Volume 27 Part 2 June 1989

JOURNAL

OF THE

ASSOCIATION OF PUBLIC ANALYSTS

Annual Report of the Council of the Association of Public Analysts for 1988

Presented at the Annual General meeting of the Association at Oxford on 15th April 1989 by the Honorary Secretary, Mr. M. Barnett.

This report reviews the activities of the Association of Public Analysts during the year ending December 31st 1988 and also discusses its future aspirations.

Some forty Public Analysts Laboratories are situated throughout the United Kingdom, and members' laboratories exist in Eire and Australia. These laboratories continue to provide the sharp edge of the scientific enforcement of a major part of statutory and other investigational activities relating to Food, the Environment, Toxicology, Consumer Protection, Occupational Hygiene and Agricultural Materials. In addition, many of our laboratories provide scientific advice including quality monitoring activities in connection with the production of a wide range of products, especially foodstuffs.

Members of these laboratories work with Local Authorities, Central Government, the European Community, the Royal Society of Chemistry, the British Standards Institute (BSI) and the National Measurement Accreditation Service (NAMAS), as scientific advisors, committee members and participants in collaborative trials.

In particular, part of these representations has been addressed to the formulation of a viable state of readiness for the anticipated Completion of the Internal Market in 1992.

A summary of the statistics of samples analysed is given in the Appendix to this report.

The Local Government Act 1985

The Local Government Act 1985 led to the abolition of the Greater London Council and the Metropolitan County Councils in England. These areas were previously served by Public Analysts Laboratories and it is useful to record, three years on, the impact that this reorganisation has had on the laboratory service. District councils within the county boundaries became the appropriate authorities responsible for the appointment of Public Analysts. In some parts, the original laboratory still serves all the district councils corresponding to the previous county. In others geographically adjacent district councils have appointed different Public Analysts and their laboratories.

It must also be recorded that some local authorities increasingly use so called

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screening tests. These tests are carried out away from the official laboratory. Since they are not carried out under the supervision of the Public Analyst, the tests are not validated and contribute nothing to legal enforcement activities. Moreover, the diversion of resources to screening tests reduces funding which is vitally necessary to officially appointed laboratories.

Sub-committee Activities and Other Issues

The Association of Public Analysts has an active committee and sub-committee structure, the members of each sub-committee having had significant experience in their subject area.

Meat and Fish Products

The composition and labelling of meat and fish products continues to provide numerous challenges for the Public Analyst as they seek to protect the consumer. Minced meat is frequently sold with some qualifying description such as "Economy", "Lean", "Extra Lean" and "Low Fat". Public analysts are concerned that, often, such descriptions do not reflect the actual quality of the food. In fact a chaotic situation exists and so renewed efforts were made to seek specific regulations. Mechanically recovered meat (MRM) is held to be a proper ingredient for meat products but questions of whether the presence of MRM should be declared in the food name or list of ingredients or whether it should count towards the product's legal meat content are still largely unresolved. Analytical techniques for measuring MRM content are being investigated. Proposals from the Ministry of Agriculture Fisheries and Food (MAFF) for fish product regulations were a major issue for our members. Members of this Association participated in trials on methods for determining ice glaze on frozen fish but are greatly dismayed that the proposal for controlling such products under Weights and Measures legislation sweeps aside issues such as added water within the fish. The main proposal for other fish products is that they should be labelled with a declaration of minimum fish content, and this proposal is welcomed, but the present draft was judged to be deficient in that inadequate attention was given to any offence where the composition did not match the declaration. Emphasis on labelling to the virtual exclusion of whether or not that labelling is accurate is no protection for consumers.

Milk and Dairy Products

PROPOSED LEGISLATION, ETC. ON WHICH COMMENTS HAVE BEEN MADE

A code of practice on hygenic production of sheep milk to include: proposals for regulations to amend and consolidate the Milk and Dairies (Semi-Skimmed and Skimmed Milk) (Heat Treatment and Labelling) Regulations 1986; Importation of Milk Act 1983, proposals for revised Importation of Milk Regulations; and the Milks (Special Designation) Regulations 1988, proposals for revised regulations on heat treated milk.

OTHER MATTERS AND ACTIVITIES

The Chairman of this sub-committee attended numerous meetings with

MAFF, the Milk Marketing Board (MMB), the Department of Trade and Industry (DTI), the Public Health Laboratory Service (PHLS), the National Farmers Union (NFU) and the Institute of Environmental Health Officers (IEHO). The purpose of these meetings was to consider Directive 85/397/EEC on Health and Animal Health problems affecting Intra-community trade in heat-treated milk and to seek agreed guidelines for the sampling and testing of pasteurised milks for enforcement purposes. These guidelines were due to be published in February or March 1989 under the imprimaturs of this Association, IEHO, PHLS, MMB, DTI and NFU but, for technical reasons, not MAFF.

The opportunity to extend and consolidate the role of Association members in the examination of food quality by asserting that the bacteriological analysis of foods is essentially aimed at assessment of the quality of those foods has been in the forefront of the APA representative's thinking on this matter. It is crucial that the opportunities now likely to be present are seized and that the Association fully supports the efforts already made in this area.

It is noteworthy that the Milk (Special Designation) Regulations 1988, adopt, apparently for the first time in Regulations made by the Minister of Agriculture, British Standard Methods of bacteriological analysis. Certainly, as a result of the earlier negotiations with MAFF, the opportunity was taken to submit to MAFF details of the other Regulations, made by DTI, calling up British Standards for which APA representatives have had some responsibility. Furthermore, the sub-committee Chairman's laboratory was involved in ring trialling the bacteriological methods required to be used when analysing heat treated milk.

In the circumstances, the continuing activity by the APA on relevant BSI Committees, especially DAC/3 and DAC/4, the latter coming under the auspices of the Microbiology Sub-committee, is perceived as crucial to long term activities of the Association members.

Drafts of the Commission Directive on sampling and methods for the analysis of raw and heat treated milk have been received, and much time taken in assessing these methods and their likely impact upon the work of Public Analysts. Although so much effort had been expended, it came as a great disappointment in November to receive the reasons why MAFF would not specify that Public Analysts were the proper officials to carry out analyses of imported milks. The Association's view was that without proper control of qualifications, and also indemnifications, the public and traders alike would not be properly protected.

MAFF again became interested in the over-run of Ice Cream. The APA reconsidered its official view, last expressed in 1956, and advised that ice-Cream should now be sold by weight, but with control by means of a solids per unit volume limit.

Microbiology

1. COMMUNITY TRADE IN MINCE MEAT

The draft directive which started life as COM (87) 658 was commented upon for the second time. It was gratifying to see our initial comments have on this occasion borne fruit.

The Directive was published in O.J. 6382/15 on 31 December 1988.

