit. In arriving at the processing times recommended in Table IV, 640 heating–cooling curves were plotted for different kinds of fruit. The fruits in Group I (Table III) are all in the high-acid group, and the oxidase-enzyme systems of the apples are inactivated at comparatively low temperatures. A relatively high ratio of liquid to solid is necessary if the heat is to penetrate adequately in the times given. The texture of gooseberries and rhubarb, processed as recommended for this Group, will be firm, so that they will tolerate further cooking without undue breakdown. The fruits in Group II comprise the soft fruits, which are packed with a higher fruit/liquid ratio, but not ' solid packs ', also the gooseberries and rhubarb, cooked sufficiently for serving without further heating, and most whole stone-fruit. The temperatures required to inactivate the oxidase-enzyme systems in the plums vary so considerably from one variety to another that it has been thought desirable to risk the possibility of slight discoloration in a few varieties for the sake of retaining a reasonably whole attractive product.

The fruits in Group III are those acid kinds that can be packed very tightly into the jars, as well as halved stone-fruit, and whole nectarines and peaches. The nectarines and peaches are not so acid as some fruits and also have oxidase-enzyme systems that are not readily inactivated by heat.

Group IV comprises figs, pears and whole tomatoes, all of which are in the higher pH ranges for fruits. In addition, the pears are very liable to enzymic discoloration. For this reason,

more stringent processing conditions are necessary. Even so, the figs should be packed in acidified syrup, otherwise there is a risk that pathogenic organisms, if present, might develop.

No spoilage has been noted in whole tomatoes when processed for the times given for the Group IV fruits (Table IV), but very occasionally spoilage has been noted in the solid-pack tomatoes, processed for the times given for Group V. Further investigations are being continued on the resistance of the spores of anaerobic organisms allied to *Bacillus thermoacidurans* at different pH levels in tomato pulp. It appears at present that the spores are not destroyed, but only inhibited, by the lower pH levels of the tomatoes, even if processed for a short while at 212° F.

The advantages and disadvantages of the different methods of processing may be summarized as follows:

Method (a): slow water-bath.—This is recommended as the most reliable method to use if the appearance of the fruit is of paramount importance, but it does necessitate the use of a thermometer if it is to be followed accurately. It is one of the most economical in fuel when only one batch of fruit is to be processed.

Method (b): quick water-bath.—This method was evolved for those people requiring a quicker process than method (*a*). The appearance of the fruit is nearly as good as that obtained by method (*a*), and the quick water-bath method does not require a thermometer (as 190° F can be taken as the approximate simmering point) and needs a considerably shorter total processing time. It is intermediate in fuel consumption for either single or subsequent processes.

Method (c): pressure pan.—Careful timing is required to avoid either under-processing or over-cooking of the fruit when this method of processing is used, therefore the minimum and maximum times in which the 5 lb. pressure should be reached have been defined. As 5 lb. is the minimum pressure recorded by many types of pressure pans this was used but even so, some breakdown of over-mature fruit may occur. Since insufficient time is given to remove all the air in the cooker, the 5 lb. pressure per sq. in. is usually a mixture of air and steam pressure, registering about 225° F, and 1 minute at this pressure is sufficient for the more acid fruits. Owing to the great differences in the temperatures of the fruit and cooker in this short time of heating, a cooling period of 10 minutes before the pan is opened is, however, essential. This point requires stressing as the instructions given by some of the manufacturers of the cookers recommend cooling the cooker quickly and removing the jars as soon as atmospheric pressure has been reached, which is often after only a few minutes. If this were carried out, the maximum temperature of the fruit in the jar would frequently be below 150° F and spoilage would be almost inevitable. This method of processing is one of the most economical in fuel, especially when using gas.

Method (d): slow oven, 250° F.—Oven processing of bottled fruit is not so reliable as the water-bath methods but often more convenient for the housewife. In the past, the processing time for this method was left largely to the experience of the preserver, who kept the jars in the oven 'until the fruit looked cooked'. It was found that the temperature of the fruit in the centre of the jar at this stage was far below the desired minimum, but when the jar was filled with boiling syrup or water there was a rapid rise in temperature and, provided that the jars were not tightly packed, this might be sufficient to prevent spoilage. The difficulty remained in judging when the fruit was sufficiently cooked.

The cooling effect of the different loads in the oven is very marked in thermostatically controlled gas or electric ovens, and in some of the heat-storage cookers this problem is so serious that oven bottling cannot be recommended. The effect can be offset in the gas and electric and some solid-fuel ovens by varying the process time according to the quantity of fruit being processed; but such variations do not overcome the difficulty of uneven heating throughout the oven, so that the fruit in tall jars tends to be overcooked at the top before that at the bottom has reached a sufficiently high temperature. The method cannot be recommended when processing fruits with light-coloured flesh, as the warm, dry atmosphere encourages enzyme activity, and the fruit is spoilt in appearance and flavour before the boiling liquid is added at the end of the process. The amount of fuel needed is very similar to that required in method (*b*).

Method (e): moderate oven, 300° F.—This method was adapted from that recommended by one of the firms supplying gas cookers. It overcomes the difficulties of processing fruits with light-coloured flesh found in method (*d*), since the boiling syrup or water is poured on the fruit before being processed in the oven. This also gives a more even penetration of heat, can be used for 'solid-pack' fruits, and the time required in the oven is less than in method (*d*).

In the early experiments with this method, the jars were put on an asbestos mat on the

oven shelves, but it was difficult to allow the exact amount of headspace for the expansion of the liquid to ensure that at the end of processing the jars were full but had not overflowed. Standing the jars in trays with deep sides was shown to be undesirable, but a flat baking-sheet, lined with newspaper to absorb any liquid, had no effect on the rate of processing, and was adopted as the most convenient procedure.

This method is the most extravagant of those studied from the point of view of fuel consumption, particularly if only one batch of jars is to be processed, but it has advantages over method (*d*) in ease of manipulation, and it can be used for all fruits.

Method (f): canning.—The advantages of canning over bottling are the rapid heat-transference possible through the metal container, so that comparatively short processing times followed by rapid cooling are used. The fruit is raised to a higher temperature than in the bottling methods, but, owing to the rapid cooling, the fruit is not broken down. The 1-lb. cans may safely be processed for 5 minutes less than the time recommended for the same fruit in an A2½ can, but if the full time is given, no over-cooking is apparent. It is the most economical method for fuel consumption if several batches of cans are to be processed, but not for a single process.

Conclusions

Studies of the pH values of different kinds of fruit, the temperatures required to inactivate the oxidase enzymes and to kill the micro-organisms likely to cause spoilage, and the rates at which the heat penetrates to the coolest part of the container have been made. Based on the results, new quick water-bath and steam-pressure processes have been developed and some of the processing times recommended for bottling fruit have been amended when the slow water-bath method is used. It was shown that the oven methods of bottling cannot be controlled as accurately as the water-bath methods, and the times of processing in the oven must be varied according to the quantity of fruit being processed. Recommended times are given for one process in a domestic oven controlled at 250° F, in which the jars of fruit are filled with boiling syrup or water after heating, and in another in which the jars are filled with fruit and boiling liquid before being processed in an oven controlled at 300° F.

The amounts of gas and electricity used in processing different quantities of fruit in the low and higher pH ranges have shown that the slow water-bath and steam-pressure methods are the most economical on fuel for a single batch of fruit, whereas canning is the best if several batches of fruit are to be processed consecutively. The oven method, controlled at 300° F, was generally the most extravagant of those tested.

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SODIUM AS A PLANT NUTRIENT*

By J. J. LEHR

1. The present paper gives a critical re-examination of different data and conceptions on the action of sodium in relation to deficiency symptoms and yield response.

2. The importance of sodium for different agricultural crops is discussed in relation to the replacement of potassium and independent sodium effects.

3. The results of pot experiments on oats, reported in the literature, indicate that sodium has an independent function other than that of replacing potassium. Both the nitrate and chloride of sodium appeared to be suitable for oats.

4. Field experiments testing sodium for early potatoes in Holland showed little effect on yield of tubers, but there were effects on the tops. Even at high levels of potassium there were responses in yields of main-crop tubers from dressings of sodium. The effect of sodium was studied by comparing sodium nitrate with calcium nitrate. When sodium chloride was applied to potatoes, either as common salt or with 20–40% muriate of potash, there were decreases in yield and starch contents of the tubers.

5. Results are given of recent Dutch experiments with fodder beet, testing sodium as nitrate of soda. The influence of soil type and addition of farmyard manure is discussed.

More than a century ago the founders of agricultural chemistry, when defining the elements vital for plant growth, such as nitrogen, potassium, phosphorus, calcium, magnesium and iron, included sodium among them. The first evaluation of sodium was therefore positive and little questioned, but physiological investigations, initiated in about 1860, did not confirm that sodium is strictly essential for plants, although a certain physiological activity could not be denied. It now appears that the negative conclusions on the essentiality of sodium, which obtained in this first period of physiological research, are no more conclusive than the positive evaluation from the early science of agricultural chemistry.

As we know, various essential elements were easily overlooked at that time, because water culture or sand–water culture techniques were very defective, and this coincided with inadequate analytical methods. Bertrand[1] has pointed out that the older analytical methods used for sodium, which were all of an indirect type, did not permit the determination of small quantities of this element and thus the impression was wrongly created that in many plants sodium is not a normal constituent. Bertrand analysed 450 different species of plant and found sodium in them all, although the content varied considerably, from more than 10 g. to less than 0·1 g. of sodium per kg. of dry matter. It is also obvious that the older analytical methods were unable to serve as a check on the complete absence of sodium in culture experiments and it is doubtful, therefore, whether the control solutions employed in the early physiological experiments were completely free of sodium. We cannot, of course, expect sodium to behave like a trace element, but the question of essentiality is still in dispute and has not yet been adequately tackled with modern techniques.

It must be emphasized that physiological investigations failed to find symptoms of sodium deficiency, that is symptoms of disease. Further, it is reported in the literature that certain plant species reached maturity in water cultures without the addition of sodium; nevertheless in the presence of sodium a certain yield-increasing action was found, especially if there was an insufficient supply of potassium. On the basis of these results, sodium was generally defined as beneficial, stimulating and, more especially, potassium-replacing. The reservation is still made that sodium can only partially replace potassium in some special functions but not in all. This definition places sodium in a position of complete dependence on potassium and closely links its practical effect with sufficiency or insufficiency of potassium. This conception is still found in most textbooks on physiology and agricultural chemistry.

Co-operation of potassium and sodium

It cannot be denied that the actions of sodium and potassium are closely associated. This is also apparent from their co-operation in relation to deficiency symptoms. In many crops sodium has the capacity to prevent, to defer for a long time, or to reduce considerably the occurrence of potassium deficiency. This part of the sodium effect is seen in all our experiments with fodder beet, sugar beet, table beet, oats, barley, Westerwold rye-grass, English rye-grass, turnips (autumn variety), lupins, red and white clover, potatoes, marrow-stem kale and rapeseed. Figs. 1 to 7 show some examples of this capacity. Most of the experiments were carried out with nitrate as the sodium carrier and the sodium action is demonstrated

* Read before the Agriculture Group on 18 November, 1952

by comparing sodium nitrate with calcium nitrate. Similar examples are reported for sodium chloride and sodium sulphate.

As already stated, there is never any question of complete replacement: a certain minimum of potassium is always required. If this minimum is not available the addition of sodium may even aggravate the symptoms of disease. (This phenomenon was observed in July, 1952, in an experiment with mangolds and kale on Lord Rosse's estate at Birr, Ireland. The crops

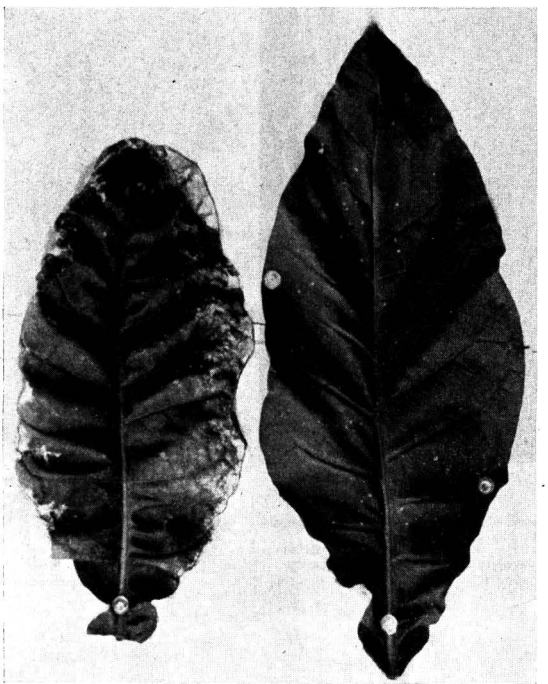

FIG. 1.—*Tobacco leaves from pot trial with humic sandy soil without potash dressing*

Left: Symptoms of potassium deficiency are seen in a leaf from plant dressed with nitrate of lime
Right: Normal leaf from plant dressed with Chilean nitrate of soda

showed marked signs of potassium deficiency and without potash fertilization common salt had an adverse effect. On the other hand, an appreciable improvement was obtained with common salt in combination with potash.) In many cases, however, the potassium present in the soil, if combined with a sodium dressing, is sufficient to eliminate the deficiency. As far as is known, no similar example has been reported in which deficiency symptoms of one element can be removed by the presence of another element. This demands a critical approach, as our definition of the essentiality of nutritive elements is based on the occurrence of specific disease symptoms and on the irreplaceability of the element concerned.

The co-operation between potassium and sodium is tentatively shown in Fig. 8; each column represents the minimum total amount of univalent cations needed for healthy development of certain crops. According to prevalent conceptions the need of univalent ions can be completely filled by potassium, but some of the functions of potassium can also be exercised by sodium, as is shown by the unshaded section of each column. Consequently, only that quantity of potassium which is irreplaceable by sodium is essential to plant life. As far as physiological activity is concerned, sodium behaves like a normal main element, and it may therefore be asked whether it is certain that sodium has no essential function of its own which may have escaped the attention of former investigators, and whether, as with potassium, a minimum quantity of sodium is required for the normal development of plants.

FIG. 2.—*Barley plants grown without potash fertilizer on trial field at Halle, Holland*

Left: Plant dressed with nitrate of lime shows severe damage from potassium deficiency
Right: Plant fertilized with Chilean nitrate of soda shows healthy development and no signs of deficiency

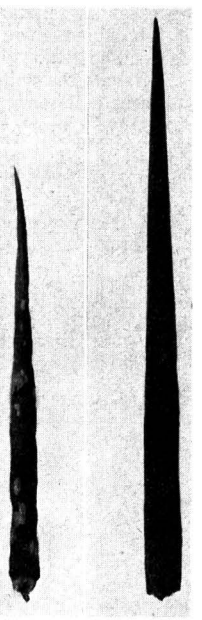

FIG. 3.—*Barley leaves taken from the plants seen in Fig. 2*

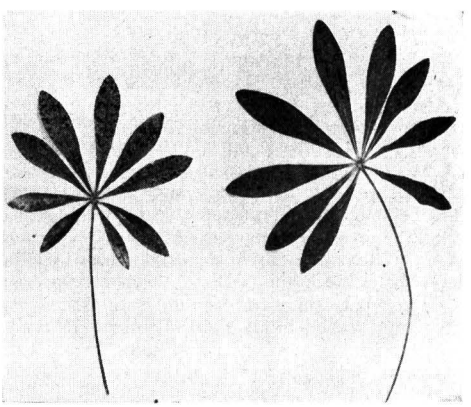

FIG. 4.—*Lupin leaves from plants grown without potash dressing—field experiment at Halle, Holland*

Left: Symptoms of potassium deficiency occurred on plots dressed with nitrate of lime
Right: Leaf from plot dressed with Chilean nitrate of soda had a healthy appearance and only on drying were some dark spots visible on the surface

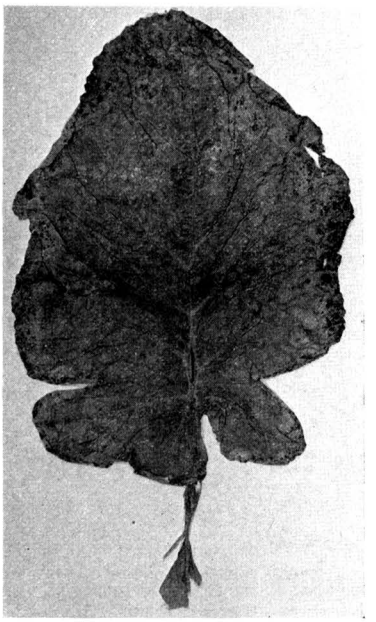

FIG. 5.—*Marrow-stem kale : dried leaves from sodium/potassium experiment at Halle, Holland*

