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Presented at the Annual General Meeting of the Association of Public Analysts at Southampton on 23–25 April 1987,

By the Honorary Secretary, Mr K. T. Chisnall.

House of Lords Select Committee—Science and Technology in Local Government

The Association submitted both written and oral evidence to this Committee whose report was published on 12 December 1985 and debated in the House one month later. The report was welcomed by the Association of County Councils for its recognition of the range of scientific services provided by local authorities. However, the recommendation that all local authorities should set up Science and Technology Committees and that the status of Public Analysts in the organisation should be specified was considered unnecessary, and a matter for local management decision. Recommendations for joint or co-operative provision of scientific services by local authorities were accepted by the Association of County Councils as principles but not to be made compulsory. The Select Committee's investigations provided a welcome opportunity for the Association to express views about the level of work and organisation of the Public Analyst service, and for these to be examined independently and conclusions drawn. It was pleasing to see that the Select Committee found that the overall level of scientific and technical expertise in local government is good and in some authorities excellent, but was concerned to hear that such services are in danger of being adversely affected by financial constraints.

Local Government Act 1985

Last year we reported that although the Local Government Act 1985 led to the abolition of the Greater London Council and the Metropolitan County Councils, there was some optimism that the laboratory services that had been built up in the Metropolitan Counties would be retained.

In the run-up period to the passing of the Act, the House of Lords Select Committee on Science and Technology had taken a close look at Science and Technology in Local Government including the Public Analyst service. In its report, the Select Committee expressed the view that there should be a move towards regionalisation of the Public Analyst service. They also pleaded for a greater awareness of scientific matters in local government in general. To this end they recommended involvement of the Public Analyst in the management team of the local authority and the setting up of Science and Technology Sub-Committees.

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In the event, the abolition of the Metropolitan Counties has led to the retention of three out of the four local authority maintained metropolitan laboratories, in joint arrangements between the successor authorities. The Merseyside laboratory, however, was closed on 31 March 1986. This must be regarded as a serious loss as for many years it had been one of the major local government laboratories in the country. In October, Liverpool re-opened the laboratory, but with only a quarter of the former Merseyside staff, and it is still not clear what arrangements for a Public Analyst service will be made by some of the districts. Such fragmentation is a retrograde step at a time when fewer, better equipped laboratories are needed. It will take many years to regain the lost expertise.

There have been some readjustments in the two Metropolitan Counties that use consultants' laboratories but not as far-reaching as the changes in Merseyside. It must, however, be noted that there is evidence of the increased use of in-house screening tests in addition to the use of the officially appointed Public Analyst. Duplication of resources between such mini-laboratories and a properly equipped Public Analyst laboratory must inevitably lead to overall increased costs to the ratepayers.

Finally, it must be recorded that, with one exception, administrative structures have been established that deny direct access of elected members to their Public Analyst who must operate through an officer of another, non-scientific, discipline. The Association feels that the recommendations of the House of Lords Select Committee were along the right lines. In a time of increasing need for good scientific advice, any move that makes the source of that advice more remote is to be regretted.

Agriculture

Public interest in levels of residues in food from agricultural treatments remains at a high level. During 1986 Public Analysts were again active in determining residues of pesticides in meat products, cereals and vegetables. Participation with the Ministry of Agriculture, Fisheries and Food continued in a number of surveys. Debate is still continuing on how best to control the level of residues in food. A discussion document now circulating seeks to ascertain the views of interested organisations in regard to the implementation of Part III of the Food and Environment Protection Act. Many Public Analysts feel that the present proposals do not satisfy the public demands for statutory limits to the extent that they are put forward primarily for the protection of trade interests rather than protection of the consumer. The strengthening of the Food Act rather than the proposed actions under the Food and Environment Protection Act would have been more relevant to public interest and public safety.

The present proposals suggest that Central Government agencies will have the primary role in monitoring residues of pesticides in food. Sampling and enforcement officers already exist at Local Authority level. It is only necessary to provide financial resources to permit them to bear the increased work load. To set up a parallel system run by the Ministry is not only wasteful, it is a misuse of resources. Under these proposals the Government will effectively control the

sampling officers, the analysts and the fate of the crops, thus acting as judge, jury, executioner and probably as arbiter in appeal situations.

The need for monitoring activities independent of Government was clearly seen in three panic situations in 1986, viz. methanol in wine, diethylene glycol in wine, and radiation levels in foods. There is a need for a strong independent monitoring system for evaluation of residues from agricultural treatments in food. The qualifications, skills and expertise available in Public Analyst Laboratories and the working relationship at local authority level with Food Sampling/Enforcement Officers should be fully utilised.

Another important piece of legislation in the agriculture area of work was the new Feeding Stuffs Regulations 1986. This set of regulations consolidated existing controls and incorporated provisions from EEC directives extending the control to additives, premixtures and complementary feeding stuffs.

Completion of the Internal Market

During 1985 the European Council welcomed Lord Cockfield's proposal to complete a single European market by 1992, recognising as a high priority the need to remove physical, technical and fiscal barriers to trade. At the same time proposals for amendments to the Treaty of Rome were initiated (the Single European Act), which included proposals for qualified majority voting on the Council to avoid delays in decision-making created by the current unanimous vote requirement.

The European Commission, charged with the task of implementation, has issued discussion documents and proposals by which the "Completion of the Internal Market" might be achieved. A major principle is that if a product is lawfully manufactured and marketed in one member state, it should be allowed to be freely sold throughout the Community.

The Commission recognises that the aims of national legislation on health, safety and the environment are similar if not identical, and that the concept of mutual recognition, supported by harmonisation in essential areas, should be adequate to entitle the free movement of products.

With regard to foodstuffs, legislation will concentrate on "horizontal" directives to protect the health and safety of consumers. To this end, draft framework directives have now been issued dealing with food additives, materials and articles coming into contact with food, foods for particular nutritional use and labelling. The latter is particularly significant, as, in the Commission's view, provided labels give consumers adequate information, there is no further requirement for compositional standards or derogations which restrict the free movement of goods.

The Association has expressed concern in concert with the local authorities and other enforcement professions over the possible implications of some of these proposals, particularly with regard to the accountability of the Commission to elected members and expert advisory bodies.

In addition, recent proposals for the system of inspection and control of food are, as currently drafted, far from satisfactory. The Association has expressed its deep concern over these matters to the Ministry, especially regarding the potential for self regulation by the industry and the failure to recognise and fully

incorporate the Public Analyst's independent scientific investigation of foodstuffs traditional in the U.K. and essential to the proper protection of the consumer.

Milk and Dairies

The Association is involved within BSI in reviewing the methods for the determination of the freezing point of milk, which is used to assess the presence of extraneous water. Several laboratories have taken part in a number of collaborative trials to validate analytical methods being adopted by BSI. These include nitrogen in cheese and acidity, lactose, chloride and ash in milk.