2. NATURAL MINERAL WATERS

i. The second draft of the Guidelines for the Recognition and Exploitation of Natural Mineral Waters was discussed at a meeting chaired by MAFF in April 1988. Nothing has been heard since.
ii. A collaborative trial on the estimation of the total viable colony count in Natural Mineral Waters was under taken in May 1988. The results are awaited with interest.

3. INTRA-COMMUNITY TRIALS IN HEAT-TREATED MILK

The first draft of the chemical and microbiological methods required for the implementation of Directive 85/397/EEC on Health and Animal Health Problems Affecting Intra-community Trade in Heat Treated Milk was scrutinised and commented on by the committee and the Milk and Dairies Sub-committee in April 1988. Following this, a meeting in October of interested parties (Trade and Enforcement), under the Chairmanship of MAFF, discussed the collated UK comments.

It was disappointing to see that the second draft of the methods, issued in December 1988, ignored all comments other than those of an editorial nature.

4. CURRENT INTERESTS

i. BS 4285 concerning Microbiological Examination for Dairy Purposes is under review.
ii. The European Suspension Test, first brought to the sub-committee's attention in 1987, has now been issued under the BSI imprimatur as DD 177: 1988 (Draft for Development: Method of test for the anti-microbial activity of disinfectants in food hygiene).
iii. A third collaborative trial on the Natural Mineral Water Methods, this time on *Pseudomonas aeruginosa*, is in preparation.

Food Labelling

Food is labelled in order to relate information. In recent years the public awareness of modern food production technology has resulted in the spotlight of the media turning to the use of food additives, and the response by a number of food producers has been to adorn labels with words such as "natural", "traditional" and "country-style". Analysis continues to play a vital role in examining such claims. However, no amount of label reading in isolation from scientific examination of a food can result in an investigation of value. For example, kippers described as containing no artificial colours were in fact found to contain a colouring agent derived from plant material, this being completely artificial to the herring and to any smoking process.

Yet another phenomenon to greet the consumer is the use of two or more descriptions to describe one product. Usually one of the descriptions is accurate, whilst the other may be false or misleading. A recent court case appeared to suggest that such a practice is acceptable. How the purchaser can decide between such descriptions remains a mystery.

The Association's labelling sub-committee has dealt with the following issues during the year.

1. A proposed directive on foods for particular nutritional uses.
2. Nutrition claims in the advertising and labelling of food.
3. EEC proposals for a directive on Compulsory Nutrition Labelling
4. EEC proposals for a directive on Nutrition Labelling Rules.
5. "Real Fruit" Gums.
6. Champagne flavoured chocolate.
7. Extra lean mince.
8. Declaration of added salt, sugar, etc.
9. Labelling of four alcoholic beverages.

Water

Public Analysts have extensive experience and expertise in the examination of water in all of its forms. Such capability and capacity will be available and ought to be utilised within the new regulatory systems to control both the quality and safety of drinking water and the prevention of pollution of surface watercourses.

During the course of the year, initial appointments were made to the new National Rivers Authority to be responsible for enforcing pollution control legislation. The Association anticipates that this organisation will appreciate the value of the national network of Public Analysts Laboratories for the provision of independent high quality forensic data and will avoid the unnecessary, and highly expensive, duplication of scientific enforcement facilities.

Public concern with respect to the safety and quality of drinking water resulted in a significant increase in the demands for independent tests and advice. In common with our Environmental Health colleagues, the Association takes the view that water undertakings must be subjected to a rigorous system of statutory compliance monitoring by the Local Authorities. Any system based largely on self-regulation, as may shortly be implemented, is unlikely to provide sufficient public reassurance. Relatively little financial stimulus to an existing and proven framework would produce a dramatically improved enforcement service, consistent with the aims and intentions of the European legislators.

Many Public Analysts have also become increasingly involved in testing and consultancy services to local authorities, designing essential maintenance treatment and monitoring systems to prevent Legionnaires Disease, etc. in public buildings.

Occupational Hygiene

The growing importance of the practical aspects of compliance with the Health and Safety at Work Act is demonstrated by the involvement of Public Analysts in the provision of testing and consultancy services. Asbestos management, lead exposure, solvent fumes, sick building syndrome investigations, Legionnaires Disease prevention and lighting adequacy are just a few of the areas of involvement.

The requirements for scientific services will increase further with the implementation of the Control of Substances Hazardous to Health Regulations. Many County Councils have already established scientifically directed central control groups to implement requirements to protect their staff. Public Analysts, many of whom employ staff with additional qualifications in

occupational hygiene, are able not only to carry out monitoring and analytical investigations, but also to provide a comprehensive occupational hazards assessment service.

Consumer Hazards

PROPOSED LEGISLATION, ETC ON WHICH COMMENTS HAVE BEEN MADE

The Furniture and Furnishings (Fire) (Safety) Regulations 1988;

The Ceramic Ware (Safety) Regulations 1988.

Review of the Cosmetics Directive, paper commissioned from Professor Molle.

LEGISLATION, ETC. NOTED

During 1988, the DTI approved standards mentioned in Notices 1 and 2 issued in February and August. In all, some 29 standards were approved of which APA involvement was instrumental in BS 6748. Thirty-nine standards are under consideration for approval and, of these, 14 have or are being produced under the responsibility of standards committees on which APA is represented.

OTHER MATTERS AND ACTIVITIES

The Vice-Chairman of this sub-committee, in his capacity as UK/BSI representative on the Toy Safety Committee (TC52) of the European Committee for Standardisation (CEN), has continued to play an active role in the process for the adoption of EN71, parts 1, 2 and 3. This will form the basis of BS5665: 1989, which will replace the withdrawn BS5665: 1987. Meanwhile, BS5665: 1978 and 1979 remain current, despite all of which the International Standards Organisation (ISO) have circulated ISO/DID 8124, parts 1, 2 and 3—Draft for the Safety of Toys—which largely duplicates the work of CEN in the revision and adoption of EN71.

Controversial standards for metals release are, however, likely to be difficult to enforce unless the unsatisfactory results of a preliminary collaborative trial of a simulated stomach-acid leach test can be dramatically improved.

In April 1988, BSI set up a Committee (FHM/47) to examine standards for materials in contact with foods and, in view of the perceived burden of work, established two working parties, of which FHM/47/1 deals with extraction of plastics materials by foods and food simulants and FHM/47/2 is concerned with evaluation of heavy metals leached from painted and plastics surfaces. The APA representative on both working parties has been the Chairman, whose laboratory method for fat component analysis using HPLC appropriate when testing plastics with olive oil, and whose protocol for a ring trial of his method for evaluation of heavy metal release from painted surfaces, emulating the BS 6748 method which he and Dr Rix of the Laboratory of the Government Chemist (LGC) had produced, have contributed to the work of the committee.

Together, with a representative from the LGC, our Association represented the UK at the 30th meeting of the Methods of Chemical Analysis Group for Cosmetics in Brussels, 25 and 26 January 1988, and reports were presented of the LGC organised trials of methods of analysis for colouring agents, insolubility

of pigment lakes, identification of benzyl alcohol, determination of 6-methylcoumarin, of selenium disulphide and of zirconium, aluminium and chloride in complexes.