Potassium deficiency was very marked on plots dressed with nitrate of lime in the absence of potash

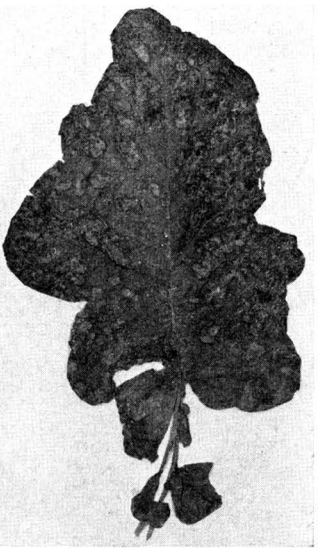

FIG. 6.—*Marrow-stem kale : dried leaves from sodium/potassium experiment at Halle, Holland*

Symptoms of severe potassium deficiency still occurred with nitrate of lime plus a low potash dressing

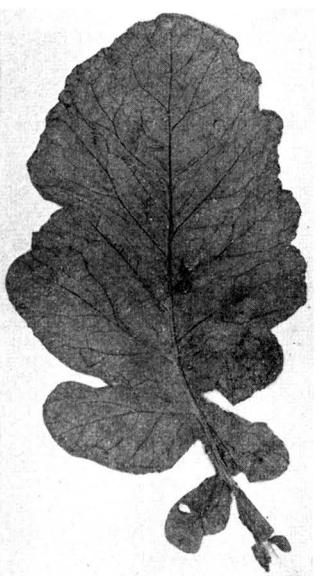

FIG. 7.—*Marrow-stem kale : dried leaves from sodium/potassium experiment at Halle, Holland*

No sign of potassium deficiency was seen in plants dressed with Chilean nitrate of soda in the absence of potash

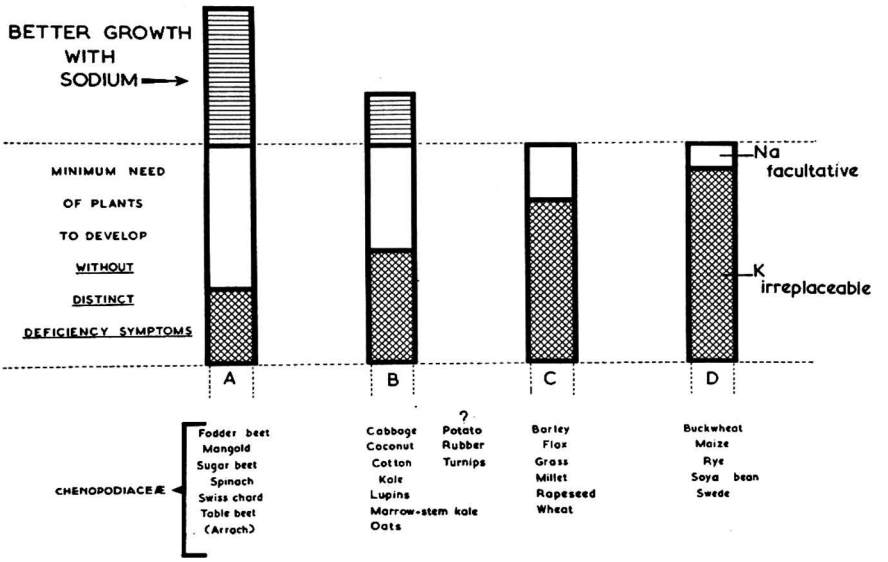

Fig. 8.—*Tentative scheme for classification of crops according to potassium-replacing power of sodium and independent sodium-effect on yield*

Before this question is discussed the relative needs of different crops for potassium and sodium must be considered. The crops can first be classified according to the proportion of potassium which can be replaced by sodium; groups classified according to the importance of sodium are then obtained, as shown in Fig. 8.

Group A has the largest sodium : potassium ratio, and represents those crops having the highest capacity to absorb sodium. All the members of this Group are Chenopodiaceae, the family which is often described as halophytic. Although there can be little doubt about the sodium-loving character of these crops the classification of other crops in Groups B, C and D is still somewhat arbitrary, and this part of the diagram should only be considered as a working scheme. A special feature of Group A—probably also applicable to Group B—is that, in the presence of sufficient potassium, sodium is still able to increase yields. The columns representing these Groups have been extended to indicate this effect.

Harmer & Benne[2] made another classification of crops based on the degree of benefit derived from sodium in the absence and presence of sufficient potassium (Table I).

Table I

Effect of sodium applied as a nutrient on several crops[2]

Number	Degree of benefit in deficiency of potassium		Degree of benefit in sufficiency of potassium	
	1. None to very slight	2. Slight to medium	3. Slight to medium	4. Large
1	Buckwheat	Asparagus	Cabbage	Celery
2	Corn	Barley	Celeriac	Mangel
3	Lettuce	Broccoli	Horse-radish	Sugar beet
4	Onion	Brussels sprouts	Kale	Swiss chard
5	Parsley	Caraway	Kohlrabi	Table beet
6	Parsnip	Carrot	Mustard	Turnip
7	Peppermint	Chicory	Radish	
8	Potato	Cotton	Rape	
9	Rye	Flax		
10	Soya bean	Millet		
11	Spinach	Oat		
12	Squash	Pea		
13	Strawberry	Rutabaga		
14	Sunflowers	Tomato		
15	White bean	Vetch		
16		Wheat		

Nitrate of lime without potash dressing

Nitrate of lime with 400 kg. per hectare of 40% muriate of potash

Nitrate of lime with 800 kg. per hectare of 40% muriate of potash

Chilean nitrate of soda without potash dressing

FIG. 9.—*Dried leaves of fodder beet from sodium/potassium field experiment*

Disease symptoms—apparently potassium deficiency—may occur very persistently in fodder beet even with heavy dressings of potash, but seldom when nitrate of soda is applied without potash; this probably indicates that sodium is essential to this crop

[*The production of these illustrations in colour has been made possible by the courtesy of the Nitrate Corporation of Chile Ltd.*]

Both schemes have approximately the same groups of crops, though there are some striking differences, for example spinach. Harmer & Benne also consider their classification to be tentative, but it offers a valuable starting point for further investigation.

Sodium as an essential element

When the question is considered whether sodium has any independent function in the plant, quite apart from its power to replace potassium, it is obvious that symptoms of sodium deficiency should first be investigated in the crops of Group A. References made in the recent literature on sodium suggest a certain essentiality of this element for some crops:

No top yields of barley without sodium chloride[3] (Wagner, p. 328).

Sodium indispensable for sugar beet[4] (Stoklasa & Matousek, p. 16).

With sugar beet a fair amount of sodium is presumably always necessary for satisfactory foliage development, even if sufficient potassium is present[5] (van Ginneken & Bruinsma, p. 312).

The need for sodium of fodder beet is greater than that of any other agricultural crop; consequently, where other crops remain without sodium response, beet may have a considerable need of this element, which cannot be met, or can barely be met, by supplying more potassium[6] (van Itallie, p. 69).

Improvement of crops by sodium in the presence of potassium; a smaller proportion of roots affected by damping-off and black rot; healthier, glossier leaves, which appear more resistant to the attacks of such diseases as leaf spot of beets and blight of celery; and an improved keeping and eating quality for celery[7] (Harmer & Benne, p. 954).

Examples of combined sodium and potassium deficiency with sugar beet; probably one example of sodium deficiency only[8] (Hale *et al.*, pp. 20–21).

Symptoms of sodium deficiency in sugar beet, mangold and garden beet: leaves dull-green and appear thin; marginal and intervenal scorch similar to that from potassium deficiency; very subject to wilting[9] (Wallace, p. 71). (Wallace[9] states on page 60—'The only crops on which sodium deficiency effects may be said to be shown are the sodium-loving crops, such as sugar beet, mangolds and turnips. Where sodium is in short supply for these plants, the leaves are dark green, rather dull, wilt rapidly in drought and many tend to grow out horizontally from the crown of the plant. Some marginal brown scorch may develop.')

In pot experiments, occurrence of specific sodium-deficiency symptoms in sugar beet.[10]

Taken by themselves, these examples may not yet be considered sufficient evidence of sodium-deficiency symptoms or of the essentiality of this element for certain plant species, but they indicate that negative conclusions about sodium should not be regarded too categorically. There are, however, further indications to support the view that the significance of sodium rests on something more than a function that is subordinate to potassium.

In demonstration trials in Holland, which are carried out every year with fodder beet, deficiency symptoms are found to occur very persistently, especially on ploughed grassland; a dressing of 800 kg. of 40% muriate of potash per hectare, when combined with a dressing of 'nitrate of lime' (800 kg. per hectare) may be insufficient to prevent the disease, and deficiency symptoms occur very seldom if the potash dressing is omitted and 'nitrate of soda' (800 kg. per hectare) is applied. Specimens of dried leaves taken from one of the trial fields illustrate this (Fig. 9). It should be emphasized that the total quantity of univalent ions in 800 kg. of muriate of potash (40%) (which is 6·8 kilo-equivalents of potassium + 4 kilo-equiv. of sodium) is even higher than that in 800 kg. of nitrate of soda (9·4 kilo-equiv. of sodium).

An experiment at Rothamsted Experimental Station, reported by Crowther,[11] shows that, above a certain level of potassium fertilization, sodium chloride is more effective than potassium chloride in increasing the yield of sugar beet, if calculated on a chemical equivalent basis. In this connexion it may be useful to transcribe the results of some of our fodder-beet experiments in Holland.

In 1946–47 the average surplus yield with potassium dressings [800 kg. of nitrate of lime + 800 kg. of K40 (40% muriate of potash) compared with 800 kg. of nitrate of lime without potassium dressing] was 32·5%; the average effect of sodium dressing (800 kg. of nitrate of soda compared with 800 kg. of nitrate of lime, both without potassium dressing) was 32%. In six out of eight examples the potassium effect was greater than the sodium effect; in the remaining two examples the sodium effect was greater.

In 1948 the average reactions for potassium and sodium were 23½% and 25% respectively. The potassium effect was greater in four examples out of fourteen, the sodium effect in nine examples.

In 1951 twenty trials were carried out on a slightly modified scheme. The average results, drawn from a report by M. Rosanow (of this Laboratory), are stated in Table II.

Fig. 10 represents a more detailed analysis of these results according to particular aspects (one trial on a deviating soil type omitted).

Table II

Average beet yields per hectare

	No potash	400 kg. of 40% muriate of potash	800 kg. of 40% muriate of potash
Chilean nitrate of soda	69,629 kg.	72,143 kg.	74,106 kg.
Nitrate of lime or kalkammonsalpeter (limed ammonium nitrate)	60,432 ,,	64,197 ,,	67,588 ,,

Sodium effect: 15% Potassium effect: 12%

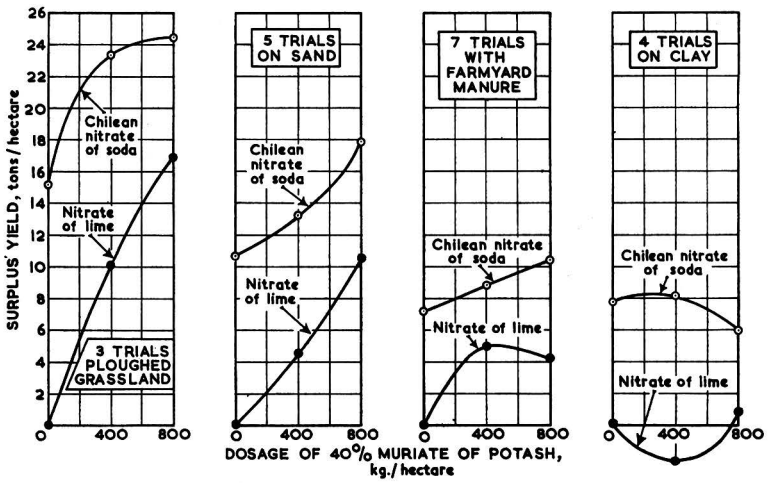

FIG. 10.—*Average results of twenty fodder-beet trials, Holland, 1951*

A remarkable feature was, that in experiments with a basic dressing of farmyard manure (20 tons per hectare), the raising of the potash dose from 400 to 800 kg. per hectare, in combination with nitrate of lime, gave negative results in five cases out of seven, but an increase in yield was obtained with Chilean nitrate of soda.

In four experiments on clay soils there was, on the average, no effect of potash fertilization against a still important positive effect of sodium.

These results show that there are conditions either in which sodium can be more effective than potassium, or in which sodium may even increase yields when potassium does not.

Effect of sodium on yield of oats and potatoes

Another method of studying the essentiality of an element is to examine the yield curves of two co-operating nutritive elements. Experimental methods described in the literature can be divided into two groups: X, in which increasing doses of potassium are used, with and without the addition of a constant amount of sodium, and Y, in which a constant sum of univalent ions (potassium and sodium expressed in equivalents) is used, but with ratios varying between 100% of sodium and 100% of potassium.

Starting from type-X experiments (Fig. 11), curve X1 shows theoretically the trend of yields when sodium has a potassium-replacing effect but no specific function of its own. At lower potassium doses there is a yield-increasing effect which decreases to zero in the presence of sufficient potassium. If the yield curves run as in X2, an independent function of sodium is indicated, because there is then a yield-increasing effect even in the presence of sufficient potassium. In experiments of type Y, curve Y1 represents the partial replacement of potassium by sodium, and curve Y2 indicates an independent action of sodium. This type of curve implies that maximum yields cannot be achieved with potassium alone, and that a certain amount of sodium is necessary.

In 1943 some pot experiments were carried out with oats[12] and compared with former experiments described in the literature; ten pot experiments are suitable for an examination by the yield-curve method.

If the results of twelve experiments (Table III) are summarized, it can be seen that nine examples support an independent function of sodium in the oat plant, but only three favour a more restricted ability to supplement potassium if this element is insufficiently supplied. Moreover, two of these three examples are not conclusive, as it is certain that a fair amount of sodium was already present in the nutrient medium.[12]

Further experimental data are desirable but a conclusion may now be drawn from this brief survey. There is little confirmation of current conceptions on sodium and it is surprising that former investigators, in their interpretation of the sodium effect, adhered to a definition which is rather negative and does little justice to the facts.

It may be noted that these oat experiments do not establish any difference, in principle, between various forms of sodium, except that no positive results are stated for the sulphate.[19] Chloride and nitrate, however, were both found to be active carriers of sodium.

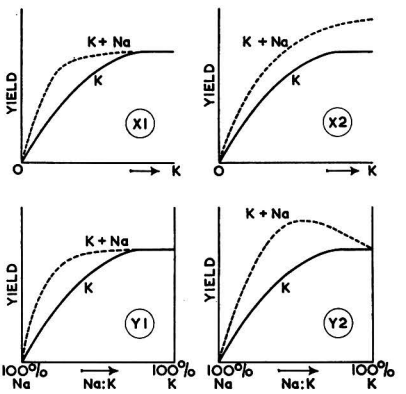

FIG. 11.—*Theoretical yield curves showing sodium/potassium co-operation*

Table III

Physiological experiments with oats

Year	Author	Type of experiment	K/Na replacement	Independent effect of sodium
1868	Wolff[13]	Y. water cultures		+
1891	Atterberg[14]	Y. sand/water cultures	+	
1898	Hellriegel *et al.*[15]	Y. sand cultures		+
1902	Wilfahrt & Wimmer[16]	X. ,, ,,		+
1904	Damseaux[17]	Y. ,, ,,		+
1918	Mitscherlich[18]	X. pot experiments		(+)
1920	Pfeiffer & Rippel[19]	Y. sand cultures	+*	
1936	Boguslawski[20]	X. pot experiments, loamy and sandy soils		+
1945	Holt & Volk[21]	X. sand cultures		+
1949	Larson[22]	X. pot experiments, loamy soil		+
1952	Lehr[12]	X. ,, ,, sand/dusarite† cultures		+
1952	Lehr[12]	X. ,, ,, sandy soil	+*	

* In these experiments the medium itself contained considerable amounts of sodium
† A carbon preparation with a high adsorptive capacity for cations

Another interesting example of the action of sodium is shown by potatoes. According to the classification of Harmer & Benne, this crop does not benefit at all from sodium, or only very slightly, even when potassium is deficient. This conclusion is probably based on American experiments with salts containing chlorine. European literature, however, contains several communications with more positive results. Nevertheless, the potato is a special example because this crop has a relatively low capacity to absorb sodium, which makes it more difficult to explain the yield-increasing effect. This may be illustrated by some analytical figures (Tables IV and V) which show the different behaviour of oats and potatoes.