Meat and Fish Products

A number of difficulties with the Meat Products and Spreadable Fish Products Regulations 1984 had been highlighted by Public Analysts, and discussions with the Ministry of Agriculture Fisheries and Food on resolving those points were promoted by the Association's Meat and Fish and Novel Protein Products Sub-Committee, which subsequently reported to members. A few amendments were accepted by the Ministry. Liaison was maintained with various bodies on "Guidelines for the Due Diligence Defence" relating to controls and labelling of added water contents in cured meats, and the Sub-Committee made detailed preparations for a LACOTS survey on cured meats as sold to the public. The Sub-Committee issued advice on several analytical and related topics including differentiating between species of meats, rapid measurements of meat/fish spoilage, and nitrogen factors for lamb, and the group also maintained an active interest in on-going work on fish foods and egg products.

Labelling of Foods

THE INFORMATIVE LABEL

The label on a foodstuff is intended to fulfil two basic functions, firstly, to allow the manufacturer or retailer to present the food so as to attract the consumer, and secondly, to allow the consumer to know what is in the package. U.K. Food law has traditionally placed few restrictions on what might appear on labels, relying to a great extent on Section 6 of the Food Act, that the label must not mislead. As a back-up however, consumers were being safeguarded, usually without their knowledge, by the imposition of compositional standards, so that a wide variety of foods, particularly in the meat and dairy fields, had a guaranteed minimum quality.

In recent years, there has been a move away from this approach, towards the concept of "informative labelling". Under this system, few products will have a guaranteed compositional quality, but the manufacturer will have to indicate more precisely on the label what is in the food. As an example, a food described as Beef Casserole would in 1967 have had to contain at least 35 per cent. of meat. With the advent of new meat products regulations in 1984, no standard now applies to Beef Casserole, and the manufacturer can put in as much or as little meat as he desires. The current requirement is to indicate on the label the content of meat that is present, but since the declaration of meat content is

invariably lost in small letters among the list of ingredients, the ability of the consumer to make ready comparisons of one product with another is diminished.

If informative labelling is to continue as a basic concept, then at the very least, compositional declarations should be required to be made alongside the name of the food and in a prominent place on the label.

THE CONFUSED NAME

Contradictory descriptions on foodstuffs have long been felt to be unacceptable, since they could mislead the consumer, and invariably devalue a traditional name. The classical case arose in 1950 when it was held that the description "non-brewed vinegar" could not be used. The basic reason for the judgement was that vinegar is a double fermented product, and therefore "non-brewed vinegar" was a contradiction in terms. One beneficial result of the judgement was that the name vinegar was protected for the traditional product.

Informative labelling is a direct challenge to traditional names and two recent cases illustrate how the onus is being thrown more and more on the consumer to untangle and interpret many of the complicated descriptions being devised by manufacturers. In the first case, the description "vegetable lard" was held to be valid since the label also declared that the food was made with "100% vegetable oils". In the second case, a slab of meat product was made by pressing and moulding together small pieces of chicken, but the description "chicken breast steaks" was held to be valid since the label also bore the legend "flaked and formed" meat. In these cases, the names "lard" and "steak" have been used for foods which are not traditionally "lard" or "steak", and although the information on the label as a whole satisfied the judges, the traditional names have undoubtedly been devalued.

NUTRITIONAL INFORMATION

According to the press, radio, television, consumer organisations, food retailers and many books on the subject, people who buy food wish to know more and more about the nutritional make-up of the food. Typical analyses for fat, protein, carbohydrate, dietary fibre, salt and sugars appear on many labels and although the figures may increase knowledge of the food itself, the consumer might still be left wondering what it all means and how he should interpret it in terms of his own diet. Articles decry the addition of salt to food, but this is only likely to be a problem to people who are already hypertensive, and will normally have the condition under control. Evidence that high cholesterol foods such as eggs increase blood cholesterol levels has been strongly contested, whilst there is a recent suggestion that too much dietary fibre added to foods is harmful in that it absorbs minerals which should be entering the body's digestive system.

Placing nutritional information on a food label is not, in itself, a health hazard, but the hysteria which surrounds the subject is likely to cause more worry than the information on the label is intended to allay.

Eating a balanced diet, with moderate amounts of food, would be better for the nation's health than reading reams of figures on nutritional information.

Compilation of this information is expensive, and the money might be better spent on a programme of education which took a balanced and constructive view of all foodstuffs—from basic to convenience, and also stressed the importance of physical exercise.

NATURAL IS A POINT OF VIEW

With the increase in consumer consciousness on matters concerning food, the spotlight has been switched on to additives and the absolute necessity for their presence. Perceived wisdom is that foods without additives are better than foods which contain them and any food that is "natural" is better than one that isn't.

Many natural or single foods such as wheat, milk, tea, coffee, strawberries and cheese have extremely upsetting effects on a large number of people, whilst evidence that additives are a significant cause of allergic reactions is not substantial. Nevertheless, to describe a food as "natural" carries a premium which manufacturers earnestly seek, but, to date, the word has not been defined in terms of foodstuffs and cannot have a precise meaning.

Guidelines for manufacturers and consumers alike on the meaning of jargon terms, such as "natural", "low in X", "free from X" are being actively pursued.

Additives and Contaminants Sub-committee

The work of this Sub-Committee during the past year revealed a bias towards microbiological aspects of Draft British Standards, the microbiological examination of meat and meat products being a major topic. This, and a growing awareness within the Economic Community in this field, prompted an assessment within the APA of involvement in this work. A questionnaire revealed that 36 laboratories had some involvement in microbiology, and 24 devoted separate laboratory space to this aspect. Eighteen employed full time staff for microbiology, and 21 employed graduates in the subject. In view of the increasing interest in this field, it was proposed that a separate Microbiological Committee be set up, and this will be implemented in the coming year.

Other matters dealt with related to proposed E.C. Directives for infant formulae and follow-up milks, hygiene of egg products, heat-treated milk, food additives, materials and articles intended to come into contact with foodstuffs, antioxidants and hormones.

In the field of plastics for food use, progress has been towards testing for overall migration with the use of specific migration for "components" known to have toxic properties. A test method for overall migration has recently been produced by the Packaging Industries Research Association (P.I.R.A.) and, if shown to be satisfactory in forthcoming collaborative testing, may be included in future statutory controls for plastic materials intended for use with foodstuffs.

Environmental Monitoring of Radiation and Radioactive Contamination

During the year the Environment Sub-Committee has continued to put forward APA comment on matters relating to environmental pollution to appropriate national bodies. The Sub-Committee has also been active in the

field of Quality Assurance in organising a collaborative trial for the determination of lead in dust which is to be published in 1987.