BSI Membership

The APA is now represented on two of the BSI standards committees whose work impinges directly upon consumer safety—TCM/- and FHM/-.

The work programmes of these standards committees extended to 112 and 27 pages of tabulated data, respectively. In particular the APA is actively represented on committees concerned with glazed ceramics and vitreous enamel ware (FHM/12), also ceramic ware (FHM/29), babies' dummies (FHM/42), materials in contact with food (FHM/47), toys (TCM/15) and fibre mixtures, particularly lambs' wool in mixed wool (TCM/21).

Scheduled quinquennial revisions of many standards are overdue and the need to revise, and then trial, existing methods of test to afford standards with established repeatability and reproducibility of test procedures, as well as the need to devise the trial of novel methods, introduces massive work loads, all, subject to the exception reviewed in BSI paper 88/00031, unfunded.

If the Government wants sound standards to be taken into Europe by BSI as the basis upon which CEN and CENELEC can adopt fair and effective standards to protect consumers, and ethical traders alike, the cost of essential work must be appropriately funded. Otherwise, "DIN" will "WIN" and "BSI" will hardly have had a chance to "TRY" to win the standards race into Europe.

Environment

The environment sub-committee has again been particularly active this year in the field of Radiation and Radioactivity monitoring. Members of the sub-committee have worked through the local authority associations to formulate the provisions for the Local Authorities Radiation and Radioactivity Monitoring Advice and Collation Centre (LARRMACC). Public Analysts involved in local monitoring schemes have been concerned for some time with improving their internal quality assurance schemes by wider collaboration and to maximise the benefits of the data produced at local level. LARRMACC will achieve those aims and other objectives by centrally advising and co-ordinating the activities of local authorities involved in radiation monitoring and in particular prescribing national quality assurance criteria for sampling and analysis.

Public Analysts will welcome these activities as a necessary extension of their own attention to quality assurance and as an important part of their general approach towards Accreditation of all their functions.

Public Analysts also have a commitment to drinking water quality monitoring, which varies from area to area. In parts of the UK laboratories work directly with statutory water undertakings, in other parts they work with district councils in enforcing the provisions of the Water Act, particularly in relation to private supplies. The Association awaits the publication of the regulations for Water supplies which it is understood may create a new enforcement arm through authorisation of "technical assessors". Technical assessors will have particular

responsibilities related to assurance of the chemical and biological quality of supplies.

The Association believes that Public Analysts are well placed to be considered by the Department of the Environment (DOE) for appointments as technical assessors—in being able to provide the necessary locally based and locally committed scientific expertise. Some individual local authorities have already taken the initiative by proposing this course of action to the DOE and further developments will be monitored by the Association.

A European Seminar

The Association of Public Analysts appreciates that it is necessary to recognise the ever increasing boundaries in food production and food distribution. It is important that the methods of operation continue to ensure that the general public and honest traders are well protected against dangerous or substandard products and against unfair competition. It is necessary to ensure that the systems of monitoring the quality of foods and identifying problem areas are recognised and acceptable within and across national boundaries.

With this concern in view the Association of Public Analysts funded two members to participate in a seminar held in Brussels in 1988. This seminar discussed the problems arising out of the need for mutual recognition of "quality marks" and "standards" in the immediate future and in advance of the integration of systems within the European Community by 1992. The seminar was attended by delegates from many different disciplines and from all countries operating within the European Community and the European Free Trade Association. It served to highlight that there are many different methods of approach, but there is an increasing willingness to try to ensure that methods of operation are compatible and unlikely to lead to uneven enforcement throughout Europe.

The systems of monitoring food quality vary throughout Europe and the appointment of Public Analysts by local authorities, which is the practice in the United Kingdom, is unique within Europe. It has been suggested that steps should be taken to try to form a European Association of Public Analysts. However, there are difficulties due to the fact that the UK is the only country which requires that persons acting as analysts of food within their area should hold a diploma obtained after successfully undertaking an examination on the analysis (including microscopy) of Food Drugs and Water (MChemA). It will be necessary to enter into a dialogue between interested parties in regard to the mutual recognition of Higher Diplomas of this type and it is hoped that the Royal Society of Chemistry, which controls the examination in the UK, will ensure that the existing standard of technical ability is maintained in the future.

Another important aspect which relates to the acceptability of results coming from laboratories and the acceptance of certificates of marks of quality prepared by the laboratories, is the maintenance of adequate quality control of the results obtained and accreditation of the procedures used by the laboratory in its routine method of operation.

The seminar was a first step towards recognising the many difficulties and the

considerable work required to be undertaken to ensure that the systems develop in a satisfactory manner.

Future Food Law

The next few years will see major changes in the organisation and operations of the Public Analysts' Laboratories. The Food Act 1984 is currently under review and the EC Directive on the Official Control of Foodstuffs is being finalised. Both activities will have effect on the whole of the enforcement system. However, for Public Analysts there are two major issues: firstly, the designation of "Official Laboratories"; and secondly, their role in Factory Inspection.

As soon as the Food Control Directive is in force, MAFF will be required to advise the EC Commission of the UK's Official Laboratories. For Public Analysts it is thought that three criteria of achievement might be necessary:

(i) the requirement for the statutory Mastership in Chemical Analysis (M Chem A) qualification;
(ii) the achievement of NAMAS Accreditation for laboratory procedures; and
(iii) satisfactory performance in proficiency testing trials organised by MAFF.

Finance necessary for accreditation, proficiency testing, internal quality assurance, collaborative testing, training and method development is significant in terms of the achievement of recognition as "official laboratories". Public Analysts acknowledge that 10 to 25 per cent of their overall efforts may be spent in these areas, dependent on the stage of development.

Enforcing Authorities will need to recognise those costs as part of the overall importance of the enforcement system.

The new Food Act and the Control Directive will also introduce more formally into the enforcement system the requirement for Factory Inspection. Public Analysts have been active in the Local Authorities' Co-ordinating Body on Trading Standards (LACOTS) in drafting Guidance Notes on Inspection of Food Production Factories for Local Authorities. As Food Scientists, Public Analyst Laboratory staff are uniquely placed in the enforcement chain to provide the scientific expertise so necessary to effective factory inspection. The Association wholeheartedly supports the LACOTS advice to MAFF that:

> "LACOTS would emphasise that food enforcement and particularly in-factory enforcement will, at local authority level, be a multi-disciplinary affair. Representatives of the three involved groups—TSOs, EHOs and Public Analysts—will together provide the necessary expertise (with appropriate further training where needed) to carry out effective factory enforcement".

The Association believes that given a multi-disciplinary approach, with the skills to be contributed by the different professions within the enforcement systems, factory inspection can be effectively carried out by local authorities, as part of a general approach to Food Law enforcement at all stages of the distribution chain.