Thus, sodium can comprise more than half of the total amount of univalent ions in the oat straw, and potassium and sodium can more or less replace each other equivalently. This phenomenon has already been described by Maschhaupt.[24]

Table V gives the analyses of potatoes ('Eigenheimer' variety) from the same trial field (1950).

The potato plant appears to have a slight capacity to absorb sodium even at very low levels of potassium in the soil. There is no question of an equivalent replacement, and the contents of the foliage suggest that potassium is by far the most important nutrient for this crop.

Table IV

Contents of potassium and sodium in oats (1948) *at heading stage in milli-equiv. per* 100 *g. of dry matter*[23]

	Chilean nitrate of soda			Nitrate of lime		
	K	Na	Total	K	Na	Total
			'Express' variety			
Control	31	64	95	34	5	39
K1	60	39	99	60	6	66
K2	79	25	104	98	3	101
K3	100	15	115	120	3	123
			'Mansholt' variety			
Control	35	64	99	44	8	52
K1	63	52	115	76	5	81
K2	88	23	111	85	4	89
K3	107	14	121	115	3	118

Table V

Contents of potassium and sodium in potatoes (1950) *in milli-equiv. per* 100 *g. of dry matter*

	Chilean nitrate of soda			Nitrate of lime		
	K	Na	Total	K	Na	Total
			Tubers			
Control	30	10	40	31	4	35
K1	32	10	42	26	5	31
K2	43	8	51	47	5	52
K3	53	4	57	54	5	59
			Foliage			
Control	9	11	20	7	6	13
K1	28	7	35	11	5	16
K2	87	5	92	71	4	75
K3	124	4	128	114	2	116

The figures agree with those obtained by Metz[25] in a pot experiment with potatoes. Only in some extreme cases did he find a higher sodium content in the foliage (up to 24 milli-equivalents per 100 g. of dry matter), and the highest figure for potassium was 108 milli-equivalents. Metz attributed the yield-increasing effect of sodium (as sulphate) to a liberation of potassium from the foliage, which is thus released for the tuber. In the field experiment at Halle, Holland, this theory could not be confirmed. Though appreciable yield increases were obtained at the K0 and K1 levels (30% and 23% respectively), resulting in an increased recovery of potassium by the tubers, the potassium content in the foliage did not show any decrease. (The potassium levels referred to in this paper may be defined as follows: K0 = control or no potassium dressing, K1 = low to moderate potassium dressing, K2 = normal potassium dressing, and K3 = high potassium dressing.)

Ten experiments with potatoes were carried out, all on fields undergoing long-term trials with a rotation of crops. To study the effect of sodium, Chilean nitrate of soda was compared with nitrate of lime, or in some cases with 'kalkammonsalpeter' (limed ammonium nitrate) at increasing potassium levels. Potassium was supplied as sulphate except in one experiment. Very little effect was obtained in experiments with early potatoes, as is shown in Table VI.

The effect of potassium (yield increase with nitrate of lime : K3–control) amounted to 7% in the first experiment but was negative for the plots dressed with Chilean nitrate of soda. In the second experiment there was no potassium effect and in the third only a slight potassium effect. The fourth experiment showed a marked response from potassium dressings—27% increase on the average for both nitrogen fertilizers.

Although, in general, sodium dressings did not increase the yield of early potatoes, main-crop tubers gave surplus yields fairly regularly (Table VII).

In six field trials, all on sandy soils, the sodium effect amounted on an average to 9·6% for plots without potassium or with a low potassium dressing, and to 5·8% for plots dressed with normal or high quantities of potash. The latter figure is not spectacular but it has

Table VI

The effect of sodium (as Chilean nitrate of soda) on yield and starch content of early potatoes

Year	Place	Average effect on tuber yield: control	Average effect on tuber yield: other potassium levels	Average effect on starch content	Average effect on starch yield: control	Average effect on starch yield: other potassium levels
1948	1. Varsseveld	17%	average 2%	average − 0·3%	16%	average − 5%
1949	2. Wognum		average ½%	not determined		not determined
1949	3. Heer Hugowaard		,, ,,	not determined		not determined
1950	4. Wageningen		,, ,,	average − 0·8%		average − 5%

1. 1st year expt. on sandy soil (Eersteling variety): comparison with nitrate of lime
2. 1st ,, ,, ,, clay soil (Eersteling ,,): ,, ,, limed ammonium nitrate
3. 2nd ,, ,, ,, clay soil (Rode Eersteling variety): ,, ,, ,, ,, ,,
4. 2nd ,, ,, ,, sandy soil (Doré variety): ,, ,, ,, ,, ,,

certain economic importance and is also comparable with the effect of potash dressings in the one-year and two-year trials (on an average 7%). Besides, there is reason to assume that, in experiment No. 8, a condition of overdosage of sodium was reached by the regular application of sodium nitrate, and, in experiment No. 9, the plants had to be harvested early on account of the dryness of the local climate. On the control plots the starch content appeared to have been little influenced by sodium (average + 0·1%) but, when combined with a potash dressing, sodium tended to lower this content (average − 0·4 to − 0·45%). In addition, there was a decrease of 0·5%, on average, due to the potash dressings (K_2, K_3)–(K_0, K_1).

The results are not yet sufficient to formulate a final valuation of the economic importance of sodium dressing for potatoes generally, but it seems fairly safe to conclude that there is good reason for the use of sodium dressing for main-crop potatoes. Obviously, sodium does not accelerate the formation of tubers in the early stage.

In looking for an explanation of this difference the following facts are important. In some experiments (Nos. 1, 6 and 8) it was observed that the foliage of plants dressed with nitrate of soda remained green after the plants that had received nitrate of lime had withered. In this way the growth period was prolonged by seven to ten days. Yield determinations of experiment No. 4 (early potatoes) showed an average surplus yield of 14% for the foliage of the plants dressed with nitrate of soda. The explanation of the different behaviour of early and main-crop varieties may therefore be twofold: 1, better assimilation by the larger leaf surface and conversion of foliage into tuber at the end of the vegetative period, and 2, additional production of tubers is reached by the prolonged vegetative period of plants fertilized with nitrate of soda.

So far we have dealt with experiments carried out with nitrate as the sodium carrier. The literature, however, shows that potatoes also respond to dressings of sodium sulphate or sodium carbonate.

Table VII

The effect of sodium on yield and starch content of main-crop potatoes (experiments on sandy soil)

Year	Place	Average effect on tuber yield: K_0, K_1	: K_2, K_3	Average effect on % starch content: K_0	: K_1, K_2, K_3	Average effect on starch yield: K_0, K_1	: K_2, K_3
1944	5. Halle	6·5%	4·9%	0·8	− 0·1	7·6%	2·1%
		—	6·0%	− 0·9	− 0·6	− 4·8%	3·2%
1946	6. Volkel	—	10·2%	—	− 1·0	—	2·9%
1946	7. Volkel	5·5%	6·9%	− 0·2	− 0·4	3·9%	3·8%
1950	8. Halle	26·7%	2·8%	− 0·2	− 1·9	22·0%	− 3·1%
1952	9. Gerritsland	6·5%	1·5%	1·0	− 0·1	6·0%	1·0%
1952	10. Lochem	14·4%	8·5%	0·2	0·1	15·6%	7·6%
	average	9·6%	5·8%	0·1	− 0·45	8·4%	2·5%

5. 2nd year experiment; Eigenheimer and Gloria varieties
6. 1st ,, ,, ; phosphate trial; Bintje variety
7. 1st ,, ,, ; Bintje variety
8. 8th ,, ,, ; Eigenheimer variety
9. 5th ,, ,, ; Eigenheimer ,,
10. 4th ,, ,, ; Eigenheimer ,,

Effect of chlorides on yield and starch content

Experiments with common salt or with potassium salts containing sodium chloride, such as kainite, are generally described as unfavourable, especially with respect to their influence on the percentage of starch. The field experiment at Lochem in 1952 (Table VII, Expt. No. 10) was devoted to this question and instructive results were obtained. Chilean nitrate of soda and nitrate of lime (both 500 kg. per hectare) were compared at three potassium levels (control, 90 and 180 kg. of K_2O). Potash was applied in three forms: 60%, 40% and 20% muriate. Included also were plots with nitrate of lime + 60% muriate of potash + a quantity of common salt supplying an amount of sodium equivalent to that in the sodium nitrate dressing. Further, there was a treatment with Chilean ' potassic nitrate of soda ' (10% of K_2O as nitrate, remainder $NaNO_3$).

For comparison of the different grades of potash, the content of sodium chloride is calculated as follows:

180 kg. of K_2O as K60 (60% muriate of potash) corresponds to 10 kg. of sodium chloride
180 kg. of K_2O as K40 (40% ,, ,, ,,) ,, ,, 147 kg. of sodium chloride
180 kg. of K_2O as K20 (20% ,, ,, ,,) ,, ,, 510 kg. of sodium chloride
344 kg. of sodium chloride contains approximately the same quantity of sodium as 500 kg. of sodium nitrate

The inclusion of potassium salts and common salt raised the problem of the time of application. When chlorine-containing potassium salts are used on potatoes it is the general practice to apply early, so that the adverse effect of the chloride is reduced by leaching. This entails the risk of losing some of the potassium, a risk which is even greater with sodium. As the main purpose was to determine the fertilizer value of material as chloride, we chose the middle course, as the following time-table shows: 7 March, muriate of potash applied; 21 April, planting; 25 April, common salt and nitrogen fertilizers applied; 12 May, first appearance of plants. The results of this experiment leave no doubt that chlorides act unfavourably, for both yield and starch content. Although sodium nitrate increases yield (Fig. 12), common salt decreases it markedly, except when combined with a double dressing of 60% muriate of potash. At the same time, 40% and 20% muriate appear to be less satisfactory than the 60% grade, except for 40% muriate when combined with nitrate of lime.

As regards the influence of different fertilizers on starch content, a marked increase was obtained with potassium as nitrate (see Fig. 13: Chilean 'potassic nitrate'). These plots produced the highest quantity of starch of the whole experiment. The single dressing of muriate of potash (60%) did not affect the percentage of starch either way, but the double dressing lowered the content. As the decrease was still more pronounced with 40% and 20% muriate of potash there is no doubt that chloride has an adverse influence on the starch content. In this experiment there was no adverse action from sodium, the starch content with sodium nitrate being, on an average, 0·1% higher than with nitrate of lime. Sodium as chloride, on the other hand, greatly depressed the starch content, although this was offset to a certain extent by the application of 60% muriate of potash.

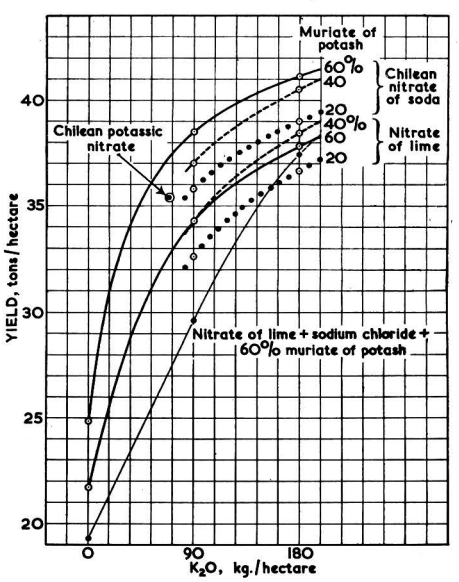

FIG. 12.—*Comparative yields of potatoes in sodium/potassium experiment at Lochem, Holland*

In the classification of crops (Fig. 8) it would be reasonable to place oats in Group B, because sodium can replace a fair amount of potassium and can even produce appreciable surplus yields in conditions of adequate supplies of potassium. It is a little more difficult to indicate a proper place for potatoes; the capacity of this crop to absorb sodium and its low potassium replacement

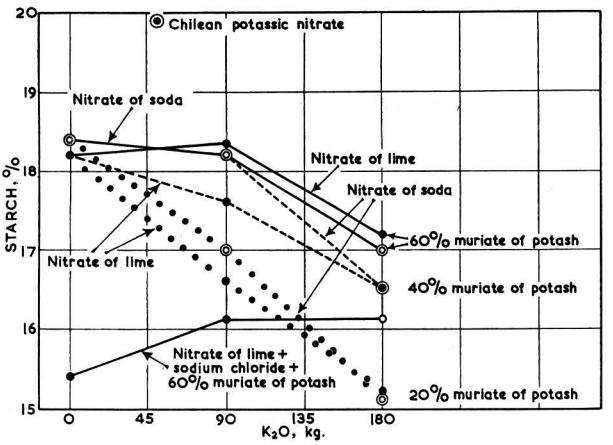

FIG. 13.—*Starch content of potatoes in sodium/potassium experiment at Lochem, Holland*

suggests Group C. Nevertheless, potatoes show a certain benefit from sodium in the presence of potassium, a feature which is not associated with Group C. Either an additional and intermediate group between B and C must be made, or the scheme be amended so that Group C covers some independent function of sodium and its ability to give extra yield. Before this problem can be dealt with, further research will be necessary to confirm the present findings and to clarify the position of other crops in Group C.

Acknowledgment

Figs. 3–7 and 9 are reproductions of leaves from a collection made and prepared by J. M. Wybenga, to whom the author is indebted for his kind assistance.

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SOME NOTES ON THE DETERMINATION OF METHYL KETONES

By N. J. BERRIDGE, M. ZIELINSKA and J. BARRETT

Four main classes of previously known methods of determining methyl ketones have been tested and improvements have been made in some of them. The method based on pH measurements of mixtures of the ketones with hydroxylamine hydrochloride solution was shown to be most suitable for numerous routine determinations such as might be required in chromatography.

It has been known for some time that methyl ketones occur in rancid fats, particularly as a result of the activity of moulds.[1, 2] It was therefore not surprising that they should be found in blue-vein cheese, nor that they should contribute to its flavour.[3] In order to help in the chemical examination of such materials it would be useful to have a ready means of analysis for methyl ketones. Some of the known methods give values that depend on the identity as well as on the quantities of the ketones present in a mixture, and with other methods the figures obtained cannot be related directly to flavour because of the different flavours of different ketones. Thus the ketones must be separated before progress can be made. Adsorption or partition columns offer the most promise and for the majority of these it would be necessary to break up the effluent into many samples for separate analysis. A simple, reliable and rapid method of analysis is therefore a prerequisite. Several methods taken from the literature and, in some cases, modifications of them, have been examined from this point of view and the results are presented in this paper.

(1) Determination with salicylaldehyde

Salicylaldehyde forms intense colours in the presence of methyl ketones and concentrated acid[4] or alkali.[5, 6] Some years ago Täufel *et al.*[4] attempted to make the method quantitative by the use of sulphuric acid, and they also studied its specificity. From the work of these authors it may be surmised that the method is very sensitive to the actual technique of handling, and this was found to be so. Some skill was needed to avoid charring of the samples when sulphuric acid was added and though this was readily acquired the intensity of colour was still subject to fortuitous variations. When distillates from butter or cheese were tested, atypical colours were produced. They were too yellow, although charring had been avoided, and none of the filters available permitted the measurement of the typical pink colour in the presence of the yellow.

Schmalfuss *et al.*[7] used fuming hydrochloric acid to avoid the risk of charring. The concentration of the acid was not specified, but it is important since too high a concentration produces pink colours in the absence of methyl ketones. This was noticed when hydrochloric acid gas was bubbled into the reaction mixture.

It has recently been shown[8] that the reaction between salicylaldehyde and acetone in the presence of potassium hydroxide can be made more reproducible if light and air are excluded, and if at least five hours elapse between warming and the final measurement of light absorption. Working with different reaction conditions Thin & Robertson[9] appeared to find such precautions unnecessary; perhaps this was because their estimations were carried out at room temperature.

It can readily be observed in experiments with salicylaldehyde that the colour develops in the oily aldehyde phase, which tends to separate during the heating of the mixture. Reactions in a heterogeneous system are more difficult to control than those in a homogeneous system. The systems under test could be made homogeneous by the addition of sufficient alcohol, and after a few experiments a reagent mixture of ethanol, hydrochloric acid and salicylaldehyde was chosen as showing promise. The mixture itself becomes pink on being set aside or on heating alone, so that blank determinations had to be made with every batch. This reagent gave reproducible results, with reasonable adherence to Beer's law, and, though useless for mixtures, it is apparently suitable for determining single ketones.

Experimental

Reagent.—A mixture of ethanol (30 ml.), 10N-hydrochloric acid (20 ml.) and salicyl-

aldehyde (2 ml.). The reagent was used within an hour of mixing.