Prior to 1986 some Public Analysts had carried out, or been involved in examining the need for, environmental monitoring of radiation and radioactive contamination in their localities. Such monitoring was particularly aimed at examining the effect of nuclear industry on its close environs. Concern, in many quarters, about the need for independent monitoring was heightened by the Chernobyl accident. Following arrival of Chernobyl pollution in the U.K., many local authorities began to examine the extent of Government and Industry monitoring in their areas and to consider the establishment of programmes of measurement to be carried out by the local authority itself. Public Analysts have worked as part of local authority teams to assess the requirements of independent programmes and to design and implement a range of different types of programmes for monitoring.

The monitoring requirements of different local authorities vary. Programmes being established range from single issue studies such as measurement of caesium contamination in lamb or measurement of "background" external gamma radiation on land to more complete environmental studies which attempt to evaluate external and internal exposure of local people due to radiation and radioactivity from local, national and international sources of emission.

Consumer Safety

During the year the Association has commented on numerous draft proposals for legislation. Additionally the Association has raised several points and has expressed concern about the use of lead in articles used by children but not covered by the Toys Safety Regulations. This is being pursued with the Department of Trade and Industry.

In line with its policy on accreditation, the Association has suggested that NATLAS accreditation for specified tests shall automatically qualify a laboratory as a test house for the purposes of the Consumer Safety Regulations.

Occupational Hygiene Services

Compliance with Health and Safety legislation increasingly places greater emphasis on practical scientific/medical investigations of workplace health risks. The Health and Safety Commission in stressing this requirement has called for a concerted effort to ensure the adequacy and recognition of specialist services. Scientific Advisers, who are considerably experienced in this work, are well aware that, with respect to chemical risks, Local Authority responsibilities are no less diverse or onerous than those of industry. Indeed, the need to protect school children and the aged is a particular reason for a professional approach to the co-ordination of health and safety services. Amongst the varied investigations conducted by Public Analysts are asbestos risk, toxic metals in paint and fumes, solvent fumes from printing operations and craft work, boiler house and incinerator gases, pesticide sprays and swimming pool treatment chemicals. County Council Scientific Advisers are particularly experienced and qualified to

meet what is now becoming recognised as an essential need for a practical rather than an administrative approach.

Analytical Quality Assurance

The Association recently published its document "A Protocol for Analytical Quality Assurance in Public Analysts Laboratories". This document will form the basis of all quality assurance procedures within the Public Analyst Service. Additionally the Association has accepted the principle of accreditation as part of its policy. Discussions are taking place with the National Testing Laboratory Accreditation Scheme (NATLAS) Executive with a view to agreeing the protocol for accreditation.

Conclusion

The Association has given great consideration to the House of Lords Select Committee Report on Science and Technology in Local Government and has agreed a policy, issued as a Policy Document, designed to take the service into the twenty-first century.

The Policy envisages a move towards accreditation of laboratories and a formal analytical quality assurance scheme. Also in order to make the best use of available resources, it is clear that there must be rationalisation of the service.

APPENDIX I

STATISTICAL SUMMARY 1986

Foods (including complaint samples and those submitted under the Imported Food regulations)	90400
Milks (including those examined for antibiotics and those taken under the Milk (Special Designation) Regulations)	17500
Drinking Waters	14700
Mineral Waters (Natural Mineral Waters Regulations 1985)	100
Swimming Pool Waters	3200
Environmental Pollution (water, trade effluents, tip leachates, ground waters etc.)	44300
Environmental Pollution (waste disposal, reclaimed land etc.)	31200
Feeding Stuffs and Supplements (Agriculture Act and Medicines Act)	5600
Fertilisers (all kinds)	2200
Consumer Protection and Trade Description Acts samples	6200
Cosmetic Products Regulations samples	500
Health and Safety at Work samples	30200
Miscellaneous (Health Authorities, HM Coroner, other Local Authority departments)	27500
TOTAL	273600

APPENDIX II

REPRESENTATION OF PUBLIC ANALYSTS ON OUTSIDE ORGANISATIONS

A. Local Authorities

1. Local Authorities' Co-ordinating Body on Trading Standards (LACOTS).
   (a) Quality Standards Panel.
   (b) Labelling Sub-panel.
   (c) Working Party on Sampling Techniques.
   (d) Working Party on Meat Products.
   (e) Safety Panel.

2. Association of County Councils (ACC).
   (a) Consumer Services Committee, Public Analyst Adviser.

3. Association of Metropolitan Authorities (AMA).
   (a) General Services Committee, Public Analyst Advisers.
   (b) ACC/AMA Joint Waste Disposal Panel.

4. Convention of Scottish Local Authorities (COSLA).
   (a) Scottish Food and Drugs Coordinating Committee.
   (b) Public Analyst Adviser.

B. Central Government

1. Ministry of Agriculture, Fisheries and Food (MAFF).
   (a) Food Advisory Committee.
   (b) Steering Group on Food Surveillance, Heavy Metals Working Party.
   (c) Steering Group on Food Surveillance, Quality Assurance Sub-committee.
   (d) Steering Group on Food Surveillance, Sub-group on Mycotoxins.
   (e) Advisory Committee on Pesticides.
   (f) Veterinary Products Committee, Feeding Stuffs Sub-committee.
   (g) Veterinary Products Committee, Feeding Stuffs Sub-committee, Methods of Analysis Panel.
   (h) Working Party on Due Diligence.
   (i) Committee on Analytical Methods for Pesticides and Veterinary Products.
   (j) Working Party on Pesticide Residues, Sub-group on Bromide Residues.
   (k) Working Party on Pesticide Residues, Sub-group on Pesticides in Animal Products.
   (l) Working Party on Pesticide Residues, Sub-group on Cereals.
   (m) Working Party on Pesticide Residues, Sub-group on Fruit and Vegetables.
   (n) Analytical Panel on Mycotoxins.

2. Department of the Environment.
   (a) Radioactive Waste Management Advisory Committee.
   (b) Advisory Committee on Safe Transport of Radioactive Materials.
   (c) Steering Committee on Environmental Lead Monitoring.
   (d) Working Party on Pesticides in Drinking Water.
   (e) Standing Committee of Analysts (water analysis).
   (f) Environmental Sub-committee. Joint with National Water Council.

3. Department of Trade & Industry.
   (a) National Measurement Accreditation Service/National Testing Laboratory Accreditation Scheme (NATLAS/NAMAS), Chemical Technical Committee.

C. European Community

1. The Community Bureau of Reference; Consultative Committee on Reference Materials for Food Analysis.
2. Working Party on Cosmetic Products.
3. European Committee for Standardisation (CEN), Committee on Safety of Toys. Technical Committee 52/WG1.