APPENDIX

STATISTICAL SUMMARY 1988

Figures for 33 Laboratories

Total number of samples	250 153
Including:	
Foods (including complaint samples and those submitted under Imported Food Regulations)	69 794
Milks (including those examined for antibiotics and those submitted under the Milk [Special Designation] Regulations)	12 603
Drinking Waters	21 615
Mineral Waters	577
Swimming Pools	3 456
Environmental Pollution (water, effluents, tip leachates)	50 020
Environmental Pollution (other samples)	25 143
Feeding Stuffs (Agriculture and Medicines Act and Feed Supplements)	2 838
Fertilizers (all kinds)	835
Consumer Protection, Trade Description Acts	8 998
Cosmetic Regulations	604
Health and Safety at Work Act samples	26 985
Miscellaneous (e.g. H.M. Coroner)	26 685

J. Assoc. Publ. Analysts, 1989, **27**, 47–53

An Evaluation of Methods for the Determination of the Total and Soluble Lead Content of Dry Paint Films

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A collaborative trial is described which evaluates (1) the precision of a method for total lead content of paint films, (2) the official method for soluble lead content of paint films and (3) a co-operative trial to evaluate the precision which was achieved by the use of various methods chosen by the participating laboratories.

The Toys (Safety) Regulations 1974[1] prescribe a maximum limit for the total lead content of dry paint films on toys of 2500 parts per million. Also, The Pencils and Graphic Instruments (Safety) Regulations 1974[2] provide a limit of 250 parts per million for the soluble lead content of any coating of paint.

The latter Regulations indicate a method for dissolving "soluble matter" contained in any coating. There are, however, few published procedures for determining the total lead content of dry paint films on toys. BS.3900 : Part B4[3] describes a method for determining total lead in paint which requires 5 g of paint. Similarly BS.3900 : Part B5[4] includes a method for the extraction of soluble lead which also requires 5 g of paint. Such an amount of sample is rarely available and, generally, analysis must be carried out on whatever quantity can be removed from a toy. This lack of paint has given rise to concern about the precision of methods used to determine the total lead content. The statutory method for soluble lead is given in outline only. It does not stipulate a minimum quantity of paint, although the minimum quantity used is self limiting by the amount of solution produced for analysis.

The method specifies the size of the sieve through which the comminuted paint must be passed. This procedure has been criticised by Public Analysts as being difficult to carry out. It is likely that particle size would have a major effect on the soluble lead content of the paint film, therefore some form of size grading is essential. No precision data appear to have been published on this method.

This paper describes a collaborative trial by eight Public Analyst Laboratories carried out to gain information on:

(a) the precision of the official method for soluble lead content.
(b) the precision of an agreed method for determining the total lead content. The method was previously recommended for use in a survey of lead in painted consumer goods[5].

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(c) the precision which would be achieved by Laboratories using their normal screening method of analysis. A free choice of method was available to Laboratories.

Sample Preparation

Liquid paints (green) were supplied by a local toy manufacturer. After an initial analysis they were mixed, where appropriate, in various proportions to give appropriate levels of total lead content in the dry matter, coated thinly on to large sheets of glass and allowed to dry. The air-dried paints were scraped from the glass and oven dried at 100°C, allowed to cool and ground to pass a 500 μm sieve. The final sample materials were subjected to repetitive analysis for total lead to ensure that the process produced an adequately homogeneous dried paint. The approximate "target" levels of total lead content were 2500 mg/kg (the statutory limit for toys) 5000 mg/kg and 10,000 mg/kg. The ground paints were sub-sampled into eight portions using a "cone and quarter" technique so as to ensure that each laboratory had paint samples with equivalent levels of particle size. Approximately 2.5 g of each paint was supplied to each of the participating laboratories.

Instructions to Laboratories

The eight laboratories taking part in the trial were instructed to:

(a) determine the total lead content, in duplicate, by the method specified in Appendix I.
(b) determine the soluble lead content, in duplicate, using the official guidance specified in The Pencils and Graphic Instruments (Safety) Regulations 1974 (*note:* in addition it was specified that the pH of the final extract should be less than 1.5 but not lower than 1.0). See Appendix 2.
(c) determine, in duplicate, the total lead content by a method of choice.

For dilution guidance, the laboratories were informed that the total lead ranges in the samples were likely to be:

A 1500–2500 mg/kg
B 10,000–12,000 mg/kg
C 4000–6000 mg/kg

When returning results laboratories were asked to supply:

(i) a copy of the procedure used as the method of choice (together with analytical quality assurance data where this is available).
(ii) all calculations, and
(iii) any comments or constructive criticisms.

Results

See Tables I, II and III.

Discussion and Conclusions

All analytical results were included in the statistical treatment of the results. No results from samples A, B or C have been rejected as outliers.

TABLE I

LEAD CONTENT OF DRY PAINT FILMS. TOTAL LEAD CONTENT (SPECIFIED METHOD) (*mg/kg*)

Laboratory	Sample A	Sample B	Sample C
1	2324, 2242	11,932, 12,524	6088, 6178
2	2050, 2150	12,700, 12,950	5450, 5400
3	2193, 2259	13,046, 13,046	5620, 6230
4	2120, 2133	12,523, 12,406	6012, 5832
5	2230, 2200	13,700, 13,600	6310, 6420
6	2115, 2164	12,794, 12,839	6238, 6307
7	2564, 2513*	13,951, 13,511	7161, 6425
8	2200, 2202	12,535, 12,633	5939, 6061
Mean	2228	12,918	6104
Standard deviation	137	540	425
Range	2050–2564	11,932–13,951	5400–7161
Coefficient of variation (%)	6.2	4.2	7.0
Repeatability (*r*)	116	566	703
Reproducibility (*R*)	400	1582	1250

* The results are slightly above the statutory limit and this Laboratory is classed as a "straggler" by Dixon's Test[6] on Laboratory means. The results were included in the statistical analysis.

Repeatability and reproducibility are as defined by BS.5497 : Part 1[6].

TABLE II

LEAD CONTENT OF DRY PAINT FILMS. SOLUBLE LEAD (*mg/kg*)

Laboratory	Sample A	Sample B	Sample C
1	40, 40	209, 213	207, 208
2	31, 33	157, 188	197, 197
3	42, 58*	183, 200	187, 197
4	40, 43	263, 238†	221, 234
5	50, 54	279, 284†	223, 222
6	49, 48	220, 215	234, 225
7	54, 48	240, 221	224, 228
8	44, 49	203, 214	213, 216
Mean	45	220	214
Standard deviation	7.4	34	14.3
Range	31–58	157–284	187–234
Coefficient of variation (%)	16.5	15.5	6.7
Repeatability (*r*)	13	35	14
Reproducibility (*R*)	21	100	40

* Results classed by Cochrans test[6] as stragglers but not as outliers. The results were included in the statistical analysis of the results.

† Contains results above the statutory limit of 250 mg/kg.