Procedure.—Ketones were diluted in two stages to give aqueous solutions of a concentration between 0·04 and 0·4 millimolar. With methyl *n*-amyl ketone the first dilution was made in ethanol. The ketone solution (2 ml.) was mixed with 5 ml. of reagent, the mixture was heated in a water bath at 80° for 15 minutes, then removed and allowed to cool rapidly. Ethanol (5 ml.) was mixed with the now pink solution and the light absorption determined immediately by the Spekker absorptiometer with the green filter. Unknown solutions, such as cheese distillates, standard solutions with known amounts of ketone, and 'blanks' with distilled water were heated together in the same bath, with the same reagent.

Results.—Fig. 1 shows the standard graph obtained with methyl *n*-propyl ketone. Table I shows the effect of increasing the time of heating, which increases not only the colour of the blank but also the difference between the blank and the ketone solution. Table II gives the colour intensities of several ketones, and in Table III results from various methods are compared for a number of cheese distillates.

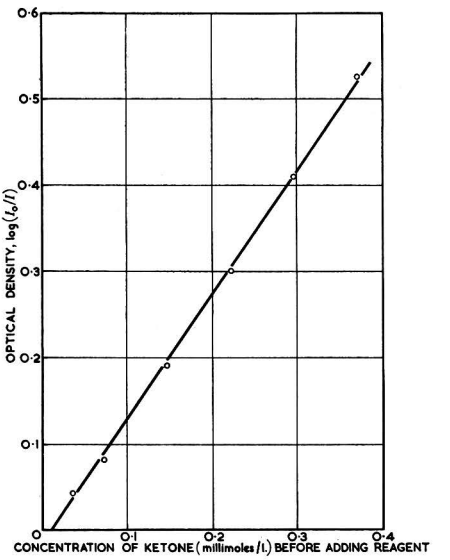

FIG. 1.—*The absorption of green light by the salicylaldehyde derivative of methyl* n-*propyl ketone, plotted against ketone concentration*

Table I

Effect of heating time on the colour produced by salicylaldehyde and methyl n-*propyl ketone*

Time at 80°, min.	Optical density difference*
10	0·57
20	1·07
30	1·52
40	2·00
50	1·77
60	2·36

* ($\log I_{blank} - \log I_{ketone\ solution}$) determined after dilution and calculated back to original volume

Table II

Effect of kind of ketone (concn. 0·45 millimolar) on colour intensity with salicylaldehyde

Ketone	Optical density (as in Table I)
Acetone	0·04
Methyl ethyl	0·30
Methyl *n*-propyl	0·14
Methyl *iso*butyl	0·01
Methyl *n*-amyl	0·21
Methyl *n*-hexyl	0·23

Table III

Comparison of ketone content of steam distillates of cheese determined by different methods

Distillate No.	Ketone expressed as methyl *n*-amyl ketone (μg.) per ml. of distillate: Salicylaldehyde–sulphuric acid method[4]	Salicylaldehyde reagent, described in text	Dinitrophenylhydrazine method
1 W	21	104	85*
1 B	9	98	85
13 W	0	82	114
13 B	4·5	64	171
2 C	0	25	85
2 N	0	25	114

* This distillate gave 34 when treated with hydroxylamine

(2) Determination by oxidation

Yields varying from 102 to 108% were obtained for the total volatile acids produced by oxidizing methyl ketones with alkaline hypobromite. The total methyl ketones can therefore be determined in this way, but the method would be too tedious if it did not include the

possibility of separating the mixture of acids produced and of relating them to the composition of the mixture of ketones. The results of experiments dealing with this aspect will be presented in a subsequent paper.

Experimental

Reagents.—(1) Alkaline hypobromite freshly prepared by adding 6·5 ml. of bromine dropwise to a solution of 13 g. of sodium hydroxide in 50 ml. of distilled water. The mixture was shaken vigorously during the addition and cooled in ice.

(2) Sulphuric acid, 20% (v/v).

(3) Potassium metabisulphite, 10% (w/v).

Procedure.—The ketone (0·1 ml.) and 6 ml. of the alkaline hypobromite were sealed in an ampoule which was then rotated in a vertical plane at 60 r.p.m. for five hours. This time was necessary to ensure that the higher ketones were completely oxidized. The mixture was then transferred to a vessel immersed in ice-water, and the ampoule rinsed with several volumes of water. The sulphite solution was added from a burette until the mixture was colourless, then a further 3–4 ml. was run in. Sulphuric acid was now added until pH 2·0 had been reached (glass electrode). If the pH went much below 2·0 (i.e. pH 1·6) bromine was liberated which could not then be discharged by the addition of sulphite solution. If the bromine appeared during the titration before pH 2·0 was reached, more sulphite was added. Finally, at pH 2·0, an excess of 2–3 ml. of sulphite solution was added to prevent the liberation of bromine during the distillation which followed. The acidified solution was steam-distilled in the usual way until no further significant quantities of acid appeared in the distillate. This was then titrated with standard alkali from pH 3·0 to pH 9·0 to avoid including the sulphurous acid.

Results.—Table IV shows the yield of volatile acid from known ketones and from butyric acid used as a control. Table V gives the values obtained with cheese distillates by the oxidation method and by the sulphuric acid–salicylaldehyde method of Täufel *et al.*[4] It is probable that much of the acid was produced from substances other than ketones and the method therefore lacks specificity.

Table IV

Yield of volatile acid when known ketones are oxidized

R group of the methyl ketone	Total yield of volatile acid (per cent. of theory)
Ethyl	104
n-Propyl	102
*iso*Butyl	108
n-Amyl	107
Butyric acid control (subjected to whole oxidation and recovery process)	103

Table V

Apparent methyl ketone content of acid-free distillates from blue cheese by the oxidation method and by the method of Täufel et al.[4] *The distillates were rendered alkaline and extracted exhaustively with ether*

Cheese	Apparent methyl ketone content, μg./g. of cheese	
	By oxidation to fatty acids	By salicylaldehyde–sulphuric acid method
Stilton 1, Sample A	1100	12
Stilton 1, Sample B	1200	9
Stilton 11A	1400	11
Danish Blue, Sample A	3500	37
Danish Blue, Sample B	1000	39

(3) Determination with 2 : 4-dinitrophenylhydrazine

The coloured 2 : 4-dinitrophenylhydrazones of the methyl ketones may be extracted from aqueous solutions with immiscible solvents such as benzene. If the aqueous solution is sufficiently acid the colour in the organic liquid due to the free base may be reduced to a very low or at least to a constant level. The colour of the separated organic solution may then be related to the ketone content if the type of ketone is known. (This is somewhat similar

to the method of Greenberg & Lester,[10] who used carbon tetrachloride to extract the dinitrophenylhydrazone in the determination of acetone.) The limitation arises because different ketones give different intensities of colour. This is again a method that can be used for isolated ketones but not for mixtures.

Experimental

Reagent.—This was prepared by saturating 2N-hydrochloric acid with 2 : 4-dinitrophenylhydrazine and adding an equal volume of 10N-hydrochloric acid to the filtered solution.

Procedure.—The ketone was diluted in benzene to a concentration between 0·0005 and 0·01 molar and 5 ml. of the solution was shaken vigorously with 2 ml. of the reagent for 5 minutes at room temperature. After the mixture had been set aside for 20–24 hours at room temperature, to allow full colour development, 1 ml. of the top layer was diluted to 10 ml. with fresh benzene and its light absorption was measured on the Spekker absorptiometer with the violet filter.

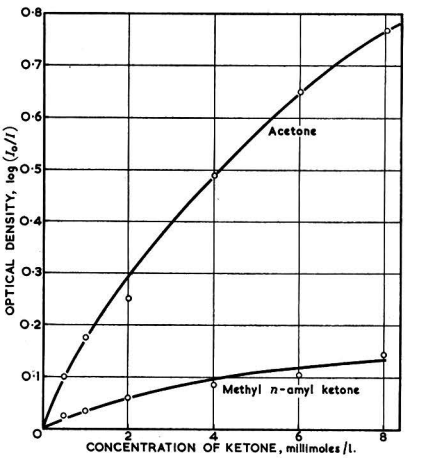

FIG. 2.—*The absorption of violet light by the 2 : 4-dinitrophenylhydrazones of acetone and methyl* n-*amyl ketone plotted against ketone concentration*

Results.—Fig. 2 shows curves relating absorption to concentration for acetone and methyl *n*-amyl ketone. Results obtained from a few cheese distillates are reproduced in Table III.

(4) Determination with hydroxylamine hydrochloride

A number of workers[11–13] have shown that hydrogen ion is liberated in nearly stoicheiometric proportions when carbonyl compounds react with hydroxylamine hydrochloride because the resulting oxime is a much weaker base than the parent hydroxylamine. Hydroxylamine itself is not a strong base and the hydrochloride is partly hydrolysed in dilute solution giving, at a concentration of 0·05M, a solution of pH 3·6 with a moderate buffering power. The addition of a ketone to such a solution, therefore, causes a regular fall in pH which can be related to the quantity of ketone added. This has been done by Roe & Mitchell,[14] who showed that many ketones produce approximately the same fall in pH at the same equivalent concentrations; these authors used a standard experimental graph to relate the pH change to the ketone content of unknown mixtures. Maltby & Primavesi,[15] who have also reviewed the early literature on the use of this reagent, have determined the conditions for complete titration of the liberated acid. Trozzolo & Lieber,[16] on the other hand, propose a treatment with excess of partly neutralized hydroxylamine in boiling alcohol and a back-titration of the unchanged reagent. A modified titration procedure is described by Feuell & Skellon.[17] These methods appear well adapted for many carbonyl compounds, including those which react slowly, but seem unnecessarily cumbersome for some simple methyl ketones and inconvenient for analysing the effluents from a column. Since in the method of Roe & Mitchell[14] the pH of the mixture containing methyl ketones did not change after five minutes it seemed reasonable to suppose that a titration could then be made. Theoretical figures could not, however, be obtained except with acetone, although the figures given by Roe & Mitchell for the change in pH were confirmed for the ketones tested, provided that sufficient methanol were present. Subsequently all experiments were carried out at a final methanol concentration of 68% (v/v).

The pH-difference method is sensitive to small changes in the composition of the hydrochloride solution such as may occur for example on ageing. Frequent standardization is therefore essential, but it is inconvenient because the relationship between the variables is curvilinear. It has been shown that a slightly different method of calculating the results gives a straight line over a tenfold range of ketone concentration and thereby facilitates standardization. In this method the pH values of the standard mixtures of ketone and hydroxylamine hydrochloride are plotted against $\log\left(\frac{0{\cdot}05}{[\text{ketone added}]} - 1\right)$ where 0·05 is the normality of the hydroxylamine hydrochloride and square brackets denote concentration. The resulting

line is straight between the ketone concentrations of 0·0007M and 0·008M and therefore requires fewer points to determine it than the curve originally given. Frequent standardization with three or four ketone solutions during a series of determinations is thus simplified.

Experimental

Reagent.—Hydroxylamine hydrochloride (A.R.) 0·05M, in methanol, prepared by diluting a 0·5M-aqueous solution to 10 volumes with 75% (v/v) methanol. The pH of the resulting solution was always approximately 3·6.

Procedure.—For the preparation of the standard graph, 0·1 ml. of an alcoholic solution of ketone was added to 10 ml. of the hydroxylamine solution to give final concentrations ranging from 0·0001M to 0·015M, and the pH values were measured after not less than 5 minutes at room temperature. The usual glass electrode was employed but particular care was paid to the electrode system. It was flushed frequently with potassium chloride solution and the junction between the solution under test and the potassium chloride solution was made in a tube of 2·5-mm. bore. The instrument was also checked frequently against the standard buffer. These precautions were taken so that the second decimal place of pH values could be relied upon.

Unknown solutions were treated in the same way. When these could not be alcoholic the necessary changes were also made in the standard solutions, but most of the experience with this method has been with gas–liquid partition chromatography, to be described in a later paper, in which the ketone is added as a vapour and questions of diluent do not arise.

Results.—During the earlier part of the work results were interpreted according to the method of Roe & Mitchell with whose figures they were in agreement. The validity of the rectilinear interpretation, and the effect on it of changes in the pH of the reagent, are illustrated in Fig. 3.

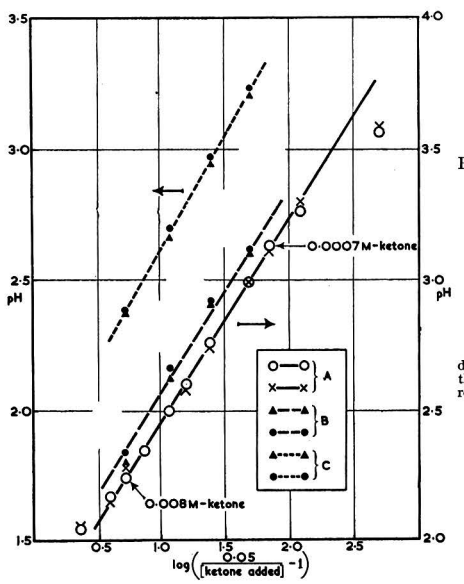

FIG. 3.—*The pH values of mixtures of hydroxylamine hydrochloride and ketones plotted against* $log\left(\frac{0{\cdot}05}{[ketone]} - 1\right)$

A {acetone / methyl *n*-hexyl ketone} reagent at natural pH, i.e. 3·6

B {methyl *n*-propyl ketone / methyl *n*-hexyl ketone} reagent at pH 3·4

C {methyl *n*-propyl ketone / methyl *n*-hexyl ketone} reagent at pH 3·8

The reagent for B and C was not merely that for A adjusted to different pH values, but an entirely different solution. This is why the pH readings for B are higher than those for A, although the reagent had a lower initial pH

Discussion

Although the methods described in the present paper can be used for the estimation of methyl ketones, it is clear, particularly from the results in Table III, that it is useless to apply them directly to mixtures such as may be obtained by distillation of blue-vein cheese or rancid fats. It is first essential to separate the ketones from one another and from other carbonyl compounds. This may be done by chromatography and for this purpose the determination

with hydroxylamine offers considerable advantages in simplicity without any sacrifice of reliability.

A completely different approach to the general problem of detecting low concentrations of vapour in a gas stream has been made by Griffiths *et al.*[18] Among the techniques they examined, that of Phillips[19] was the most sensitive. It depended on the measurement of the difference of surface potential of two different metal plates in the gas stream. This procedure appears to offer a number of advantages for gas–liquid partition chromatography, though, as yet, it seems not to have been applied in this field.

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SENSORY TESTS AND CONSUMER ACCEPTANCE*

By J. M. HARRIES

Some implications of the distinction between the consumer-acceptance test and the analytical taste-panel test are discussed. Examples are given of its impact upon some of the systems used by the Scientific Adviser's Division of the Ministry of Food. The direct-difference type of test is briefly considered and mention is made of an attempt to develop a scale of intensity, of limited applicability, from such tests.

Most writers on the subjective assessment of foodstuffs distinguish between the consumer-acceptance test, on the one hand, and the specialist grading test or analytical laboratory taste panel, on the other.[1] It is the author's experience that this distinction, once made, is easily forgotten, and that it can often be used to resolve problems which arise at all stages in the design of either type of test. In this paper the relationship between the two types of test is a central theme, and certain aspects of both types are discussed.

Consumer-acceptance and analytical taste-panel tests

The number of people involved is considerably greater in the consumer-acceptance test and these people are required to be representative of the consuming public; in the analytical panel a few people are used who are often required to possess some special acuity of taste or

* Read at a Symposium on Flavour Assessment organized by the Food Group, the Biological Methods Group of the Society of Public Analysts and the Biometric Society on 11 March, 1953

perception. The method of interpretation of data from the two types of test is also different. In analytical tests an average result is required, and since the value of an average depends upon the scatter of the individual readings about that average it is essential that the judges taking part should agree with each other to some degree. The extent to which they disagree contributes towards the experimental errors of the investigation. In the consumer-acceptance test, however, an average is neither possible nor feasible. If, for example, the opinion of the consumer is required in a straightforward preference test, the answer is not likely to be as simple as 'A is preferred to B' but rather that a certain proportion of the public prefer A and a certain proportion prefer B. The question of agreement between the people taking part does not arise, and the experimental error of the test is necessarily a sampling error of a proportion, not of an average.