D. Royal Society of Chemistry

1. National Council.
2. Law and Parliamentary Committee.
3. Professional Affairs Board.
4. Qualifications and Education Board.
5. Benevolent Fund.
6. Examinations and Institutions Committee.
7. Liaison Committee (with APA).
8. Applications Committee.
9. Disciplinary Committee.
10. Ethical Practices Committee.
11. Working Party on Mastership in Chemical Analysis Qualification (M.Chem.A).
12. Analytical Division Council.
13. Registration Committee.
14. Health, Safety and Environment Committee.
15 M.Chem.A. Examination Board.
16. Analytical Methods Committee (AMC), Chairman.
    (a) AMC Meat Factors Sub-committee.
    (b) AMC Veterinary Residues Sub-committee.
    (c) AMC Animal Feeds Sub-committee.
    (d) AMC Antibiotics in Animal Feeds Sub-committee.
    (e) AMC Statistics Sub-committee.
    (f) AMC Metallic Impurities in Organic Matter Sub-committee.

E. British Standards Institution

1. Local Government Liaison Officer—Disinfectants.
2. Disinfectants Standards Committee, DIC/–
3. Disinfectants, Test Method, DIC/11.
4. Disinfectants, Specifications, DIC/12.
5. Chemical and Health Council, C/–.
6. Toy Safety Committee, TCM/15
7. Fertilisers Committee, CIC/37.
8. Technical Committee (TC) for Ceramic Ware, Glassware and Glass Ceramic Ware in Contact with Food, FHM/28/29.
9. TC on Land Quality.
10. Fillings (Rag Flock, etc.) TCM/10.
11. Meat and Meat Products FAC/6.
12. Freezing-point of Milk DAC/2.
13. Dairy Apparatus DAC/3/12.
14. Dairy Products DAC/3.
15. Land Control EBC/47.
16. Cereals and Cereal Products, FAC/4.
17. Spices and Condiments FAC/7.
18. Tinned and Metallic Cooking Ware FHM/12.
19. Analysis and Sampling of Iron, Manganese and Chrome Ores.
20. Sampling and Analysis of Fluorspar, Bauxite and Aluminium Ores.
21. Committee on Laboratory Ovens.
22. Food and Agriculture Committee. FAC/21.

F. Other Organisations

1. European Food Law Association, Chairman of UK Section.
2. International Committee for Uniform Methods of Sugar Analysis (ICUMSA), National Committee.
3. Meat and Livestock Commission, Serological Testing Committee.
4. Committee of Polytechnic Heads of Analytical Chemistry Departments—ACOT Scheme.
5. Nottinghamshire College of Agriculture, Food Science Advisory Panel.
6. International Standards Organisation (ISO) Committee for Analysis and Sampling of Iron, Manganese and Chrome Ores.
7. ISO Committee for the Sampling and Analysis of Fluorspar, Bauxite and Aluminium Ores.
8. International Union of Pure and Applied Chemistry, (IUPAC), Applied Chemistry Division (Secretary).
9. IUPAC, Food Chemisty Commission (U.K. National Representative).
10. IUPAC, "Pure and Applied Chemistry" Editorial Advisory Board.
11. AOAC, International Co-ordination Committee.
12. IFST/RSC Joint Mastership in Food Control Board.
13. IFST Public Affairs Committee.

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The Adulteration of White Pepper with Rice Starch

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A standard for white pepper is proposed to prevent the addition of adulterants, particularly rice starch; the recommended standard is that undried white pepper should contain not less than 3·5 per cent. trans-trans piperine and that the ratio of potassium to calcium should be not more than 0·45 on a weight basis. The proposed standard is not applicable to black pepper.

Pepper, both black and white, has been adulterated with a variety of substances; the methods used to determine such adulteration have been reviewed[1]. A common adulterant of white pepper is rice starch and the detection of this material is difficult as the small (5–10 μm) polygonal grains of rice starch are similar in size and shape to the starch grains present in white pepper[2]. White pepper naturally contains a large but variable content of starch; for example, a range of 45–64 per cent. was reported by Egan *et al.*[3] A direct determination of total starch can therefore only indicate gross adulteration.

White pepper, unlike many other spices including black pepper, contains more calcium than potassium[4,5,6] with a typical ratio of potassium to calcium of about 0·3 whereas rice starch contains more potassium than calcium, with a typical ratio of potassium to calcium of about 18–45, both ratios calculated on a weight basis. Thus the addition of rice starch to white pepper will increase the potassium to calcium ratio. White pepper contains about 4 per cent. of piperine (2-trans-4-trans-N-piperoyl piperidine) which is responsible for its pungent taste; the addition of any adulterant will reduce the piperine content. In the current investigation therefore, a range of genuine and adulterated white pepper samples were examined for piperine content and potassium to calcium ratio, and on the basis of the results found a standard for white pepper is suggested.

Method

The samples examined consisted of black and white pepper (including samples from Sarawak, China and Brazil), rice starch, corn flours and mixtures of known white pepper content. The genuine samples of white pepper were from freshly ground pepper corns, and represented a significant proportion of the white pepper available in Australia. As pepper is grown in a limited number of countries, the white pepper available in Europe would be expected to have a similar composition to that available in Australia. The piperine content of the pepper samples was determined by high performance liquid chromatography

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(HPLC)[7] using a Lichrosorb RP-8 reversed phase column, 250 × 7 mm OD, 5 μm particle size, with a mobile phase composed of 345 ml water, 160 ml acetonitrile and 40 ml of tetrahydrofuran, and a flow rate of 2 ml/min; the detector wave-length was set at 345 nm. Piperine was extracted from the sample with boiling ethanol, and phenazine, as internal standard, was added to an aliquot of the ethanolic extract. The calcium and potassium contents of the samples were determined by atomic absorption spectroscopy (AAS) and flame photometry respectively, using the procedures described by Egan *et al.*[8] Samples (8 g) were ashed in platinum dishes at 600 °C and the residues were extracted with 5 N hydrochloric acid. These solutions were diluted to give suitable concentrations for AAS and flame photometry.