SPECIFIED METHOD FOR TOTAL LEAD (TABLE I)

The most significant results are those from sample A since the mean is close to the statutory limit of 2500 mg/kg. The calculated values for repeatability and reproducibility indicate a need for great care in the interpretation of lead contents in the range 2000–3000 mg/kg using this method. Indeed, Laboratory 7

TABLE III

LEAD CONTENT OF DRY PAINT FILMS. METHOD OF CHOICE

Laboratory	Total lead (*mg/kg*) Sample A	Sample B	Sample C
1	2000, 1996	10,918, 11,051	5136, 4970
2	2325, 2160	8285, 6995	4640, 4490
3	1803, 1853	11,453, 11,339	5069, 5203
4	2337, 2308	13,698, 13,861	6522, 6272
5	1960, 1560	5070, 6440	2400, 3340
6	2120, 2160*	12,800, 12,800*	6240, 6310*
7	3007, 1635†	10,982, 8958	3832, 2730
8	2084, 2069	11,919, 12,274	5975, 6012
Mean	2086	10,552	4946
Standard deviation	334	2646	1306
Range	1635–3007	5070–13,861	2400–6522
Coefficient of variation (%)	16.0	25.1	26.4

* Laboratory routine method is the specified method therefore the results are as Table I.
† Contains both the highest and lowest result and one result exceeds the statutory limit.

found sample A to be slightly higher than the prescribed limit. Such a result would justify a great deal of further analysis on the sample.

The amount of paint used in the method, i.e. 200 mg, is rather more than may on occasions be available from a toy. It is probable that the precision of the method when less than 200 mg of paint is used would be lower.

It is difficult to explain why the repeatability of sample C exceeds that from sample B[7].

SOLUBLE LEAD METHOD (TABLE II)

The restriction on pH was included because it has been found that with a pH below 1, the soluble lead content can rise dramatically.

However, Laboratory 8 has commented as follows: "The request to restrict the pH range between 1–1·5 was not found to be practicable since a pH meter is ruled out due to limited (approximately 10 ml) amount of solution. Limited range pH paper with known standards proved to be dubious".

The comment by Laboratory 8 is reasonable and this point has always been considered as a drawback in the method.

Although the total lead content of sample B is approximately twice that of sample C, the average soluble lead content of the two samples are almost identical. The precision of the results on sample B are much worse than those on sample C.

There are a number of factors which might affect the soluble lead content of paint films. Two of the main factors are the form of the lead in the paint and the particle size of the paint (i.e. the surface area available for contact with the acid).

The paint used in the preparation of sample C was a mixture of A and B whereas a single paint was used in preparing sample B. Both samples were

ground in the same manner and sieved through a 500 μm sieve, but no attempt was made to ascertain the particle size of the two dried paints. Again, from the repeatability and reproducibility, it can be seen that great care must be taken in the interpretation of results close to the statutory limit for pencils and graphic instruments. Results from sample B range from 157 mg/kg–284 mg/kg, with Laboratory 5 reporting two results above the statutory limit and Laboratory 4 a single result above the statutory limit. It is possible that in future legislation, further use may be made of soluble lead content rather than total lead content. If this is so, the method must be specified in more detail.

METHOD OF CHOICE (TABLE III)

The coefficients of variation indicate that when analysts are given a free choice of method, the precision of the results is much worse. This is not surprising as a general array of varying methods was used. Two laboratories (2 and 5) used a wet oxidation procedure which gave noticeably lower results at the higher lead levels. Both laboratories expected this to be the case and only used wet oxidation since their routine method was similar to that specified.

The reason for the lower results by wet oxidation is probably due to the insolubility of lead sulphate. BS.3900:Part B4:1986 specifies both wet oxidation and dry ashing methods for determination of lead content. The wet oxidation procedure specified in this British Standard involves a final complexation stage with ammoniacal EDTA to render the lead sulphate soluble.

Laboratory 6 routinely uses the specified method and therefore did not submit further results.

The remainder of the laboratories used methods based on an ashing procedure similar to the provided method, subject to the following modifications:

Lab. 1 Magnesium nitrate solution was used as an ashing aid. The ash was evaporated with equal volumes of concentrated hydrochloric acid, and concentrated nitric acid prior to extraction with 1% hydrochloric acid.

Lab. 3 No ash aid was used and extraction was carried out with 20% hydrochloric acid.

Lab. 7 No ash aid was used. The sample was ashed at 500°C for two hours, cooled, extracted with concentrated nitric acid and filtered.

Lab. 8 The method was the same as the specified method except
(a) the paint and sodium carbonate are moistened and dried prior to initial ashing.
(b) If the sample is not completely ashed, it is moistened re-dried, and re-ashed.

Lab. 4 The ash was transferred to a 250 ml beaker, boiled with 40 ml of 5·5 N hydrochloric acid for 15 min, filtered and made up to 100 ml in a volumetric flask.

Internal quality assurance data was supplied by two of the laboratories taking part.

The general lack of precision suggests that in future legislation if a limit for total lead is to be retained, a well defined method should be specified.

Acknowledgements

The Author thanks Mr G. Keen and the staff of Hereford and Worcester County Laboratory for their help with sample preparation, etc. Also the following Public Analysts and their staff for their participation:

H. M. Bee, County Analyst, Staffordshire.
M. J. Billington, Public Analyst for the seven District Councils of the West Midlands Region.
K. T. Chisnall, County Analyst, Derbyshire.
N. Harrison, County Analyst, Leicestershire.
G. Hooke, Ruddock & Sherratt Ltd., Chester.
D. W. Lord, County Analyst, Lancashire.
D. J. Petford, Clayton, Bostock Hill & Rigby Ltd., Birmingham.

References

1. "The Toys (Safety) Regulations 1974", SI. 1974 No. 1367, HMSO, London, 1974.
2. "The Pencils and Graphic Instruments (Safety) Regulations 1974", SI. 1974 No. 226, HMSO London, 1974.
3. British Standards Institution, "Determination of Total Lead in Paints and Similar Materials", BS3900: Part B4, London 1986.
4. British Standards Institution, "Preparation of acid extracts from liquid paints and coating powders", BS3900: Part B5, London 1986.
5. "Lead in Painted Consumer Goods", LACOTS circular to Public Analysts Liaison Groups LCS/SH/B6.13.
6. British Standards Institution, "Precision of Test Methods", BS5497: Part I, London 1979.
7. Bee, H. M., "Critical Appraisal of the Collaborative Testing of analytical Methods", *J. Assoc. Publ. Analysts*, in press.

Appendix I. Specified Method for Total Lead in Paint

Weigh 200 milligrams of material into a cleaned silica dish. Cover with an equal quantity of finely ground ANALAR sodium carbonate and gently ash over a Bunsen until fuming ceases. Transfer to a muffle furnace at 450°C for 1 h. Moisten the cooled ash with distilled water, cover with a clock glass and add 2 ml of ANALAR or foodstuffs grade concentrated nitric acid. Rinse the clock glass on to the silica dish and add 0·2 ml of ANALAR or foodstuffs grade concentrated hydrochloric acid and evaporate to dryness on a water bath.