The fallacy of using averages as a means of arriving at the consensus of opinion of a consumer-acceptance panel may be illustrated as follows. Fig. 1 represents a hypothetical case where four samples have been scored on a scale of acceptability by a consumer panel. The graph, which is highly idealized, shows the proportions of the panel members who allotted the various degrees of acceptability to each of the samples. If the results were averaged, the averages would be identical. One of the four, sample D, shows a greater dispersion of individual readings about the average than the other three. If these four samples were compared two at a time in a preference test, opinion would be equally divided and each one of the pair would obtain 50% of first choices. If all four were compared at the same time, however, sample D would be given first choice by those who are more strongly in favour of D, whereas those who are more strongly antagonistic to D would share their first choices almost equally between A, B and C. Sample D would therefore obtain a working, though not an absolute, majority, even though the average acceptabilities of all four samples are the same.

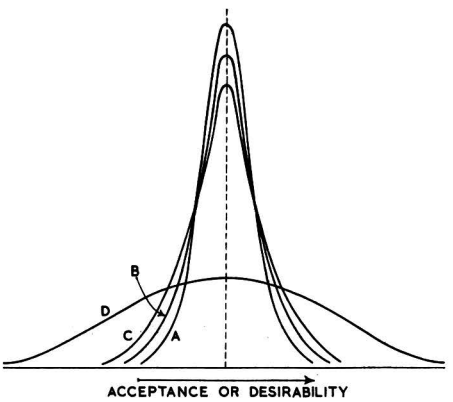

FIG. 1.—*Idealized distribution curve showing degrees of acceptability allotted to 4 samples, A, B, C, D, by a consumer panel*

This is one example of a series of theorems known to psychologists which might be applied with advantage to the forecasting of consumer preference.[2] This concept of dispersion in a consumer-acceptance test has an interesting analogy in the economic concept of elasticity of demand. The latter is usually related to the price of a commodity, but there is evidently such a thing as elasticity of acceptability on quality. It is clear, for example, that considerably different dispersions will be obtained in the testing of oysters and of bread. People are likely to be more indifferent to the latter and to have stronger views about the former. Similarly, different dispersions might be obtained with different grades of the same foodstuff, as for example with jams of different sweetness. Thus in a consumer-acceptance test, dispersion of the individual readings reflects a property of the foodstuff—the degree of indifference to it; in the analytical panel, dispersion of individual readings is treated as experimental error.

Acceptance and preference are both economic concepts. An acceptance level will vary with standards of living, not only from one social group to another but from time to time for the same group, largely determined by the forces of supply and demand. Preferences are largely a matter of degree or strength. The ordering of characteristics of a particular foodstuff into a scale based on likes and dislikes is therefore considered to be not sufficiently stable for scientific investigations, since results are required that can be reproduced with some degree of accuracy.

The function of an analytical panel is to analyse. The usual procedure followed at the Scientific Adviser's Division of the Ministry of Food in the formulation of a system of scoring is to find as many precise, mutually exclusive, and exhaustive descriptions as possible. It is usually found that a body of technical terms is already in use by the trade. Definitions of these terms frequently vary, but these and any original descriptions are discussed at some length with the members of the panel during a training period to ensure that all members define the terms used in the same way, and fairly rigidly. They may then be placed in some

order, as has been done in the scale described by Shewan *et al.*,[3] but this is not always possible. It is not, however, essential, and the resultant system may be based upon, and analysed according to, presence-or-absence criteria. An example of such a system is given in Table I, which shows part of the system used for ' scoring ' dehydrated potato. Members of the panel are asked merely to note which of the characteristics shown are applicable to the sample under consideration. The results are summarized by means of the mode (or the most ' fashionable ' characteristic) of any particular group. Statistical analyses and tests of significance can be carried out on the basis of relative frequencies of occurrence. If each characteristic were given a number and the numbers then averaged, apart from the assumptions involved in such a procedure, the result could conceivably fall on a number indicating a characteristic which was not applicable to this sample in the opinion of any of the judges. This method of arbitrary allocation of numbers along a scale is, however, used when other systems are unsuitable, and in such cases fairly rigid tests of internal consistency are carried out.

Table I

Part of score sheet for dehydrated potato

General appearance

1. Strips more than 1 in. long
2. Strips somewhat fragmented ½–1 in. long
3. Strips less than ½ in. long
4. Strips fully reconstituted (surfaces not concave)
5. Strips not fully reconstituted (surfaces concave)
6. Appearance generally mushy
7. Surface dry in appearance
8. Surface slimy in appearance
9. Translucent appearance
10. Number of major blemishes

Natural flavour

23. Full potato flavour
24. Weak potato flavour
25. Flavourless
26. Slight earthy flavour
27. Strong earthy flavour
28. Sweet

Foreign or ' off ' flavour

29. Rancid
30. ' Cardboard '
31. Scorched
32. Bitter
33. Sulphite
34. Sour
35. Other foreign flavour (specify)

36. Weak
37. Moderate
38. Strong

} Intensity of foreign flavour

In the literature on organoleptic evaluation there are many accounts of attempts to combine the scores for a number of properties into an overall score of general quality. The view submitted here is that every foodstuff may be examined for each of its properties separately, and any reports should be content to deal with each property on its own merits. If the need for a combination arises, it will refer to a specific question relating to a specific consuming population. In such a case the weight allotted to each property should be decided by that population, and can be made known to the investigator by means of a consumer-acceptance test. A comparison of overall quality of two or more foodstuffs will only be necessary when a decision has to be taken as to which is most desirable to a consumer, and it is reasonable to suppose that the consumer himself is the best judge of what is meant by ' quality ', what part is played by texture, what by flavour, etc., and this weighting will itself vary from consumer to consumer and from time to time. Thus the term ' overall quality ' has no place in analytical evaluation, but is proper to a consideration of consumer acceptance, and when the results of an analytical taste panel are reported the procedure at the Scientific Adviser's Division of the Ministry of Food is to state a result for each property of the foodstuff without any combination, which might hide more than it would reveal.

The difficulty with such a system as that illustrated in Table I arises when it is realized that many of these characteristics may be present in different degrees of intensity. In such cases an arbitrary scale of intensity is introduced, but the introduction of many of these will make the overall system lengthy and cumbersome. It has been found, however, that an analytical panel can be given very complicated instructions on the scoring of a product since the same people are generally used time and again, and they can soon memorize lengthy scoring systems. In a consumer-acceptance test the system used must be kept simple, since there are a large number of people and there is no opportunity to train them in the use of a system and ambiguity may easily develop. The emphasis in the analytical system is on analysis; cumbersomeness is often a necessary adjunct.

Direct-difference tests

When it is possible to present samples simultaneously, i.e. when there is no time factor such as storage involved in the experiment, and when the foodstuff under consideration is fairly homogeneous, there is one kind of test that is particularly useful. This is typified by the triangular test extensively used in America. If, for instance, we wish to compare two types of a particular food where type A has undergone a specific treatment and type B has not, and acts as a control, and if the investigator wishes to know whether the treatment has had any effect on the organoleptic properties of the foodstuff, two samples of A and one of B, coded at random, may be presented to a panel of judges. The judges are told of this and are asked to specify which is the odd sample. If a judge cannot distinguish in any way between the samples, he will have a one-third chance of giving the correct answer by guesswork alone. What is more relevant is that we know from the binomial theorem the expected fluctuations of the number of correct results in a group of judges of given size in the absence of any real ability to differentiate between samples. A statistical test of significance is based on this. There is much literature on the subject of the use of these tests for choosing those judges with greatest powers of discrimination.[1] We use them more often to test for differences due to specific treatments. We do not, however, often use the triangular test, but prefer to present two samples of one type and three of the other, when the chance of success of any individual in the absence of any real discrimination is reduced to one-tenth. If ten people are used in such a test then we expect one correct result more or less by chance alone; and if we obtain four correct results we say that there are only five chances in a hundred that this could have happened had there been no difference between the samples; if five correct, the chances are one in a hundred; and if six correct the chances are one in a thousand. The use of these tests is limited to those commodities that have little or no sampling variation, i.e. a variation that would itself allow of discrimination not due to the treatment being studied. They have been used with success in investigations on orange juice, dried milk, potatoes (mashed), jam, custard powder and eggs (dried).

We consider these tests to be objective. Though based on a subjective judgment they are objective in that all investigators would interpret the results in the same way. (The subjective equivalent would be to give the judges two samples, one of each type, and ask them to state whether or not there was a difference between them.) These direct-difference tests, as they have been called, are particularly suitable for the investigation of fine flavour differences. They supply the investigator with a direct statement as to whether the treatment has resulted in a difference in eating properties, and this is frequently all that is required. They may tell the investigator, if approximately extended, the direction of any difference that may exist, but not its magnitude.

It may now be considered how far the results of such a test can be extended. If the result is not significant, i.e. according to the panel there were no differences due to treatment, then we cannot, of course, assume that the consumer will find none unless the panel was itself representative of the public. If, however, the judges were trained and experienced tasters of this foodstuff, it is usually concluded that the proportion of the consuming public that could tell the difference is probably small, though a few people may exist who can do so with ease. If we obtain a significant difference due to treatment, then a consumer test must be carried out if a knowledge is required of the consumer's attitude to the treatment under consideration. The analytical test is not, and can never be, a short cut to the consumer-acceptance answer.

Some limitations of organoleptic techniques

Whether the technique used is that of a scale, a presence or absence test, or a direct-difference test, the answer obtained from the analytical panel invariably contains a clause that is common to all scientific experiments—' within the limitations of the experiment '. And one of the limitations of experiments in flavour assessment is that the results do not necessarily apply to the consuming public. In most investigations, however, flavour and other properties of a foodstuff are important only in so far as they can be detected by or approved by the consuming public. This does not mean that analytical or laboratory panels are a waste of time. On the contrary, as a preliminary they can be most valuable in that they may save an immense amount of effort. The application of the results of a specialist test to the consumer field, however, must be qualitative not quantitative.

The limitation mentioned above is of course due to the fact that different people have different sensitivities or discriminations. That this is so is shown in many ways, but notably by the fact that those investigators who have tried to establish threshold levels for the various

tastes all give different results. There are two aspects of this limitation which are of particular interest. The first of these is a consideration of how severe it may be. Table II is typical of many results which may throw some light upon this problem. It shows an analysis of variance of the results of an experiment with potatoes in which an arbitrary scale of intensity of an off-flavour is used. There are several interesting features apart from the treatment effect, which was of prime importance when the tests were carried out, such as the effect of time of day upon the performance of the tasters, or the tests of internal consistency normally carried out with such data. The point of present interest is that in each of these analyses the variation due to observers is less than the variation due to samples within treatments. Apart from the controlled treatments, the samples were identical, so that the mean square for samples represents what is sometimes called 'normal biological variation'. This is but one illustration of what seems to be a fairly general state of affairs—that the limitations of an experiment in which organoleptic techniques are employed are usually no more severe than those imposed on any experiment in which biological material is sampled, though, of course, this biological variation itself varies considerably from one commodity to another.

Table II

Analysis of variance of results from an experiment with potatoes when an arbitrary scale of intensity of an off-flavour is used

Source of variance	Degrees of freedom	10.30 a.m.		11.30 a.m.		3.0 p.m.	
		Mean square	*F* ratio	Mean square	*F* ratio	Mean square	*F* ratio
Between treatments	3	1·8014	3·07	4·9906	8·90	0·4097	1·19
Between samples within treatments	8	1·6031	2·73	3·3447	5·96	0·7917	2·30
Between judges	3	0·2986	—	0·5764	1·03	0·4653	1·35
Residual	33	0·5865		0·5612		0·3441	
Total	47						

Another item of interest in Table II is that, when the significance of the treatment effect is tested, we ignore completely the variation due to observers. This variation may be considerably larger than that due to any other source, but it does not matter how much the observers differ in their estimates of the samples included in the experiment, considered as a whole; it is the comparisons they are able to make between the samples of different treatments that are of interest in this type of test. This ignoring of the variation due to observers means that the treatment effects are more likely to prove significant, and this is valid only if the test is considered as a laboratory or analytical test. In a consumer-acceptance test, if such a statistical technique were used, then it would be wrong to ignore the variation due to observers; indeed, this would then become of prime importance.

An interesting aspect of this limitation due to differing sensitivities is that it may be possible to use it. In the direct-difference tests described above, it was stated that with a two-out-of-five test with ten people, four correct results would indicate a significant difference between the two types of foodstuff. The question may be asked whether six correct results would indicate a greater magnitude of difference if, for example, the treatment had been intensified, eight correct results a still greater magnitude of difference, and so on for increasing numbers of correct results, i.e. how far a scale of intensity might be developed by the use of the proportion of correct results in a direct-difference test over and above the number required for significance. Clearly such a scale would depend upon different people being able to recognize the difference at different intensities.

Fig. 2 illustrates an experiment that was carried out in an attempt to examine this question. Two-out-of-five tests were made with sugar solutions of various strengths. In each test a solution of strength M/10 was compared with solutions varying from M/12 to M/15, and the Figure shows the number of correct results obtained

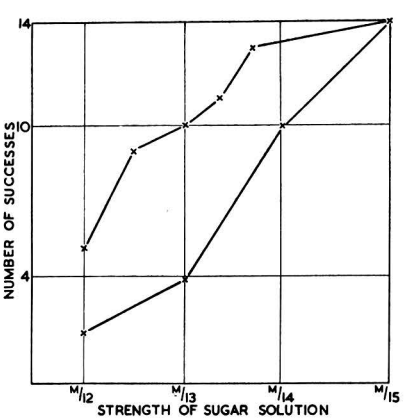

FIG. 2.—*Numbers of correct results in direct-difference tests with sugar solutions of various strengths*

out of a possible maximum of fourteen in each case. The results seemed to follow the two lines shown: the lower line showing the results obtained when the differences between the samples in successive tests were increased until all the people taking part could differentiate successfully, and the upper line the results obtained when the differences between the samples in successive tests were then decreased. The experiments are not yet complete, and these are the first rough results, but they seem to indicate that it may be possible to devise a scale for the measurement of relative intensity of sensation based on the different powers of discrimination of individuals. It may be noted that the ' hysteresis ' effect apparent in the graph, which may be the result of practice or training, is stated by Pieron[4] to be of general occurrence in the study of threshold levels.

What is important is that there should be a gradient, and it is hoped that the average gradient will prove to be relatively stable. If, however, a scale of intensity is developed along such lines, it will be an analytical instrument for comparative measurement, and successful differentiation between two samples by a laboratory panel by means of such a scale would not necessarily mean that the consumer could distinguish between them.

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THE OBJECTIVE APPROACH TO SENSORY TESTS OF FOOD*

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The use of a technique, previously described, for assessing the quality factors of iced white fish is discussed. Results are given to show that the explicit training of a panel of assessors to agree is a chief factor in achieving accuracy. The validity of comparing results from different investigations is then examined, with reference to such factors as the internal consistency of the panel, the use of control samples or standards and of certain physicochemical criteria.

Introduction

At the outset it may be useful to explain where our interests lie in the field of the sensory assessment of food. This paper arises from a study of the present-day methods of fish preservation with a view to their better understanding and improvement. We are therefore constantly faced with the problem of evaluating the eating quality of fish. In much of our previous work in this connexion, little attempt was made to find explicit principles that might lead towards reproducible results, and indeed it is now felt that many of the data then obtained would not stand up to rigorous analysis. Initially we sought a physical, chemical, bacteriological or other method for assessing quality, but it soon became obvious that the results obtained by any such method would ultimately have to be referred back to sensory judgments, and closer study of this method of assessment was seen to be of paramount importance. The

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present paper is based on the subsequent experience gained in some four or five years' work with trained taste panels, who carried out experiments on various aspects of the quality of fish.

Sensory assessments in general, and of food in particular, are often contrasted unfavourably with the more traditional physical measurements such as those of weight, time, distance or temperature. They are usually identified with subjective assessments. But physical measurements invariably involve human observers, so that the mere occurrence of inconsistent observations attributable to subjective errors cannot completely explain the scepticism with which sensory assessments are often regarded, as, for instance, at the recent Symposium in London on Subjective Judgements.[1]

Our problem is that, just as we may have to say that a given kind of fish has certain physical, chemical or bacteriological characteristics, we must also be able to say that it has such and such a flavour, odour or the like. Indeed, sensory assessments are required that are largely independent of the time, the place and the observer, i.e. assessments that can be called relatively objective. Clearly we may look to the physical sciences for guidance, because much objectivity has in fact been achieved there, with essentially the same problems. Not long ago there were no instrumental techniques for describing many of the so-called physical dimensions, but only sensory assessments, e.g. the use in Galileo's time of pulse rates to measure short periods of time.[2a] Moreover, no instrumental measurements are absolutely objective, and physical measuring instruments require constant checking and research on the conditions of their operation so as to achieve reasonably consistent results. Most sensory assessments, as usually made, in fact differ from present-day instrumental measurements, but only because well standardized scales of measurement are given for the latter, whereas for the former there is little advance information. One has first to construct descriptive classifications—or, in particular, numerical scales—and secondly to establish the conditions necessary for their objective use. It should be recognized that the assessment of a flavour of which one has previously had no experience is a radically different task from measurement along some traditional physical scale. An assessor cannot be presented with entirely new flavours if his results are expected to be comparable from one occasion to the next.