TABLE I

CALCIUM, POTASSIUM AND PIPERINE CONTENT OF WHITE PEPPER, STARCH AND WHITE PEPPER AND STARCH MIXTURES

Sample	Calcium *mg/kg*	Potassium *mg/kg*	K/Ca	Piperine *per cent.*
Genuine white pepper (10 samples) range:	1520–3000	340–860	0·19–0·44	3·64–4·35
Mean and standard deviation:	1980 ± 470	640 ± 170	0·33 ± 0·07	3·98 ± 0·28
Retail white pepper (15 samples) range:	1500–3000	510–900	0·27–0·44	3·72–4·46
Mean and standard deviation:	1890 ± 460	650 ± 140	0·35 ± 0·05	4·01 ± 0·23
Retail white pepper:				
Sample A	1440	750	0·52	3·13
Sample B	1750	770	0·44	3·17
Sample C	690	1630	2·36	0·55
White pepper & starch mixtures:				
10 per cent. maize starch	1500	680	0·45	3·81
20 per cent. maize starch	1380	640	0·46	3·31
30 per cent. maize starch	1250	640	0·51	2·92
50 per cent. maize starch	880	540	0·61	2·14
70 per cent. maize starch	560	480	0·84	1·32
10 per cent. rice starch	1500	790	0·53	3·67
20 per cent. rice starch	1130	890	0·68	3·33
30 per cent. rice starch	1130	930	0·82	2·88
50 per cent. rice starch	880	1130	1·29	2·12
70 per cent. rice starch	560	1260	2·24	1·28
Rice starch (5 samples) range:	30–60	1060–1800	18–45	0
Corn flour,* from maize or wheat (5 samples) range:	20–140	25–60	0·38–2·79	0
Corn flour,* from wheat, not gluten free (5 samples) range:	570–1150	240–250	0·21–0·44	0
Black pepper, genuine (10 samples) range:	15,400–20,800	4000–7200	2·79–3·85	4·33–5·28

* In contrast with U.K. practice, corn flour in New South Wales and other Australian States is defined (e.g. in the New South Wales Pure Food Act) as "starch powder derived from any variety of cereal grain". (Editor).

Results and discussion

The reproducibility of the HPLC method for the determination of piperine[7] was found by analysing ten separate samples of a genuine white pepper; the results had a mean value of 4·07 per cent. range 3·98–4·17, sandard deviation 0·085. The piperine, calcium and potassium contents of the samples examined are summarised in Table I. From the results found the following standard is proposed:

> Undried white pepper should contain not less than 3·5 per cent. of trans-trans piperine and the ratio of potassium to calcium should be not more than 0·45 on a weight basis.

The value of 3·5 was obtained by deducting twice the appropriate standard deviation from the corresponding mean values found for the genuine white pepper samples, and for the retail white pepper samples considered to be genuine, and rounding the mean of the two results, 3·485, to 3·5. The value of 0·45 proposed for the K/Ca ratio was selected to include all the values found for the genuine and retail samples which met the proposed standard for piperine content. The majority of retail samples of white pepper examined complied with this standard but two samples (Table I, retail samples A and B) were suspect and one sample (retail sample C) was grossly adulterated. Mixtures of white pepper and increasing percentages of rice starch show a gradual decrease in piperine content and an increase in the potassium to calcium ratio. All of these mixtures failed to comply with the proposed standard. Similar mixtures with maize starch also showed a decrease in piperine content but there was a less rapid increase in the potassium to calcium ratio; the sample with 10 per cent. added maize starch would comply with the proposed standard but microscopic examination of the sample, stained with iodine, showed the maize starch as conspicuously larger starch grains when compared with genuine white pepper. The standard is not applicable to black pepper which contains much higher concentrations of both potassium and calcium, and also a slightly higher content of piperine. The analysis of similar mixtures of starches with black pepper, not reported here, showed a decrease in piperine content but no useful alteration in the potassium to calcium ratio.

Acknowledgement

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Qualitative Analysis of Synthetic Colourings in Food

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Synthetic colourings may be extracted from aqueous or readily soluble foods using a SEP-PAK(R) sample preparation cartridge or from more complex foods using a liquid anion exchange solution in butanol. In both cases, permitted synthetic food colourings may be tentatively identified by thin-layer chromatography. Natural colourings did not cause interference in the extraction or identification stages. The method is suitable for rapid screening of foods for quality control purposes.

There are a number of methods available for the extraction and identification of synthetic colourings in foods. The qualitative extraction methods include wool-dyeing[1], polyamide powder[2], ion-pair extraction[3] and the use of a liquid anion exchange resin[4]. Synthetic colourings may be extracted directly from simple confectionery products using a reversed-phase sample preparation cartridge (SEP-PAK, C_{18})[5].

The extracted colourings may be identified by paper chromatography (PC)[1], thin layer chromatography (TLC)[2], high performance liquid chromatography (HPLC)[6], and visible absorption spectrophotometry[7].

The wool-dyeing method is generally the method of choice for extracting synthetic colourings from foods prior to identification by TLC. Whilst this is a fairly rapid method for readily soluble foods, soft drinks and sugar confectionery, it is not generally applicable to more complex foods such as meat products and baked goods unless the sample has been pre-treated to remove fats and starches. The method also involves heating the dyes in alkaline solution in order to concentrate the extract and these conditions have been shown to cause severe losses of Indigo Carmine[5].

A method has been proposed in which the colourings are extracted with a liquid anion-exchange resin dissolved in butanol and then back-extracted from the resin into dilute aqueous ammonia[6]. The extracted dyes are then purified and concentrated by column chromatography using polyamide as stationary phase[6]. This method is rather time-consuming, particularly with the latter purification stage, but it was proposed for the quantitative measurement of synthetic colourings in foods prior to HPLC and provided high recovery of colourings with good reproducibility.

In this work a modified version of the liquid anion exchange resin extraction method is proposed. This includes replacing the time-consuming column chromatography purification stage by concentrating the extract with a sample preparation cartridge. The sample preparation cartridge additionally offers a

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rapid and direct means of extracting synthetic colourings from liquid or readily-soluble foods prior to identification by TLC. These methods have been applied to a wide range of foods and observations made on the effect of the presence of natural colourings in conjunction with synthetic colourings. The proposed method provides a rapid screening method for quality control or survey purposes.

Reagents

Use analytical grade reagents.

1. SEP-PAK C_{18} sample preparation cartridge (Waters Associates Ltd).
2. Standard dye solutions, 0·1 per cent. m/v aqueous solutions of food grade colourings (Williams of Hounslow Ltd).
3. Natural colourings: Beetroot Red (Roche Products Ltd), Anthocyanin (Roche Products Ltd), Chlorophyll (Bush Boake Allen), Carotenoids (Roche Products Ltd).
4. Ammonia (S.G. 0·88).
5. Dilute ammonia. 10 per cent. v/v aqueous dilution of ammonia (S.G. 0·88).
6. Methanol.
7. Absolute ethanol.
8. Diethyl ether.
9. Heptane.
10. Hydrochloric acid, 2 M.
11. Anion exchange resin solution. 20 ml of Amberlite LA-2 (BDH Ltd) is thoroughly mixed with 380 ml of *n*-butanol. The solution is vigorously shaken with 160 ml of distilled water and 8 ml of concentrated hydrochloric acid in a 1 litre separating funnel. The lower aqueous phase is separated and discarded.
12. Sand, acid-washed GPR 40–100 mesh (approx.) (BDH Ltd).
13. Mobile phase for use with cellulose plates. Dissolve 2 g of trisodium citrate in 85 ml of distilled water and 15 ml of ammonia (S.G. 0·88). This solution should be prepared fresh immediately before use.
14. Mobile phase for use with silica plates. Prepare a solution containing *iso*propanol, ammonia (S.G. 0·88) and distilled water in the ratio 7 : 2 : 1.