Extract the residue several times with boiling 10% v/v nitric acid into a 100 ml calibrated flask, cool, make up to volume and filter through a 7 cm No. 541 filter paper. (NB: 10% v/v nitric acid is 100 ml of concentrated nitric acid (AR) (SG.1.42) diluted to 1000 mls with water.)

Determine the lead content of the filtrate by atomic absorption spectrophotometry using suitable calibration procedures. Carry out a blank determination throughout the procedure.

Before proceeding to the trial samples, laboratories should have experience of this procedure using reference material or spiked samples.

Appendix 2. Method of Dissolving Soluble Matter Contained in any Coating or Substance

1. A sample of the coating or substance, as the case may be, shall be so comminuted as to be capable of passing through a seive of wire cloth of 0·5 mm (500 μm) aperture, provided that, in the case of a sample (other than a sample of coating) containing any wax, oil or other similar matter, that wax, oil or matter shall first be removed by means of methyl chloroform (1,1,1-trichloroethane).
2. The comminuted sample shall be added to fifty times its weight of an aqueous solution (at a temperature not lower than 20°C nor higher than 22°C) of hydrochloric acid containing 0·25 per cent. by weight of hydrogen chloride (0·07 N HCl) and the mixture shall be shaken for one minute. The mixture shall then be tested for acidity and, if its pH value is more than 1·5, an aqueous solution of hydrochloric acid containing 7·3 per cent. by weight of hydrogen chloride (2N HCl) shall be added drop by drop (the mixture being shaken after each drop is added) until the pH value is 1·5 or less. The mixture shall then be shaken continuously for 1 h.
3. After shaking, the mixture shall be allowed to stand for 1 h, and shall then be filtered. The resulting solution is analysed.

J. Assoc. Public Analysts, 1989, **27**, 55–68

The Determination of Crude Fibre Content of Animal Feeding Stuffs: A Study of Experimental Factors and Proposals for Modified Methods

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The experimental parameters affecting the determination of crude fibre in animal feeding stuffs by the statutory procedure have been investigated. The separate effects of time of digestion, reagent strengths, ratio of reagent volume to sample size and filtration media have been studied. A more rapid, improved method for the determination of crude fibre is also proposed and evaluated.

Crude fibre is an important parameter of the composition of an animal feeding stuff, since it represents a summation of those constituents of a feed which cannot be readily digested by the animal and so will not contribute to the available energy value of the feed. A knowledge of the energy value of a feeding stuff enables an economic assessment of different animal production systems to be made and assists in providing a deeper understanding of the biological processes involved in animal nutrition. Currently, attempts are being made to produce equations, based on the proximate constituents of a feed, to predict the metabolisable energy of a wide range of compound feeds for use with poultry, pigs or ruminants[1], and recently promulgated U.K. regulations include a formula for calculating the energy value of compound poultry feeds[2]. Crude fibre is an important factor in some of these equations.

Originally, fibre was regarded as inert and non-nutrient, that is, in effect, a diluent. Later work, however, showed that ruminants depend on insoluble material to promote digestion in the rumen. The crude fibre content gives a measure of the digestibility of a feeding stuff, which is of primary importance in animal nutrition, but only one factor controlling the expected animal growth performance[3].

The nature of fibre has been extensively studied[4–6], and the term crude fibre is taken to include the non-digestible constituents of the feed or forage including cellulose, hemicellulose, pectin and lignin, which together form the cell walls of plants. Digestibility is difficult to assess *in vivo* and so laboratory methods involving treatment with acids, alkalis, detergents and enzymes have been proposed in an attempt to simulate the animal's digestive process[7–13].

Lignin and hemicellulose are readily attacked by dilute solutions of alkali, whilst cellulose is resistant. Many starches, sugars and related substances are solubilised in hot acidic solution, whilst cellulose and lignin are resistant to this treatment. Detergents readily solubilise proteins and fat, and a number of

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amylolytic and proteolytic enzymes are also available for digestion. Using these reagents, alone and in combination, it is possible to separate total fibre into more closely defined analytical fractions. Some workers now prefer to characterise the various chemical constituents of fibre separately by chromatographic means[14].

Crude fibre is defined as the percentage of matter remaining after treatment with acidic and alkaline solutions under standard conditions and is measured by the loss in weight on ashing of the dry residue obtained after such treatment. Other equally empirical definitions, such as acid detergent fibre or neutral detergent fibre, have been proposed by Van Soest[8,9] in an attempt to define the physiologically active constituents of total dietary fibre in human foods. Acid detergent fibre includes cellulose and lignin whilst neutral detergent fibre also includes hemicellulose. However, it is difficult to correlate these fractions with animal performance and there is no proof yet that the analytical methods proposed are any more reproducible than the familiar, longstanding procedure for crude fibre, first described in 1864. Meanwhile, crude fibre is still the only form for which a statutory declaration is mandatory and it is the figure which is familiar to many farmers as one important indicator of feed quality. Whilst many animal nutritionalists would welcome a change from crude fibre to say neutral detergent fibre, amendments to the EEC Council Directive on the marketing of feeds and the provision of a new official method of analysis would be required. Preliminary experiments in this direction indicate that much work would be needed to accommodate the wide variety of available feeding stuffs in an intensive collaborative study. Although much has been completed, there is no agreement at present on the detailed procedure to be used. Any new method is unlikely to be significantly better in terms of reproducibility.

Hallab and Epps[15] have similarly examined some of the factors affecting the determination of crude fibre by the traditional method. They found that variations in time, concentration and volume of reagents had only a minimal effect on the crude fibre value obtained but could make no suggestions to improve the manual method for determining crude fibre.

A semi-automatic method, which employs equipment supplied by the Tecator company[16], has been suggested. This has shown more rapid and consistent results and avoids transference losses. However, adoption of this system, as a statutory reference method, has the disadvantage of relying on one particular piece of equipment which is initially expensive and can be costly to maintain. Furthermore, initial experiments have produced results that were consistently higher than those obtained using the existing statutory method. This positive bias, although small, was by no means constant but varied from one feeding stuff to another.

The empirical nature of fibre determination has given rise to a large number of different experimental procedures in use in animal feed control laboratories and, in particular, filtration steps. Consequently, concern has arisen over the effects of such variations on the analytical figures produced. The statutory method[17] stipulates a time limit for filtration which often cannot be achieved. If filtration exceeds this time limit, the determination must be repeated. In some cases it is not possible to perform the filtration within the specified time limit and

no result can be obtained. Furthermore, the reproducibility of such a test is poor and this is reflected in the limit of variation permitted under the regulations.