To establish the required kind of technique, the following procedure can be envisaged: (i) Take a given limited array of sensory phenomena, e.g. the various flavours, odours etc. of fish that are known to occur during the process of spoilage under given conditions of storage. (ii) Deliberately devise descriptions for these phenomena, and possibly attach numerical symbols to them for greater convenience. (iii) Train people to use the same description for any given phenomenon. (iv) Observe empirically whether the descriptions are used consistently, and discover the factors which, if controlled or otherwise taken care of, will increase this consistency.

We shall now discuss this procedure in terms of our own experience, stressing that the validity of the results can be proved or disproved only empirically.

The choice of descriptive terms

In a paper on the dependability of food judges, Overman & Li[3] state that ' if a judge considered two different flavours equally desirable, with the result that he gave both samples an identical score, it is evident that his ability to discriminate would be partially obscured '. This remark suggests the variety of things that may be assessed. Do Overman & Li wish to investigate the personal desires of their selected judges, to estimate the ' desirability ' of the samples for some larger consumer population, to establish the discriminatory thresholds of their judges, or to differentiate between the samples of food independently of any possible ' desirability ' ? Clearly, it is essential to make the well-known differentiation between consumer tests and sensory tests as such. In the sensory tests, samples of food are classified according to their flavour, odour etc., and in the consumer tests they are classified according to their desirability. If we wish to achieve objective descriptions—i.e. independent of the observer and of the time of assessment—personal preferences, and hence the idea of consumer reactions, must be excluded. But the importance of the more impersonal sensory assessments is that one knows that they can always be directly related to actual consumer reactions. (In this they differ from most instrumental measurements.) To interpret such laboratory classifications of flavour etc. one might use trade experience, although more precise results could perhaps be established by a few deliberate consumer-tests.

Different situations undoubtedly require different kinds of descriptive classifications of sense perceptions. But we shall refer only to the classifications devised for the assessment of the spoiling of fish. The early stages of their development are described elsewhere[4] but, in brief, previously published descriptions and further detailed observations of actual spoilage changes were used to derive scoring systems for the general appearance, odour and texture

of the raw fish, and for the odour, flavour and texture of the cooked fish. The following score sheet (Table I) for the odour of cooked fish is a typical example.

Table I

Cooked fish (approx. 6–8 oz. middle cut of fish steamed en casserole in resistance-glass dishes (7 in. in diameter) over boiling water for 35 minutes

Odour (10 *marks*)*	Score marks
Strong, fresh, ' seaweedy ' odours	10
Some loss of fresh ' seaweediness '	9
Lack of odour, or neutral odours	8
Slight strengthening of the odour but no sour or stale odour ; ' wood shavings ', ' woodsap ', vanillin or terpene-like odours ; slight salt-fish or cold-storage odours	7
' Condensed milk ', caramel or toffee-like odours	6
' Milk jug ', ' boiled potato ' or ' boiled clothes ', or metallic odours	5
Lactic acid, ' sour milk ' or *o*-toluidine-like odours	4
Some lower fatty acid (e.g. acetic or butyric acids), ' grassy ', ' soapy ', ' turnipy ' or ' tallowy ' odours	3
Ammoniacal (trimethylamine and lower amines) odours	2
Strong ammoniacal (trimethylamine etc.) and some sulphide odours	1
Strong putrid and faecal odours (ammonia, indole etc.)	0

* These descriptive terms, although capable of irrelevant associations, are those used spontaneously and agreed upon by the original panel at the Torry Research Station. Other panels may well tend to use other, but probably similar, terms. A more precise terminology, replacing ordinary descriptive terms by suitable chemical analogues, is being continuously pursued

The important point here is not the ordering of the classes and the numerical scores, which will be commented upon briefly at the end of the paper, but the descriptive terms used. Their choice is difficult, partly because certain flavours or odours may be altogether new, partly because appropriate descriptive terms for sense perceptions that are reminiscent cannot always easily be agreed upon. Discussions of descriptive terms generally, such as those of Wagner[5] and Crocker,[6] repay study here.

For our own purposes, at least, we consider that the descriptive terms should exclude value judgments, not only such as ' excellent ', ' good ' or ' bad ' but also, as far as possible, such indefinite gradings as ' strong ', ' weak ' or ' mild '. The aim has been to find terms which, even in ordinary, everyday experience, are unambiguous ; for example, there are many chemicals whose flavour and odour are generally agreed upon, and which can serve as useful analogues, especially if actually present. In this way it was hoped to facilitate consistent use and interpretation of the terms.

It is interesting that the flavour classification[4] is much less specific than that for odour, and in fact contains a relatively large number of grading terms such as ' some ' and ' strong '. But this is not surprising, since only a small number of different kinds of taste were noted ; those were mainly the so-called primary tastes, ' sweet ', ' sour ' and ' bitter ' (no ' salt '). This, and also the large variety of odour responses, is in accord with Adrian's remarks.[7]

After a descriptive classification is set up and used, it can, with growing experience, be altered and generally made more precise. As an extreme example of such an alteration, a flavour of a quite ' new ' kind might occur during the routine work of a trained panel, new in the sense that no descriptive term for it had previously been agreed upon. A new descriptive term would have to be defined, for the trained panel as such could not, of course, deal with this situation, since the members' individual assessments might not agree, and the technique would go out of control. It should be noted that all this is not unusual even with physical scales of measurement, which are constantly being revised. To take a well-known example, it was found recently that the melting point of aluminium was not on the previously defined temperature scale at all, being apparently just above the maximum of the platinum resistance-thermometer range (— 183° to 660°) and just below the minimum of the thermocouple range (660° to 1063°).[2b] It will be obvious, however, that restraint is necessary in changing a given classification, as frequent alteration would nullify the purpose in aiming at objectivity, namely to be able to compare different sets of data.

Training

The mere selection of seemingly appropriate and fairly clear-cut descriptive terms is, however, not enough. Thus Vail & Conrad[8] give on their scoring cards (besides a numerical scale from 0, ' extremely poor ', to 10, ' extremely good ',) 22 descriptive terms for the flavour and aroma of poultry. They report that each person generally restricted himself to a few particular terms, the selection of terms varying from person to person. Clearly no one can

tell, except perhaps very roughly, what any term was taken to mean, and so it is almost impossible to know what one might mean by ' consistency of assessment ', let alone how to test for it. What is necessary, as already mentioned, is some attempt at standardization, and this should be promoted by training panels of assessors.

The importance of training in sensory tests of food is variously recognized, but there are some differences of opinion on what is meant. For example, in the review of the literature for the recent Conference on Sensory Methods in Washington,[9a] training appeared to be used as a synonym for experience, experience with the sensations aroused by the foodstuffs in question. At the Conference itself,[9b] training was, however, more often equated with reaching agreement on the descriptive terms used, which of course includes experience with the food. Again, Boggs & Hanson,[10] reviewing the more ' objective ' kinds of sensory test, mention this need for training judges to describe each sample in the same way. But they do not seem to implement their suggestion when they quote with apparent approval some experiments by Baten,[11] in which each judge was allowed to record his rating by placing a mark somewhere on a 6-inch line with extremes marked by ' excellent ' and ' poor '. Obviously, the agreement of different people here was left largely to chance.

By training we mean making people agree on the use of given descriptive terms and scores. One then knows, by definition, what any person's assessment ought to be, namely the same as that of any other trained person. In practice differences will of course occur, but one can examine how well the panel-members do tend to agree, and can describe their inconsistencies.

The process of training given to our panel and the statistical analysis thought appropriate have already been described.[4] The training consists essentially in the actual physical examination and discussion (in terms of the scoring system) of fish covering the whole possible range of spoilage ; for the statistical analysis it has been found that the internal consistency of a panel can be usefully described by systematic differences between the scoring-levels of the panel-members (' biases ') and by some measure of the scatter, e.g. variances or standard deviations, of their more or less random discrepancies. We should also mention that in general it has been found that the trained panel-members are not strongly biased with respect to each other, the biases being at most about half a unit on the ten-point scales used, and that each panel-member's error variance is almost always less than one unit, and often well under half a unit. One can hardly expect greater consistency on a scale on which half-units are the smallest steps used, and on which only unit steps are explicitly defined.

This sort of explicit ' training to agree ' does not seem to be very common in food research, more so perhaps in commercial grading, and various writers, e.g. Hopkins[12] in Canada, do not seem to have found training effective or practicable. We are convinced in principle of the need for it in a problem such as ours, and more or less ' clinical ' impressions have confirmed us of its effectiveness. No very systematic investigations of the effects of training have therefore been carried out, but it may be of some interest to report two sets of results collected with untrained and partially trained personnel respectively. What we expected to find was that the scoring sheet was not so good as to make training unnecessary, nor so artificial that ordinary people would not obtain roughly the same results as the trained panel.

Untrained personnel

The first set of results were collected when one of us (J. M. S.) was asked by the Scientific Adviser's Division of the Ministry of Food to select a panel for the grading of fish. The opportunity was taken to observe the scoring behaviour of 13 completely untrained persons using our score sheet which had been explained to them. Eight panel sessions were arranged as shown in Table II.

Table II

Untrained panel sessions

Session	No. of persons present	Fish tested
1	9	6 one-day old
2	10	6 four-day old
3	10	6 seven-day old
4	10	4 three-day old and 4 ten-day old
5	8	4 seven-day old and 4 fourteen-day old
6	10	3 four-day, 3 eleven-day and 3 eighteen-day old
7	9	3 seven-day, 3 fourteen-day and 3 twenty-day old
8	10	4 one-day, 4 eleven-day and 4 eighteen-day old

When the raw odour, cooked odour and cooked flavour scores are considered (i.e. about 2000 readings in all), it is found that the panel made similar decisions for these three quality factors, but beyond this the results are rather complex and difficult to describe precisely. The previous methods of analysis[13, 14] were followed and each person's bias and error variance were calculated for each panel session; the biases were found to be almost always statistically significant, i.e. the people differed systematically in their scoring level. More important than significance are the quantitative results, namely that about 50% of the 228 biases were greater than $\pm$ 0·5 (most often for cooked flavour, least often for raw odour), almost half of these being even greater than $\pm$ 1 unit. Now if two persons have biases of, let us say, + 1 and − 1 respectively (i.e. they differ by such amounts from the average of all people present), their scoring level differs by *two* units, that is, by 20% of the total ten-point range of variation. Clearly, data with systematic errors of this kind are almost useless for any kind of precise work.

If the more or less random errors are examined, the picture becomes more confused. For the earlier panel sessions where only fish of a single age-in-ice were tested, any one person tended—with many exceptions—to give all the similar fish fairly similar scores, e.g. one person would use scores 8, 8½ or 9 only, another 7½, 8, 8½, and so on. Here the random errors must be fairly 'well behaved', and are quite well described by error variances of, on the average, a little under one unit, i.e. not so very much larger than those of the trained panel. However, for the more difficult sessions, where fish of different qualities had to be assessed, about a third to a half of all the error variances turn out to be negative; this is apparently meaningless, since a variance is the square of the standard deviation, and therefore must be positive. In fact, an untrained person's scores cannot be usefully described by bias and *independent* 'random errors', since the discrepancies between the different persons appear to be correlated with scoring level, and these correlations vary from person to person. In other words, the biases—the systematic differences in scoring level—vary with the level of scoring, and differently so for different people, as illustrated by some typical results given in Table III.

Table III

Cooked-flavour scores for six fish given by three untrained panel-members A, B and C, to illustrate differential correlation of 'errors' with level of scoring

Days in ice	4	4	4	18	18	18	Means	Bias
A	7·5	7·5	5	3·5	2	4	4·9	0·9
B	5	7	5	0·5	0·5	0·5	3·1	− 0·9
C	8	8	8	0	0	0	4·0	0
Means	6·8	7·5	6·0	1·3	0·8	1·5	4·0	

In this Table the three panel-members' means or biases do not describe their scoring-level well; thus C, who would appear to be 'unbiased', has actually a bias of about + 1 for the fresh and − 1 for the stale fish. Alternatively, the 'errors', i.e. discrepancies from the fish means after allowing for overall bias, are clearly correlated; C's discrepancies are positive for fresh fish and negative for stale fish, and so on.

Although the results have been investigated in considerable detail, there seems little point in reporting the analyses, for the broad conclusion remains unaffected: namely, despite the biases already mentioned and the large discrepancies, which are even less systematic, the panel of 10 or so untrained persons do succeed on the average in putting fish more or less in their 'correct' order, where by 'correct' we mean what would have been the results of the usual trained panel for such fish. This is shown by the averages for cooked flavour given in Table IV, which are also typical of the other two quality-factors. (Fish of the same age-in-ice scored in different panel sessions are reported separately.)

Table IV

Average flavour-scores for batches of fish described in Table II

Days in ice	1	3	4	7	10	11	14	18	21
Average scores	9·2	6·4	7·9	6·4	5·7	5·0	2·1	1·0	1·3
	8·2		7·1	6·3		5·4	2·4	1·1	
				6·0					

There are some curious inversions, e.g. for the three-day- and four-day-old fish, and the older fish are probably scored lower than they would have been by the trained panel, but the general consistency of the downward trend with age-in-ice is beyond question.

Partially trained personnel

Apart from the results from the untrained personnel, some figures are available from two partially trained persons who joined a trained panel (of four members) in an investigation on storing frozen fish. Their results were not included in the analysis of the main experiment, which will be reported elsewhere. It need hardly be mentioned that one cannot, with much confidence, generalize from the behaviour of only two such persons, but the results are particularly interesting because of the availability of control readings.

There were three sessions, at each of which four sets of twelve fish were tested, being 1, 9, 14 and 20 days-in-ice respectively, and therefore 144 samples were tested in all by each person. The first two sessions were held on the same day, the third some six weeks later. Scores for cooked flavour and cooked odour only are available here; they were found to be similar and need not, on the whole, be separately described.

In the weeks before this investigation the trained panel had not been very active, and this seems to have shown itself in their being a little more erratic than usual to begin with, the average error variances in the three sessions being about 0·9, 0·8 and 0·5 respectively. (These figures may be inflated by consistent biases between panel-members, which would necessarily be small and have not been separated out here.)

Apart from a bad start, the partially trained panel-members are very consistent for very fresh and very stale fish, almost too much so in fact, i.e. they do not seem to be noticing the relatively small differences between fish of the same age-in-ice. However, for the intermediate-quality fish, which usually matter most, they are much more erratic in the first two sessions. After six weeks, and with additional experience in the interval, they showed considerable improvement. The average error variances are given in Table V.

Table V

Average error variances of two partially trained panel-members

	1 day-in-ice	9 days-in-ice	14 days-in-ice	20 days-in-ice
1st session	2·2*	2·4*	1·2*	0·4
2nd session	0·2	1·4*	6·0*	0·2
3rd session	0·4	0·8	1·0	0·3

* See text

If the two partially trained members are compared with each other, one appears to have been rather more accurate than the other during their more erratic moments in the first two sessions (marked * in Table V), when their average error variances are about 1·7 and 3·6 respectively. There is no very marked difference between them for the other results, it being about 0·2 in the other direction, and unlikely to be significant statistically. As regards bias, i.e. systematic difference in scoring level, the two members differ significantly by about 0·6 in their mean scores for cooked odour (not an unusual amount even for trained personnel), but not for flavour.

Having established that the assessments of the two partially trained panel-members are not so consistent as those of the four fully trained ones, one must now consider whether the same thing is being assessed. On the whole, the partially trained panel seem to give very much the same average scores as the trained panel, except that they tend to score the intermediate-quality fish (i.e. scores of 4, 5 and 6) about half a unit lower, and poor-quality fish (scores of 2 and 3) about half a unit higher (the latter for flavour only). The trained panel seem to have noted a drop of about half a unit from the first two sessions to the third one (except for the 20-day-old fish) which is more or less in accordance with expectation. This is echoed by the partially trained personnel for the freshest fish, but not for the 9-day-old fish (scoring 5's and 6's), and it is reversed for the 14-day-old fish (scoring about 4 and 5). It is possible that the aberrant increase on the 14-day-old fish may be due to an awareness by the partially trained persons that they previously scored such fish a little lower than the trained panel. Although these discrepancies in performance are perhaps small, a good deal of the work for which the scoring sheet is used is concerned with describing average differences of the order of one unit or even less.