Apparatus

1. Cellulose TLC plates. Glass size 20 × 20 cm spread to a uniform thickness of 250 μm from a slurry prepared by blending 15 g of cellulose (Mikrokristallin, Avicel (R) Merck) with 50 ml of distilled water.
2. Silica TLC plates. Glass size 20 × 20 cm spread to a thickness of 100 μm from a slurry prepared by blending 25 g of silica (Kieselgel 60G, Merck) with 50 ml of distilled water. Both sets of plates are allowed to dry at room temperature and are then activated before use in a fan-assisted oven at 100 °C (±2 °C) for 2 h. Once activated the plates are cooled to room temperature in a desiccator cabinet.
3. Chromatography tanks, lined with blotting paper soaked in mobile phase, with close fitting lids.

4. Syringe. 10 ml volume with Luer fitting and ground glass plunger.
5. Micropipettes. 5 μl disposable.

Procedure

(I) EXTRACTION OF SYNTHETIC COLOURINGS FROM AQUEOUS OR READILY-SOLUBLE FOODS

Dissolve 10 g of food in 90 ml of water, warming if necessary, or use 10 ml of aqueous sample. Determine the pH of the solution and if necessary adjust the pH to 2·5 with 2 M HCl. Affix the longer stem of a SEP-PAK C_{18} sample preparation cartridge to the syringe barrel and pass 10 ml of methanol through the cartridge from the syringe. Pour about 10 ml of aqueous food sample into the barrel, insert the plunger into the barrel and by holding the syringe in a vertical position squeeze the air out of the syringe and through the cartridge. Continue to pass solution through the cartridge and discard the clear eluent. Remove the syringe plunger and wash the retained colouring with two successive 10 ml aliquots of warm distilled water acidified with a few drops of 2 M HCl, by passing them through the cartridge as described above. The water wash removes sugars, flavourings, fruit acids, and other polar compounds. The colourings can then rapidly be eluted as a concentrated band by passing a solution of methanol containing a few drops of 10 per cent. aqueous ammonia through the cartridge. Again, to elute the colourings as a sharp concentrated band, it is necessary to remove air from the syringe by holding the syringe in a vertical position and depressing the plunger before eluting the adsorbed colourings. If the methanol extract appears to be cloudy, add a few drops of 2 M hydrochloric acid to re-dissolve the colourings. The purified extract can then be identified by TLC. The cartridge can be used again by re-priming with methanol but should be discarded if traces of colourings remain adsorbed.

The SEP-PAK method can be used for extracting colourings from soft drinks, boiled sweets, confectionery containing surface colouring, clear sauces, mouth wash etc.

(II) EXTRACTION OF SYNTHETIC COLOURINGS FROM INSOLUBLE AND NON-HOMOGENEOUS FOODS

Grind 10 g of sample in a pestle and mortar with 20 g of sand and approximately 5 ml of distilled water containing 1 ml of 2 M hydrochloric acid to form a homogeneous mass. Transfer the mass to a beaker and mix thoroughly with 30 ml of resin-in-butanol solution.

Allow solid material to settle and decant the resin solution through a plug of glass wool into a 250 ml separating funnel. Add 25 ml of 10 per cent. ammonia solution to the separating funnel and extract the colourings into the ammonia solution from the resin layer by vigorous inversion of the funnel. Emulsions are dispersed by careful addition of a few drops of absolute ethanol to the interface (pour ethanol down a glass rod). If there is little colour extracted into the aqueous ammonia, add 50 ml of heptane and shake again. Separate the ammonia solution and discard the butanol layer. Rinse the separating funnel with diethyl ether and discard the ether. Return the ammonia solution to the

separating funnel and wash the solution with two successive 10 cm^3 portions of diethyl ether to remove residual butanol. Separate the ammonia layer and remove excess ammonia and ether by gently warming under a stream of air or nitrogen. Cool the solution and acidify the extract to pH 3·0 with hydrochloric acid. Concentrate the extracted colours using a SEP-PAK cartridge as described in (I) above.

(III) TENTATIVE IDENTIFICATION OF COLOURINGS

Compare the Rf values of the extracted synthetic colourings with suitable standards by TLC using a stationary phase of cellulose and a mobile phase of tri-sodium citrate, water and ammonia (S.G. 0·88) (2 g : 85 ml : 15 ml). An alternative and more effective resolving system for blue and green synthetic colourings requires a stationary phase of silica and a mobile phase of *iso*-propanol : ammonia (S.G. 0·88) : water (7 : 2 : 1).

TABLE I

CURRENT STATUS OF PERMITTED SYNTHETIC FOOD COLOURINGS[8]

Synthetic colouring	EEC serial number	Colour index (1971) number
Tartrazine	E102	19140
Quinoline Yellow	E104	47005
Yellow 2G	107	18965
Sunset Yellow FCF	E110	15985
Carmoisine	E122	14720
Amaranth	E123	16185
Ponceau 4R	E124	16255
Erythrosine	E127	45430
Red 2G	128	18050
Patent Blue V	E131	42051
Indigo Carmine	E132	73015
Brilliant Blue FCF	133	42090
Green S	E142	44090
Black PN	E151	28440
Brown FK	154	—
Chocolate Brown HT	155	20285

Results and Discussion

The SEP-PAK method proved a very effective and rapid way of extracting and concentrating synthetic colourings from aqueous or readily-soluble foods. The method is also suitable for extracting synthetic colourings from complex matrices, e.g., surface coloured confectionery and iced biscuits provided that insoluble material is removed before passing the extract through the cartridge. All of the synthetic colourings were adsorbed on the cartridge provided that the pH of the extract was below 3·0. Black PN was found to have a slightly lower affinity for the reversed phase packing. Caramel leaves residues permanently adsorbed in the cartridge and it is essential that liquorice or toffee should be separated from samples before extracting the synthetic colourings. The SEP-PAK cartridges are re-usable provided that residual colour is removed by

TABLE II

Rf VALUES OF SYNTHETIC FOOD COLOURINGS USING A CELLULOSE STATIONARY PHASE AND A MOBILE PHASE OF TRI-SODIUM CITRATE (2 g) WATER (85 ml) AND AMMONIA (S.G. 0·88, 15 ml)

Food colouring	Rf value
Ponceau 4R	0·72
Red 2G	0·63
Amaranth	0·52
Carmoisine	0·21
Erythrosine	0·07
Yellow 2G	0·90
Tartrazine	0·83
Sunset Yellow FCF	0·62
Quinoline Yellow	0·29
Green S	0·93
Patent Blue V	0·97
Brilliant Blue FCF	0·88
Black PN	0·27*
Indigo Carmine	0·21*
Brown FK	0·30*
Chocolate Brown HT	0·59*

* Colours streaked, migration distance taken at the leading edge.