The current investigation by the Laboratory of the Government Chemist (LGC) critically examines the effects of various experimental parameters on the determination of crude fibre. As a result, a new rapid manual method, which presents fewer problems at the filtration stage and avoids some transference problems, is proposed and evaluated. In view of an increasing interest in the Tecator procedure and its possible adoption by the EEC as an official method, a study of some experimental parameters was undertaken and the results used for comparison with the manual methods (Tables I–IV).

Experimental

In practice[17], crude fibre is estimated by boiling the defatted feed, first in acid and then in alkali under defined conditions, the residue being filtered and washed after each treatment. The residue after digestion is then dried and the organic matter estimated by loss of weight on ashing. The necessity to filter after each boiling stage causes a number of problems. Colloidal solutions are often produced which can be slow and difficult to filter. Furthermore, transference losses whilst washing the residue from the filtration apparatus into the reaction vessel are more likely when using particular types of filtration media under certain conditions.

A number of commercially available compound feeds for cattle, poultry and pigs were selected to cover a wide range of crude fibre contents. The apparatus and chemicals used were as listed in the Statutory Method[17]. The following experimental variables were investigated in the first part of the study:

1. acid extraction time;
2. alkali extraction time;
3. acid concentration; and
4. alkali concentration.

All samples were analysed in quintuplet in a single run, a sixth analysis being used for a blank determination. The results (Tables I–IV) have been converted to a dry matter basis.

Results and Discussion

1. DIGESTION TIME

This digestion time is measured from the moment the liquid starts to boil. Digestion appears virtually complete after 30 min boiling and only relatively small variations have been observed after this time, both at the acid and alkali stages (Tables I and II). This effect is shown more clearly in Fig. 1 for three of the samples tested.

2. REAGENT CONCENTRATIONS

Historically, the presently used concentrations of sulphuric acid (0·13 M) and sodium hydroxide solution (0·31 M) (corresponding to 1·25%) were chosen as the minimum required to digest, in a reasonable time, all but the matter defined as crude fibre. Above these concentrations other substances (contributing to the

TABLE I

DETERMINATION OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS. THE EFFECT OF ACID EXTRACTION TIME ON FIBRE CONTENT

	Fibre content (*per cent.*)			
Extraction time (*min*)	5	15	30	45
Pig feed 1				
Range	6·3–6·9	5·9–6·2	5·4–6·1	5·3–6·4
Mean	6·52	6·05	5·79	5·61
s.d	0·24	0·13	0·23	0·45
Feed for laying hens				
Range	7·8–8·7	6·5–7·9	6·6–7·6	6·4–7·5
Mean	8·09	7·17	7·10	7·01
s.d.	0·35	0·55	0·46	0·44
Feed for sows				
Range	10·5–11·5	8·9–9·2	8·2–8·7	8·2–8·6
Mean	10·90	9·06	8·55	8·40
s.d.	0·46	0·14	0·20	0·18
Oat screening meal				
Range	28·2–30·2	24·3–25·0	24·1–25·1	23·3–24·1
Mean	29·0	24·7	24·6	23·7
s.d.	0·86	0·29	0·42	0·30
Broiler finisher				
Range		3·2–3·6	3·3–3·4	3·0–3·5
Mean		3·38	3·34	3·16
s.d.		0·15	0·08	0·19
Superweaner				
Range	9·5–10·9	8·7–10·1	8·0–8·6	8·2–9·2
Mean	10·02	9·28	8·38	8·82
s.d.	0·54	0·51	0·23	0·35
Pig feed 2				
Range	7·1–7·6	6·3–6·8	5·6–6·4	6·0–6·7
Mean	7·39	6·59	6·09	6·42
s.d.	0·19	0·21	0·34	0·26
Layers mash				
Range	4·2–6·8	3·6–6·8	3·6–4·8	3·6–4·6
Mean	5·45	4·60	3·96	4·01
s.d.	0·96	1·30	0·48	0·36
Low fibre layblend				
Range	4·7–5·1	4·5–4·7	4·2–4·7	4·2–4·7
Mean	4·87	4·57	4·41	4·41
s.d.	0·13	0·09	0·21	0·17
Beef fattening nuts				
Range	10·7–11·1	9·0–9·4	8·7–9·3	8·2–8·6
Mean	10·88	9·19	8·99	8·43
s.d.	0·18	0·17	0·24	0·18
Chick mash				
Range	5·1–5·4	4·5–5·1	4·5–5·3	4·6–5·2
Mean	5·24	4·88	4·76	4·99
s.d.	0·13	0·22	0·32	0·23

TABLE II

DETERMINATION OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS. EFFECT OF ALKALI EXTRACTION TIME ON FIBRE CONTENT

	Fibre content (*per cent.*)			
Extraction time (*min*)	5	1	30	45
Pig feed 1				
Range	6·1–7·2	5·4–6·1	5·4–6·1	5·3–6·0
Mean	6·41	5·87	5·79	5·66
s.d.	0·48	0·27	0·23	0·26
Feed for laying hens				
Range	7·4–8·5	6·8–7·5	6·6–7·6	6·2–7·1
Mean	8·01	7·10	7·10	6·80
s.d.	0·51	0·33	0·46	0·47
Feed for sows				
Range	10·2–11·0	9·4–10·1	8·2–8·7	8·5–8·7
Mean	10·58	9·72	8·55	8·58
s.d.	0·32	0·29	0·20	0·06
Oat screening meal				
Range	25·7–26·4	24·7–25·1	24·1–25·1	23·9–24·2
Mean	26·0	24·9	24·6	24·1
s.d.	0·3	0·2	0·4	0·1
Broiler finisher				
Range	3·8–4·0	3·1–3·5	3·3–3·4	3·1–3·5
Mean	3·86	3·41	3·34	3·32
s.d.	0·11	0·14	0·08	0·15
Poultry compound feed				
Range	3·0–3·5	3·2–3·4	3·0–3·5	2·8–3·0
Mean	3·39	3·24	3·28	2·90
s.d.	0·19	0·07	0·27	0·08
Superweaner				
Range	9·6–10·3	8·4–8·8	8·0–8·6	7·9–8·4
Mean	9·93	8·62	8·38	8·14
s.d.	0·27	0·18	0·34	0·16
Pig feed 2				
Range	6·7–7·2	6·7–6·9	5·6–6·4	5·8–6·3
Mean	6·99	6·73	6·09	6·13
s.d.	0·20	0·14	0·34	0·20
Medium hybrid layers mash				
Range	4·3–5·3	3·8–4·4	3·6–4·8	3·6–4·2
Mean	4·69	4·14	3·96	3·81
s.d.	0·38	0·22	0·48	0·23
Low fibre layblend				
Range	5·0–5·4	4·7–4·8	4·2–4·7	4·2–4·4
Mean	5·16	4·74	4·41	4·24
s.d.	0·13	0·07	0·21	0·09
Beef fattening nuts				
Range	9·7–10·2	9·0–10·3	8·7–9·3	8·7–9·6
Mean	9·92	9·45	8·99	9·17
s.d.	0·22	0·51	0·24	0·36
Chick mash				
Range	5·2–5·5	4·9–5·1	4·5–5·3	4·4–4·6
Mean	5·27	5·02	4·80	4·49
s.d.	0·11	0·06	0·32	0·04