Towards establishing objectivity

In the last section we have indicated that people assessing the flavour etc. of fish in terms of the scoring system tend on the average to agree, and that the internal scoring consistency of a panel can be much increased by explicit training. However, internally consistent results need by no means be ' objective ', i.e. more or less independent of the personnel and the time

of assessment. This kind of objectivity might be expressed in the dictum that similar samples of food should always be given the same score. But in trying to establish this there is the fundamental difficulty that one does not know whether a given sample is in fact exactly similar, and should be given the same score, as any sample that occurred some time previously or that was handled by someone else. This paradoxical situation, of apparently having to assume the point one is trying to prove, is, of course, not peculiar to these sensory assessments. The problem becomes soluble if one accepts that objectivity cannot be established by a ' crucial ' experiment—one need only imagine trying to prove by a single experiment that an hour is ' as long ' today as an hour was a hundred years ago or even just yesterday. Instead, one can hope only to accumulate many pieces of evidence which make the objectivity of the assessments, if it exists, more and more plausible, and we shall now briefly indicate some of the relevant arguments.

(i) The first point to note is the necessity of the kind of internal panel consistency already discussed. Obviously it is almost impossible to establish that the panel's scoring-level has not changed during the course of time if the panel does not agree reasonably well at any given moment.

However, as already mentioned, mere internal consistency does not imply that the scoring level has necessarily remained constant ; indeed, the occasional discussions of actual samples of fish, which are necessary to keep the panel in training, make it likely that, should the panel-members change their scoring levels, they would all change in the same direction.

(ii) The apparently obvious solution of the problem is the use of ' control ' samples or ' standards '. But this ignores the whole difficulty, namely that we cannot possibly say at present that any given sample should always have a certain score. In fact, the search for objectivity is simply a search for known standards of one kind or another.

(iii) One example of this lack of standards is that we cannot even say that all freshly caught fish should be scored 10. But here the fact that there is no ' bunching ' at the upper end of the scale, and that in general the whole 10-point range is used, is of course an extremely suggestive, although negative, symptom of objectivity. Thus, all the scoring can hardly drop by one unit, say, from one experiment to the next, because bunching at the lower end would then be bound to occur.

(iv) Again, the chief factors of spoilage appear to be the temperature and the length of storage, and by controlling these one might expect to obtain comparable samples. But we have found in two or three recent experiments that the spoilage rates under controlled conditions appear to differ (perhaps according to fishing grounds etc.) by about four or five days out of a total spoilage period of 20 days or so. The evidence here is very incomplete, and is quoted for illustration. The question is whether such differences in spoilage rate could be considered ' real ', or due to inconsistencies of the scoring from one experiment to the next. As usual with data of this kind, one would have said that both the ' real ' spoilage rates and the scoring level were constant if the observed rates had been constant ; the inconsistency of our actual observations could be due to variability of either kind, or even of both.

(v) When we consider the artificial establishment of standards, it is well known, in a general, imprecise sort of way, that quick-frozen fish stored at low temperatures (e.g. $-30°$) will show relatively little or possibly no change after several months of storage. As usual, fairly definite conclusions could be drawn if there were no apparent change in stored fish. But it would be difficult to ascribe unequivocally any drop of, say, a unit or so, either to a ' real ' deterioration or to a change in scoring level. Even in the latter case, however, it is probable that some pointers to the consistency of the scoring can be obtained from a more detailed analysis of the ' errors ' in the data. Experiments of this kind are at present in hand.

(vi) Instead of searching for a constant relationship of a given sensory variable, e.g. flavour scores, and external variables describing the treatment or the initial environment of the fish, one may investigate the relationships between two or more of the actual test-variables, e.g. flavour and cooked odour. However, any shift in scoring level might well affect all such variables to about the same extent, and any constant relationships found must be interpreted with caution in establishing objectivity.

(vii) More convincing perhaps would be a constant relationship of a sensory variable with an operationally independent one, such as some physicochemical measure. There is presumably no need to discuss here the importance of these so-called ' objective ' variables, both for a better understanding of the phenomena in question, and possibly also for obtaining quick and easily standardized indicators of eating quality.

With fish, it has for example been found that the content of ' total volatile bases ' (trimethylamine etc.) increases during spoilage, but all previous data showed the process to be very erratic. Now in some recent experiments (which will be reported elsewhere), it was found that ' total volatile bases ', after a certain logarithmic transformation, increase linearly with length of storage, and are otherwise quite regular. But the actual quantitative content of the bases varied very markedly between three different experiments, the difference being equivalent to four or five days-in-ice. The relevant point here is that it was in the same experiments that the sensorily perceptible spoilage rates were found to differ, as mentioned above, and when the values for the total volatile base are plotted against the cooked odour or flavour scores, the three experiments practically coincide. In other words, although one could not estimate from the chemical or from the sensory data the period-of-storage under controlled conditions, without possible systematic errors of 5 days or so, the average sensory score corresponding to a given chemical value is the same in the three experiments.

We should like to emphasize that much more experimental work is needed to establish such a result as definite, and we have quoted it simply as illustrating a general approach. But one may perhaps conclude that the hypothesis that objectivity within a unit or so had been established in these three experiments has not been disproved.

(viii) In conclusion, it need hardly be mentioned that the only final criteria of the objectivity of sensory or any other assessments are results that are reproducible many times. But this is by definition a long-term process, and in the meantime one requires short-cut indications that one is heading in the right direction, and for this we have tried to indicate some of the more obvious approaches. Perhaps a final caution is necessary, namely that not too much must be expected ; even the best measuring instruments occasionally go out of control.

The use of numerical scores

The use of numerical scores, or of mathematics in general, is a controversial feature of all this kind of work. We shall attempt to discuss our point of view elsewhere,[15] but perhaps a brief indication of it will be useful here.

We use mathematical methods empirically, merely to help us to represent observed data more simply and more powerfully. The objection is sometimes raised that sensory scores are not measurements in the usual sense, and in particular that they lack ' additivity ' and ' equality '. Now one does not, on the whole, desire to perform any physical additions of samples of food, and therefore the requirement of physically ' additive ' units seems quite irrelevant ; if one did want to add samples of food physically, one could easily find out, by experiment, how such processes can be described numerically. Actually, as far as we can see, these numerical scores are used in the same way as most physical measurements, for a little reflection shows how for almost every use of a given physical scale the ' equality ' and the ' additivity ' of its initial units are irrelevant. In particular, consider the physicochemical relationship mentioned at the end of the last section. There the chemical readings were transformed to logarithms and these ' non-additive ' measures were then averaged, because their relationship with age-in-ice could thus be described very simply, as a straight-line regression with constant scatter. Similarly, the sensory scores were averaged. Finally, it was found that the relationship between the (averaged) logarithms of the chemical stimuli and the (averaged) sensory responses also happened to be linear. The justification of the mathematical manipulations does not, of course, lie in this Weber-law effect, but in the fact that these particular data could hardly have been described more simply.

This necessity for mathematical treatment of the physicochemical measures shows that their peculiar virtue cannot lie in their initial numerical form, but rather in the fact that for them a great deal of ' objectivity ' has already been achieved. We believe that if any attention is to be paid to those people who say that one cannot ' measure ' in the present kind of context because of some metaphysical difficulties or other, they should be asked to state specifically what they mean, in terms that are capable of being tested empirically.

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DETERMINATION OF NITROGEN IN SOIL AND PLANT MATERIALS: USE OF BORIC ACID IN THE MICRO-KJELDAHL METHOD

By S. H. YUEN and A. G. POLLARD

The use of boric acid for trapping ammonia in the micro-Kjeldahl determination is examined. A suitable procedure, together with a modified type of micro-distillation apparatus, is described.

The buffer capacity of boric acid solutions was examined in relation to the sensitivity in the titration of ammonia dissolved in them. Two grades of boric acid, 'pure' (technical) and AnalaR, were compared; the former showed appreciable buffering on the acid side.

The pH values of solutions of both grades decreased with increasing concentration. The sensitivity of the three indicators examined for the titration of ammonia diminished with increasing concentration of boric acid as a result of the increased buffering. With concentrated boric acid, all three indicators showed wide transitional periods at the end-point, but in solutions of concentration up to 1·0% of AnalaR grade the end-points shown by all three indicators were sharp. The methylene blue–methyl red indicator, however, was generally preferable.

The ammonia-fixing capacity of boric acid was studied in air-bubbling tests and by recovery of a known amount of ammonia by distillation. A volume of 10 ml. of 1·0% boric acid fixed 5 mg. of nitrogen as ammonia sufficiently firmly to afford accurate analyses. For macro-determinations, 100 ml. of 2·0% boric acid held firmly up to 90 mg. of nitrogen.

The determination of ammonia by distillation into boric acid and subsequent titration with a mineral acid was first proposed by Winkler in 1913.[1, 2] Many research workers have since adopted this method, its attractive feature being that only one standard solution is required in the titration.

It is claimed that results thus obtained compare favourably with those given by the normal back-titration method,[3–5] although the difficulty generally encountered in the titration is the indefinite end-point given by many of the indicators used. Methyl orange,[1, 2, 6, 7] Congo red,[1, 2] bromophenol blue,[3–5, 8] and methyl red,[9–10] used by various workers, have not proved satisfactory. Several mixed indicators subsequently recommended include: tetrabromophenol blue–methyl red,[11] methylene blue–methyl red[12, 13] and bromocresol green–methyl red.[14–17]

In the present investigation the disadvantage was experienced of high 'blank' readings as well as low sensitivity with the three indicators tested (Table IA), particularly when the amounts of ammonia were small. An examination was therefore made of the buffer capacity of boric acid as a basis for improving the technique of the titration, with special reference to micro and semi-micro quantities of ammonia. Throughout this work, both 'pure' (technical, powder) and AnalaR (crystalline) grades of boric acid (Hopkin & Williams) were employed.

Ammonia-free distilled water was used in the preparation of reagents required and in all determinations.

Experimental

Buffer capacities of boric acid

In the presence of boric acid, indicators used in the titration of ammonia show an unusually wide transitional range between two distinct end-point colours. Preliminary observation of the titration of a known amount of ammonia in various concentrations of boric acid, commonly suggested in the literature, also showed that the sensitivity of the indicators tended to diminish with increasing concentration of boric acid, and that end-points were difficult to recognize in the more concentrated acid even when recommended mixed indicators were used. Buffer curves of boric acid from 0·1 to 4·0% were determined by adding 0·01N-NaOH and 0·01N–HCl to 10-ml. portions and are shown in Figs. 1*a* and 1*b*. The pH values were measured by a Cambridge bench pH meter.

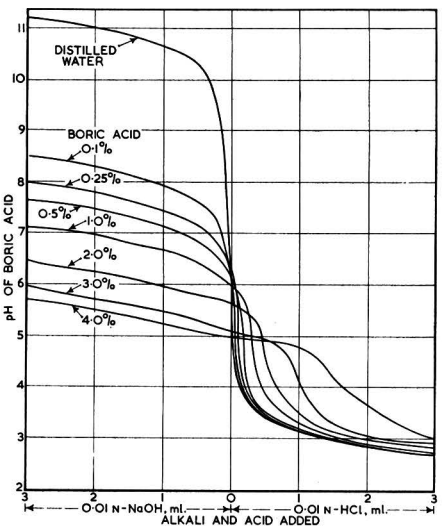

FIG. 1*a*.—*Buffer curves of boric acid, 'pure'*

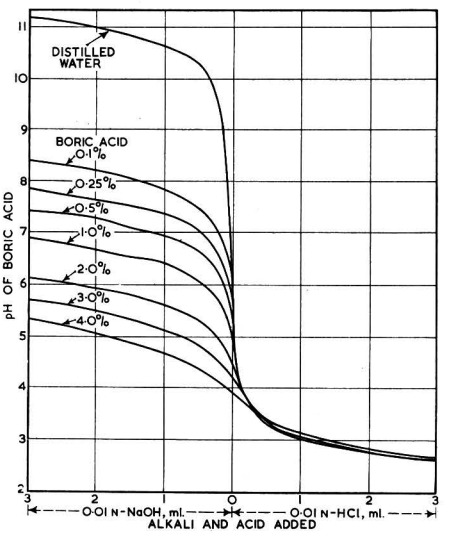

FIG. 1*b*.—*Buffer curves of boric acid, AnalaR*

It is evident from Fig. 1*a* that 'pure' boric acid, even in 0·1% concentration, had a considerable buffering effect on the alkaline side. With increasing concentration of boric acid, the buffer capacities increased by progressively smaller steps. Similar types of buffer curves were found for AnalaR boric acid, as indicated in Fig. 1*b*, step-wise differences on the acid side disappearing with the purer product.

Figs. 1*a* and 1*b* demonstrate that low concentrations of boric acid favour a sensitive titration and that with higher concentrations of boric acid there is an unusually long transitional period round the end-point. Theoretically, boric acid, as a very weak acid, should show no buffering effect with added acid; this is confirmed in Fig. 1*b*, where all pH curves of AnalaR boric acid on the acid side were practically coincident with that of the distilled water. The buffer capacity, against added acid, of the 'pure' boric acid, which research workers have commonly employed, must be due to contamination, probably with sodium salts.

pH and blank readings of boric acid

For a further examination of the relationship between the sensitivity of the titration and the concentration of boric acid, 10-ml. portions of boric acid solutions of various concentrations were directly titrated with hydrochloric acid and 'blank' tests, with distilled water, were also made with the three indicators. (For the blank tests with the micro-Kjeldahl apparatus, 10 ml. of boric acid solution was used in the receiver and 10 ml. of distilled water containing an excess of sodium hydroxide was used in the distilling flask.) The acidities of

the solutions before and after titration were recorded. The three indicators gave the same result, solutions after titration showing similar pH values. The results are shown in Table I; only the mean end-point values are given.

Table I

pH and blank readings for boric acid

Boric acid		Direct titration				'Blank' test			
%	pH	ml. of 0·01N-HCl			Mean end-point, pH	ml. of 0·01N-HCl			Mean end-point, pH
		(*a*)	(*b*)	(*c*)		(*a*)	(*b*)	(*c*)	
				A. 'Pure' boric acid					
0·1	6·02	0·04	0·05	0·05	5·15	0·07	0·06	0·07	5·18
0·25	6·25	0·11	0·07	0·08	5·24	0·10	0·12	0·10	5·24
0·5	6·15	0·17	0·15	0·15	5·20	0·18	0·16	0·19	5·20
1·0	5·96	0·29	0·25	0·32	5·15	0·31	0·30	0·35	5·10
2·0	5·63	0·36	0·33	0·40	5·19	0·73	0·75	0·72	5·24
3·0	5·16	*	*	*	—	0·76	0·80	0·80	5·16
4·0	4·96	*	*	*	—	1·50	1·46	1·45	5·22
				B. AnalaR boric acid					
0·1	5·54	0·07	0·05	0·04	5·18	0·05	0·05	0·06	5·20
0·25	5·45	0·06	0·05	0·04	4·91	0·05	0·05	0·06	5·14
0·5	5·27	0·02	0·03	0·03	4·81	0·04	0·05	0·05	5·11
1·0	5·01	*	*	*	—	0·02	0·03	0·02	4·89
2·0	4·51	*	*	*	—	0·04†	0·05†	0·06†	5·22
3·0	4·18	*	*	*	—	0·20†	0·22†	0·20†	5·32
4·0	3·90	*	*	*	—	0·45†	0·43†	0·46†	5·37

* On the acid side of end-point

† Titrated with 0·01N-NaOH

Indicators used: (*a*) methyl red;[9] (*b*) bromocresol green–methyl red mixed indicator;[17] (*c*) methylene blue–methyl red mixed indicator (see section on *Analytical procedure*)

The acidities of solutions of 'pure' boric acid increased with concentration (0·25–4·0%), corresponding with a reduction of pH from 6·25 to 4·96. In the direct titration with acid, the readings increased with increase of boric acid concentration from 0·1 to 2·0%. Although the acidity increased with the concentration of boric acid, the higher buffer capacity of the more concentrated acid required a greater amount of hydrochloric acid to bring the pH down to that of the end-point, ranging from 5·15 to 5·24. The blank tests showed a tendency similar to that found in the direct titrations, i.e. the readings increased with the concentration of boric acid from 0·1 to 4·0%. The acidities of both 3·0 and 4·0% boric acids, which were originally on the acid side of the end-point, became alkaline during the distillation, owing to the dilution effect, the distillate itself being nearly neutral. The high value of blank tests demonstrates the high buffer-capacity of the boric acid used and confirms the suggestion that a dilute boric acid solution is preferable for the determination, provided that it can fix effectively the distilled ammonia.