TABLE III

Rf VALUES OF BLUE/GREEN TRIARYLMETHANE DYES USING A SILICA STATIONARY PHASE AND A MOBILE PHASE OF ISO-PROPANOL: AMMONIA (S.G. 0·88): WATER (7 : 2 : 1)

Food colouring	Rf value
Brilliant Blue FCF	0·72
Patent Blue V	0·51
Green S	0·44

passing methanol containing a few drops of 10 per cent. aqueous ammonia solution through the cartridge.

It was found that the TLC system using cellulose plates and a mobile phase of tri-sodium citrate (2 g) water (85 ml) and ammonia (S.G. 0·88, 15 ml) was the most effective method for resolving almost all of the permitted synthetic food colourings (Table I). The Rf values were found to be readily reproducible provided that fresh mobile phase was used (Table II). Black PN and Indigo Carmine both produce a streak and have a low rate of migration. Brown FK and Chocolate Brown HT also streak heavily but migrate further. Caramel also streaks heavily but with the leading edge running with the solvent front.

The blue/green triarylmethane colourings, Green S, Brilliant Blue FCF and Patent Blue V have similar Rf values as determined using the cellulose TLC system but these colourings are readily resolved using the silica TLC system described. The Rf values for these three colourings are given in Table III.

The anion-exchange resin method has been successfully applied to a wide range of non-homogeneous foods as described in Table IV. The foods should be ground finely with the sand to ensure effective extraction of the colouring. Previous workers have used Celite as an extender but our investigations with

TABLE IV

APPLICATION OF THE ANION-EXCHANGE RESIN EXTRACTION METHOD TO FOOD SAMPLES

Sample and declared colourings	Rf values and description of separated components	Tentative identification	Observations
Mint Sauce	*On cellulose adsorbent*		Good colour uptake by the resin in butanol. Shaking the extracted solution with aqueous ammonia resulted in the formation of a pale yellow colour in the ammonia layer, whilst the resin layer remained green. Addition of heptane did not enhance movement of colour from the resin to the ammonia layer. Extract readily concentrated and eluted from SEP-PAK column.
Tartrazine	Yellow spot 0·83	Tartrazine	
	Blue spot 0·86	Unidentified on cellulose	
Green S	*On silica adsorbent*		
	Yellow spot 0·64	Unidentified on silica	
	Blue spot 0·44	Green S	
Jam filled swiss roll	*On cellulose adsorbent*		There appeared to be little uptake of colour from the sample to the resin in butanol layer. However, addition of aqueous ammonia resulted in successful back-extraction of any colour present in the resin phase. The extract was easily concentrated and the collected eluent was red/brown colour.
Tartrazine	Yellow spot 0·81	Tartrazine	
Sunset Yellow FCF	Orange line 0·60	Sunset Yellow FCF	
Amaranth	Pink spot 0·52	Amaranth	

model systems of aqueous solutions showed that a number of synthetic colourings, particularly the triarylmethane group, are strongly adsorbed on Celite even in the presence of the anion-exchange resin.

Comminuted meat products, e.g. salami, beefburgers, and meat and fish pastes were the most difficult samples to analyse because of their tendency to form stable emulsions when extracting the colourings from the resin-in-butanol solution to the aqueous ammonia solution. Partial emulsions can be dispersed by adding a few drops of absolute ethanol to the interface of the extracting solutions and agitating with a glass rod, but more stable emulsions may have to be "broken" by centrifuging. Some of the comminuted samples can be trimmed of visible fat which reduces the tendency to emulsify. For more homogeneous comminutes it is advisable to defat the sample by macerating it with sand followed by repeated extractions with chloroform before adding the resin-in-butanol.

TABLE IV — *continued*

Sample and declared colourings	Rf values and description of separated components	Tentative identification	Observations
Creamed rice pudding	*On cellulose adsorbent*		It was difficult to observe the colour uptake by the resin in butanol, but good back-extraction of yellow dye into the ammonia phase confirmed that the dye had been extracted from the sample. The extract was easily concentrated on the SEP-PAK cartridge.
Tartrazine	Yellow spot 0·83	Tartrazine	
Carotene			
Red wine (spiked sample)	*On cellulose adsorbent*		Good colour uptake by the resin in butanol. Some colour was extracted into the aqueous ammonia solution, but the majority remained in the butanol layer. Sufficient colour was extracted into the aqueous ammonia solution to allow concentration and examination on TLC.
	Dark red spot 0·52	Amaranth	
Amaranth	Very faint grey 0·82	Unidentified	

To maximise recovery of red synthetic colourings, it was necessary to add heptane to the resin-in-butanol solution before extracting with aqueous ammonia. Amaranth and Erythrosine were the most difficult to back-extract in the absence of heptane.

Recent adverse publicity has prompted a number of food manufacturers to replace synthetic with natural colourings or to use these forms in conjunction. Possible interference in this method by the main classes of natural colourings—Chlorophyll (E140), Anthocyanins (E163), Beetroot Red (E162), and Carotenoids (E160 (a–f)) was determined using model systems and also "spiking" suitable samples. Generally, the presence of natural colourings did not pose a problem to the extraction and tentative identification of synthetic colourings even when the natural colourings were present in relatively high concentrations (450 p.p.m.). Chlorophyll was generally retained in the resin-in-butanol solution and also highly retained by the SEP-PAK cartridge. Where some back-extraction at higher concentrations was found there was very little migration of chlorophyll using the cellulose or silica TLC systems. Green S and Tartrazine were readily identified in a sample of mint sauce and a sample of processed peas. Anthocyanin was partially back-extracted into the aqueous ammonia with a change in colour from red to blue and an apparent decrease in colour intensity. The Anthocyanin extracted was also highly retained on the SEP-PAK and did

not hinder elution of synthetic colourings. Dilute acidified aqueous solutions of Anthocyanin when applied directly to the TLC plates and developed showed very little migration in either system (Rf value 0·10–0·16). Amaranth was readily detected in a sample of "spiked" red wine. Aqueous extracts of Beetroot Red were not extracted into the resin-in-butanol solution and did not appear to hinder extraction of the synthetic colourings. Beetroot Red was adsorbed and desorbed from the SEP-PAK cartridge but has a low rate of migration in the TLC systems. Also in alkaline solution the red/blue betacyanins are converted to the yellow betaxanthin pigment. Carotenoid pigments were extracted by the resin-in-butanol solution but not back-extracted even in the presence of heptane. Again, when applied directly to TLC plates there was very little migration of the colouring. Where the presence of carotenoid pigments is suspected in readily soluble foods or soft drinks some preliminary extraction may be necessary to prevent the colloidal pigments blocking the SEP-PAK cartridge.