Since AnalaR boric acid was not contaminated with basic compounds, the pH values were lower than those of corresponding 'pure' boric acids. Because AnalaR boric acid had no buffer effect against added acid (Fig. 1*b*), readings of both direct titration and blank test were negligible with 0·1, 0·25 and 0·5% boric acid. The pH of 2·0–4·0% boric acid was on the acid side of the end-point, even after distillation. Back-titration with alkali was not effective because boric acid showed a buffer capacity on the addition of alkali.

It was observed that when the concentration of boric acid was low, i.e. below 1·0%, all three indicators used were equally sensitive. On the other hand, with 3·0 and 4·0% boric acid, the colour change was spread over a wide transitional range whichever indicator was employed; a colour-matching titration, with a control for comparison, was therefore necessary. Although there was no appreciable difference between results obtained with the three indicators, the methylene blue–methyl red mixed indicator was thought to be most promising, the end-point being easily identified. Methyl red alone, however, showed a poorer transitional colour, especially in the presence of concentrated boric acid of either 'pure' or AnalaR grade. The methylene blue–methyl red indicator was therefore adopted in the following work.

Recovery of ammonia by boric acid of various concentrations

The efficiency of recovery of known amounts of ammonia, namely 500 and 1500 μg. of nitrogen, distilled into 10-ml. portions of varying concentrations of boric acid, was investigated with the methylene blue–methyl red indicator. Ammonium sulphate (A.R.) was the source

of nitrogen. Recoveries in both μg. and per cent. are shown in Table II. In this Table no empirical correction was made to the titration readings.

Table II

Apparent recovery of ammonia (calc. as nitrogen) by boric acid of various concentrations

Boric acid, %	Addition of 500 μg. of nitrogen				Addition of 1500 μg. of nitrogen			
	'Pure'		AnalaR		'Pure'		AnalaR	
	μg.	%	μg.	%	μg.	%	μg.	%
0·1	505·2	101·0	498·4	99·7	1500	100·0	1500	100·0
0·25	502·0	100·4	498·8	99·8	1510	100·7	1503	100·2
0·5	516·9	103·4	502·8	100·6	1514	100·9	1507	100·5
1·0	531·3	106·3	501·3	100·3	1521	101·4	1501	100·1
2·0	559·1	111·8	491·1	98·2	1551	103·4	1495	99·7
3·0	589·0	117·8	485·3	97·1	1602	106·8	1490	99·3
4·0	623·1	124·6	483·5	96·7	1631	108·7	1475	98·3

Satisfactory recovery of ammonia within a 0·5% error is evident in Table II with 0·1 and 0·25% 'pure' boric acid and also with AnalaR boric acid up to a concentration of 1·0%.

The apparent recovery of ammonia exceeded the theoretical when the concentration of 'pure' boric acid used was higher than 0·5%. This is obviously due to the high blank tests (Table IA), which were not deducted from the titration readings shown in Table II. On the other hand, the recovery of ammonia by AnalaR boric acid diminished slightly with increase in concentration from 2·0 to 4·0%. Since a lower initial pH of these solutions results from an increase of concentration, incomplete titration of ammonia will occur when the acid employed has a concentration of 2·0% or higher, as the end-point pH of the indicator is about 5·1. Thus, for determination of small amounts of ammonia, the use of boric acid solutions more concentrated than 1·0% is not desirable since the determination is likely to be high with the 'pure' acid and low with the AnalaR grade. Further, the more concentrated the boric acid of either grade, the greater is the difficulty in matching the end-point because of the slower change in pH. In the literature little attention has been directed to the effect of concentration of boric acid on the sensitivity of the titration. Almost all workers favoured high concentrations of boric acid; for instance, for micro-determinations: 2·0[12, 16] and 4·0%; [9–11, 14] for semi-micro: 4·0%; [10, 17] and for macro-determinations: 3·0,[6, 18] 4·0,[3–5, 7, 9, 14] and 5·0% (or saturated).[1, 2, 6, 8] As shown in the previous section, when the boric acid concentration was low any of the indicators already referred to may be used without appreciable difference.

Ammonia-fixing capacities of boric acid

Since the sensitivity of the boric acid titration is closely related to the concentration of the boric acid and is greatest with low concentrations, it is preferable to use low concentrations provided that absorption of ammonia is efficient. As a very weak acid, boric acid cannot be expected to fix strongly an equivalent of ammonia. To determine the true fixing power for ammonia, air was passed, at a rate of about 250 ml. per minute, through 10 ml. of boric acid solution containing varying amounts of ammonia. For this purpose boric acid solutions of from 0·1 to 1·0% concentration, as well as distilled water, were used. Two periods of air-bubbling, 5 and 10 minutes, were adopted. Ammonium hydroxide (A.R.) was the source of ammonia. The recoveries of the added nitrogen are shown in Table III.

Table III

Ammonia-fixing capacities of boric acid: per cent. of ammonia remaining after air-bubbling

Nitrogen added, μg.	H_2O	Boric acid, 'pure'				Boric acid, AnalaR			
		0·1%	0·25%	0·5%	1·0%	0·1%	0·25%	0·5%	1·0%
		After 5 minutes' air-bubbling							
700	96·9	99·0	100·4	99·4	100·2	99·5	99·2	99·7	100·2
1400	94·7	98·6	99·1	98·4	99·3	98·3	99·6	99·4	100·3
2800	94·3	97·5	98·8	99·2	99·6	98·0	98·6	99·7	99·9
5600	93·1	96·0	98·5	98·9	99·7	97·9	98·5	99·5	99·3
		After 10 minutes' air-bubbling							
700	92·9	97·9	99·2	100·6	100·0	98·3	98·8	99·4	100·4
1400	90·6	96·3	99·1	100·1	99·2	97·2	98·5	99·5	99·5
2800	89·6	93·5	97·6	99·0	99·3	93·6	97·0	98·9	99·1
5600	89·5	92·2	97·2	97·4	98·5	91·4	96·1	96·5	97·9

The ammonia-fixing capacities of corresponding 'pure' and AnalaR grades of boric acid were practically the same in both 5- and 10-minute tests. In 5-minute tests, 0·1% boric acid did not fix ammonia completely although a 10-ml. portion of this concentration was equivalent to about 7000 μg. of nitrogen. With 0·25% boric acid, the equivalent of 1400 μg. of nitrogen was fixed with a mean loss less than 0·5%. With 0·5% acid, the equivalent of about 2800 μg. of nitrogen could be recovered after air-bubbling, and with 1% acid the equivalent of more than 5600 μg. of nitrogen was held. Greater losses of ammonia occurred in all the 10-minute tests. A 10-ml. portion of 1·0% boric acid fixed an equivalent of about 2000 μg. of nitrogen.

In a similar experiment with 10-ml. portions of distilled water, a 3% loss was found when 700 μg. of nitrogen was added, and a 7% loss occurred with an addition of 5600 μg. of nitrogen in 5-minute bubbling tests. The corresponding losses in 10-minute tests were 7 and 10% respectively.

Since the air-bubbling in the tests was very vigorous, far exceeding the bubbling taking place in ordinary distillation, it may be assumed that the fixing capacity of boric acid for ammonia in this respect is the equivalent of 1000 μg. of nitrogen for 10 ml. of 0·25% acid, 2000 μg. for 0·5% acid and 5000 μg. for 1·0% acid, with an error of less than 0·5%.

For both micro and semi-micro determinations of ammonia, 1·0% boric acid is evidently the most suitable because of its relatively strong fixing power and its negligible effect on the sensitivity of the titration. The AnalaR acid is superior to the 'pure' grade in that practically no blank reading is recorded. For macro-determinations of ammonia, 2·0% boric acid (AnalaR) is recommended to receive the distilled ammonia, and 0·1N-hydrochloric acid for the titration. It was found by a 30-minute air-bubbling test that 100 ml. of acid of this concentration effectively fixed ammonia up to an equivalent of 90 mg. of nitrogen. No empirical correction is needed in this instance when ammonia-free distilled water is used.

The ammonia-fixing capacity of boric acid was further examined by distilling a known amount of ammonia from ammonium sulphate into 10-ml. portions of 1·0% boric acid. The results of recovery are given in Table IV.

Table IV

Recovery of ammonia (calc. as nitrogen) by 1·0% boric acid

Nitrogen added,	Boric acid, 'pure'		Boric acid, AnalaR	
μg.	μg.	%	μg.	%
100	98·3	98·3	101·1	101·1
200	199·4	99·7	200·8	100·4
500	497·0	99·4	504·1	100·8
1000	985·4	98·5	998·2	99·8
2000	1992	99·6	1984	99·2
5000	4992	99·8	5005	100·1
10000	9901	99·0	9839	98·4

Values shown in Table IV agree with those of the air-bubbling tests. When 10 ml. of 1·0% AnalaR boric acid was used to receive ammonia the equivalent of about 5000 μg. of nitrogen was completely fixed, with an error of less than 0·5%. A similar ammonia-fixing capacity was shown by 'pure' boric acid, but the error was greater.

It was noticed that boric acid could absorb more ammonia, although by no means completely, in the course of distillation than it should on theoretical grounds. This is probably due to ammonia's being dissolved in the water as well as combined with boric acid. It is not desirable in practice, however, for the boric acid solution to receive more ammonia than it can hold against the air-bubbling.

Analytical procedure

Reagents.—Ammonia-free distilled water should be used in the preparation of the following reagents:

Boric acid (AnalaR), 1·0 per cent.

Sodium hydroxide (A.R.), 30 per cent.: Bottle as soon as cold and keep tightly stoppered when not in use.

Methylene blue–methyl red indicator: Mix equal volumes of 0·2% alcoholic methyl red and 0·1% aqueous methylene blue. If water-soluble methyl red is available, its aqueous solution, instead of alcoholic, may be used in the preparation of this indicator.

0·01N-Hydrochloric acid (A.R.).

Apparatus.—A 10-ml. micro-burette.

Micro-distillation apparatus: A micro-distillation apparatus, described by R. Markham,[19]

was modified by the first-named author (S. H. Y.), and found to be effective in distillation and satisfactory in operation (Fig. 2).

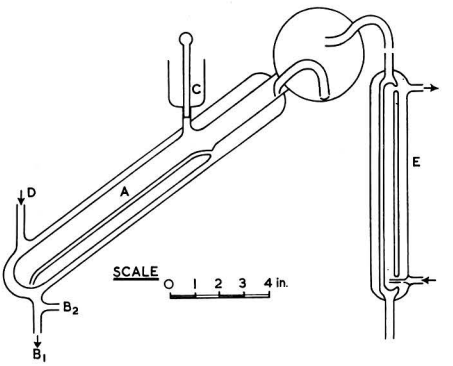

FIG. 2.—*Micro-distillation apparatus*

Preparation for distillation.—The distilling flask A is washed out by means of a filter pump connected to the water outlet B1. About 50 ml. of distilled water is added to A through the funnel C by lifting its stop-rod, while the safety outlet B2 and water outlet B1 are opened and the steam inlet D is closed. The water is sucked out by closing the safety outlet B2. The filter pump is conveniently left running continuously. The washing is repeated twice.

The distilled water in the 2-litre steam-generator is now heated over a Bunsen burner, the water outlet B1 being closed and the steam inlet D and safety outlet B2 opened. Cold water is run into the double-layer condenser E. When the water in the generator boils the burner is removed and the steam inlet D is closed. The apparatus is then ready for use.

The distillation.—Boric acid (10 ml. of 1·0%) is placed in a boiling tube (1 in. × 6 in.) and 3 drops of the mixed indicator are added (accurate measurement of the acid is unnecessary). The boiling tube is placed under the condenser E with the end of the delivery tube completely immersed in the acid. An aliquot of the test solution, containing up to 5 mg. of nitrogen, is pipetted into the distilling flask and diluted to about 25 ml. with water, and the funnel C is subsequently closed by the stop-rod. An excess of 30% sodium hydroxide solution is added through the funnel to the distilling flask and rinsed in with a few ml. of distilled water. The burner is replaced below the steam-generator while the steam inlet D is opened. The safety outlet B2 is now closed.

After distillation for about 4 minutes, 15–20 ml. of distillate will have collected. The boiling tube is then lowered and the delivery tube is rinsed. The burner is removed until the next distillation. The boric acid solution is titrated with 0·01N-hydrochloric acid. A blank test carried out in a similar manner should give a reading of less than 0·05 ml. of 0·01N-acid.

Discussion

The fundamental point in the present investigation is that the buffer capacity of boric acid in the presence of bases increases with its concentration at a rate which markedly affects the titration of ammonia present. Low concentrations of boric acid of high purity are therefore desirable for trapping ammonia distilled in micro-Kjeldahl determinations.

Several suitable indicators have been recommended for this titration. Of those tested the methylene blue–methyl red mixed indicator was generally favourable, its colour change being sharp and easily discernible. The end-point pH was in the range of 4·9–5·3. This indicator was first described by Johnson & Green in 1930[20] as a substitute for methyl red. The ratio of methylene blue to methyl red affects the colour change. Too low a ratio was found to make the colour of the end-point less distinct, and with a high ratio the change of colour was not persistent. Johnson & Green used a ratio of methylene blue to methyl red of 1 : 1·5. Later the 1 : 2[12] and 1 : 2·1[13] ratios were also adopted. In the present work the ratio 1 : 2 was found most suitable.

Since boric acid ($pK = 9·2$) is too weak an acid to hold firmly a large amount of ammonia against the bubbling that occurs during distillation, an air-bubbling test was devised to determine

the true ammonia-fixing capacity. It was found that 10 ml. of 1·0% acid fixed 5 mg. of nitrogen as ammonia without appreciable loss. For macro-determinations, 100 ml. of 2·0% acid completely absorbed an equivalent of up to 90 mg. of nitrogen. The maximum absorption of ammonia by boric acid, as reported by a number of workers, appears to be in the range of 4–8% of the theoretical equivalent of the acid. For instance, Winkler[1] stated that 0·1–0·2 g. of ammonia could be absorbed by 5 g. of boric acid in 100 ml. of water. Scales & Harrison[3] found that 95 mg. of nitrogen as ammonia could be recovered in the distillate when 50 ml. of 4% boric acid was used. Bernard[6] recommended that for absorbing amounts of ammonia ranging from 0·01 to 0·09 g., 50 ml. of 3% boric acid should be used, and that for 0·08–0·15 g. of ammonia, 100 ml. of 5% acid was required. Reith & Klazinga[14] reported that 10 ml. of 0·66M-boric acid was sufficient to hold ammonia in the range of 0 to 0·25 millimole and 50 ml. of this concentration fixed up to 5 millimoles.

It was observed from experiment that the absorption of ammonia by boric acid was considerably less rapid than that by hydrochloric or sulphuric acid. Very vigorous steam-generation often caused traceable losses of ammonia even when an effective condenser was used. For general work, a boiling tube (1 in. × 6 in.) was used as a receiver to increase the depth of liquid through which bubbles pass. Under these conditions practically no loss of ammonia occurred within the maximum fixing capacity. The error of this method was less than 0·5% in the range of 0·1 to 5 mg. of nitrogen. When the amount of ammonia distilled was less than 100 μg. the error of the determination fell to 1–2%.

Effective cooling of the condensate was also found to be important in preventing loss of ammonia. The temperature of the boric acid solution in the receiver should never exceed 40°. With the apparatus shown in Fig. 2, distillation at the rate of 3–4 ml. of distillate per minute was found suitable. The whole operation for one determination, including distillation and titration, is easily completed in about 5 minutes.

An empirical correction in the titration is necessary in the case of 'pure' boric acid (Table IA). With 10 ml. of 1·0% 'pure' boric acid the blank test was 0·32 ml. of 0·01N-hydrochloric acid. The reading was increased in proportion to the quantity of boric acid used. A blank test is preferably made whenever a fresh stock of boric acid is prepared. The pH of 1·0% AnalaR boric acid is slightly on the acid side of the end-point, but after a blank distillation the distillate shows a pH similar to that of the end-point of the indicator owing to dilution. Thus the blank-test reading is practically negligible.

Carbon dioxide in excessive amounts affects the sensitivity of the mixed indicator in the titration. Thus, the boric acid method is suitable for the collection of ammonia generated in the Kjeldahl digestion for soil and plant materials, but is less satisfactory in the determination of exchangeable ammonia in soil when magnesia is used in the distillation.

Acknowledgment

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Journal of Applied Chemistry

The following papers are appearing in the October, 1953, issue of the *Journal of Applied Chemistry*

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