If butanol remains in the aqueous extract, it reduces the retention of the synthetic colourings on the reversed-phase of the SEP-PAK causing losses during the washing stage. Therefore, after extracting the synthetic colourings from the resin-in-butanol solution into aqueous ammonia, traces of butanol are removed by shaking with diethyl ether.

Conclusions

Synthetic colourings may be extracted from a wide variety of foods using a liquid anion-exchange resin in butanol, back-extracting the colouring into aqueous ammonia and concentrating the extract using a reversed-phase sample preparation cartridge. Aqueous foods and readily soluble foods may be analysed directly using the cartridge. The synthetic colourings currently permitted may be tentatively identified from their Rf values using TLC. Natural colourings in the food did not interfere in the extraction stage nor mask the presence of synthetic colourings on TLC plates. The method provides a rapid means of screening foods for synthetic colourings by relatively unskilled personnel and is suitable for quality control purposes.

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Book Reviews

THE ANALYSIS OF AGRICULTURAL MATERIALS. MAFF/ADAS Reference Book 427. HMSO, 1986. 248 pp. ISBN 0 11 242782 6. Price: £13·00.

This is the third edition of this book first published in 1974 as Technical Bulletin No. 27. It could be described as a "Cook Book" giving 74 analytical procedures on a variety of agricultural materials together with the essential methods for preparing soil and plant materials for analysis and procedures for preparing sample solutions of plant material by wet and dry digestion. The number of individual methods included has been reduced from the previous edition but this is due to the combination of certain methods, such as available metals in soil, and the number of parameters covered has increased. There have been some changes in the methods used notably the use of a single extractant to determine extractable metals in soil.

The foreword to the book indicates that the aim is to provide organisations involved in agricultural analyses with a standard reference book of methods, and this aim is met. However, the choice of parameters to include does appear a little eccentric and one must assume this choice reflects the parameters of most importance for advisory purposes. Many of the methods are designed to assess the nutrients, essential trace elements, toxic metals and phytotoxic metals in soils together with other soil parameters essential for advising farmers or horticulturalists on the status of their ground. A second group of methods provides for the determination of the major plant nutrients and essential trace elements, together with potentially toxic and phytotoxic metals, in plant material itself. The methods for plant material are, in general, also applicable to feeding stuffs. A limited number of methods for the analysis of milk, water, and feeding stuffs are given together with methods for the examination of silage and the determination of the thousand-grain weight of cereals.

There is a warning given in the introductory section that "whilst the methods described are satisfactory for normal advisory purposes, analyses for statutory purposes must be carried out by the appropriate official methods". This is of particular importance to Agricultural Analysts. A number of parameters given are the subjects of statutory methods, in fertiliser and animal feeding stuffs legislation, and the statutory methods generally differ from those in the review book. A number of other parameters are covered by British Standard methods, and again the two differ. Whilst it is clear that the ADAS methods are generally simpler, and therefore more convenient for use in a busy laboratory, there would appear to be some logic in incorporating standard methods where these are available, particularly with the increasing emphasis on quality assurance and the use of validated methods.

An additional warning is given that methods for soil are applicable to normal

agricultural and horticultural soils but not necessarily to peats, composts etc. Private communications have indicated that ADAS do not use the given methods for the analysis of loamless composts and that the methods actually used give rise to somewhat different results. As some methods are partly empirical in nature it would be valuable to all analysts in the field if these variations were included in the next edition of the manual or possibly published as a supplement (for which there are precedents).

Many analysts will find the choice of methods in some cases to be unexpected. Atomic absorption spectrophotometry is the method used for hardness in water, a determination readily carried out by volumetric procedures. In contrast, iron in plant material is determined colorimetrically rather than using atomic absorption. A number of the methods require a volume of sample to be taken using a scoop rather than a fixed weight. While this appears to be carried out because volume is more appropriate than weight in the field, the errors involved in measuring the sample aliquot will be relatively high and determinations by weight would be preferred by many.

Though this publication contains a number of idiosyncracies it does provide a good source of tested standard methods. It should be on the bookshelf of all analysts involved in the analysis of agricultural materials and is essential reading for all giving advice to farmers or gardeners.

P. SMITH

PRACTICAL EXPERIMENTAL DESIGNS AND OPTIMISATION METHODS FOR CHEMISTS. By C. K. BAYNE and I. B. RUBIN. VCH Weinheim, 1986. 205 pp. Price: DM 110 (£47).

The purpose of this book is to enable chemists to design their experiments, based on a knowledge of statistics, rather than only using such knowledge after the experiments have been completed. The authors claim that only an elementary background in probability and statistics should be needed.

Any attempt by statisticians to meet the needs of chemists is to be welcomed, but to take advantage of this book, the chemist must be prepared to make the effort to understand the language of the statistician. To this end the book includes a useful section on analysing experimental results, together with a few worked examples.

Parameters such as average, variance and standard deviation are called "estimators", and formulae are given showing that these "estimators" themselves are subject to variation, each having its own standard deviation, and in some instances, bias. In calculating the precision of an "estimator" derived from two sets of variables, e.g. the weights of a substance and the results of titrations, guidance is given as how to use co-variance in the calculations.

With regard to the use of mathematical "language", it may be noted that the capital E is occasionally used as a sum symbol instead of the customary sigma, Σ, and it is also used to indicate an exponent. It can be disconcerting to the chemist to read that the calculated variance estimate is 2.438E-3, unless he realises that this is a way of expressing 2.438×10^{-3} or 0.002438

The major part of the book gives details of procedures for designing

sequential experiments necessary to find optimum instrument settings etc. that maximise or minimise chemical measurements. The two procedures where one or more than one factor is varied at a time, the "steepest ascent" and "simplex optimisation" methods, are described. A bibliography of these techniques is also included.

Since optimisation procedures can involve up to fifty or more separate determinations, they are stated to be only practicable if each can be carried out in a relatively short period of time. An experiment with a small experimental error will require less determinations than one based on a response with a larger error. These procedures, therefore, are likely to be of interest to chemists developing new methods rather than to analysts carrying out routine determinations.

Optimisation as described in the book relates to experimental design to achieve the most desirable results, and this should be the aim of all practising analytical chemists. It is, however, beyond the scope of the book to apply statistical considerations to the use of chemical methods so as to minimise experimental error, an optimising technique which is very necessary for analysts to consider.

H. M. Bee