TABLE III

DETERMINATION OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS. EFFECT OF ACID CONCENTRATION ON FIBRE CONTENT

Acid concentrations (*M*)	Fibre content (*per cent.*)		
	0·05	0·13	0·50
Pig feed 1			
Range	6·2–6·7	5·7–6·1	5·4–5·7
Mean	6·36	5·79	5·55
s.d.	0·24	0·23	0·11
Feed for laying hens			
Range	8·4–8·8	6·6–7·6	6·2–6·9
Mean	8·59	7·10	6·37
s.d.	0·17	0·46	0·29
Oat screening meal			
Range	27·4–28·1	24·1–25·1	24·5–25·8
Mean	27·8	24·6	25·2
s.d.	0·3	0·4	0·5
Superweaner			
Range	10·0–11·4	8·0–8·6	7·9–8·1
Mean	10·57	8·38	8·00
s.d.	0·54	0·23	0·10
Pig feed 2			
Range	6·8–7·5	5·6–6·4	6·1–6·4
Mean	7·23	6·09	6·26
s.d.	0·28	0·34	0·13
Beef fattening nuts			
Range	10·0–10·2	8·7–9·3	8·9–9·8
Mean	10·09	8·99	9·30
s.d.	0·10	0·23	0·35
Chick mash			
Range	5·0–5·7	4·5–5·3	4·3–4·8
Mean	5·31	4·80	4·38
s.d.	0·26	0·32	0·24

TABLE IV

DETERMINATION OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS
EFFECT OF ALKALI CONCENTRATION ON FIBRE CONTENT

Alkali concentration (*M*)	Fibre content (*per cent.*)		
	0·1	0·31	1·0
Pig feed 1			
Range	6·1–7·3	5·4–6·1	5·1–5·4
Mean	6·92	5·79	5·19
s.d.	0·44	0·23	0·11
Feed for laying hens			
Range	7·3–8·6	6·6–7·6	6·0–7·0
Mean	7·83	7·10	6·70
s.d.	0·57	0·46	0·43
Feed for sows			
Range	9·7–10·9	8·2–8·7	7·1–7·9
Mean	10·37	8·55	7·44
s.d.	0·51	0·20	0·37
Oat screening meal			
Range	25·4–26·1	24·1–25·1	23·4–23·6
Mean	25·8	24·6	23·5
s.d.	0·3	0·4	0·08
Poultry compound feed			
Range	2·9–3·4	3·0–3·6	2·4–2·8
Mean	3·17	3·28	2·66
s.d	0·17	0·27	0·14
Superweaner			
Range	8·7–9·2	8·0–8·6	7·9–8·2
Mean	8·93	8·38	8·03
s.d.	0·20	0·23	0·14
Pig feed 2			
Range	6·3–7·1	5·6–6·4	5·4–6·4
Mean	6·66	6·09	5·75
s.d.	0·31	0·34	0·38
Medium hybrid layers mash			
Range	3·6–5·7	3·6–4·8	2·9–3·4
Mean	4·26	3·65	3·02
s.d.	0·85	0·48	0·16
Low fibre layblend			
Range	4·9–5·0	4·2–4·7	3·9–4·1
Mean	4·95	4·41	3·99
s.d.	0·07	0·21	0·05
Beef fattening nuts			
Range	9·6–10·0	8·7–9·3	8·6–9·2
Mean	9·82	8·99	8·84
s.d.	0·17	0·24	0·22
Chick mash			
Range	5·0–6·3	4·6–5·3	4·2–4·4
Mean	5·41	4·80	4·30
s.d.	0·54	0·32	0·06

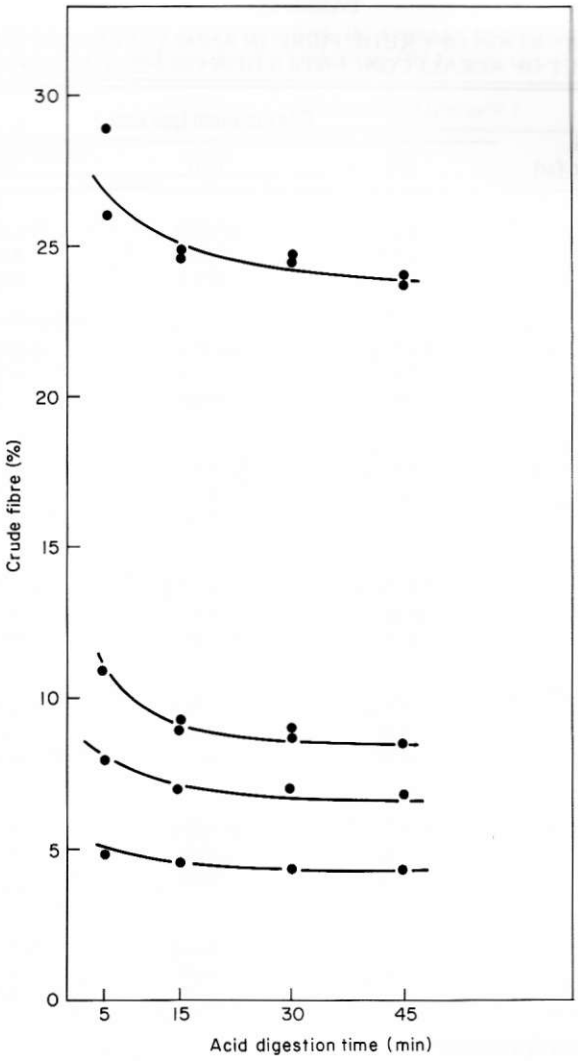

Fig. 1. Effect of acid digestion time on crude fibre content.

final crude fibre content) may also be attacked, giving low results. On the other hand, reagents of lower concentration give rise to inadequate digestion, producing high fibre results (Tables III and IV), emphasising the empirical nature of the determination. Care must also be taken to prevent evaporation losses during boiling (e.g. by using a condensing system) which, in effect, raises reagent concentrations, even at 30 min, since there is no advantage in using reagent concentrations outside the range shown in Tables III and IV.

3. SAMPLE SIZE AND REAGENT VOLUME (S/R)

Sample size and reagent volume are taken together as a ratio (S/R). Between S/R values of 1/100 and 1/150, there is very little variation in results, whether by

TABLE V

PERCENTAGE OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS. VARIATION OF FIBRE CONTENT WITH SAMPLE SIZE/REAGENT VOLUME RATIO

	Sample size(*g*)/Reagent volume(*ml*) Ratio				
Sample type	3/200	2/200	1/150	1/150*	1/100*
Soya extract					
Range	4·1–5·1	3·6–4·3	3·3–3·7	3·8–4·0	3·4–4·8
Mean	4·42	4·04	3·55	3·86	4·17
s.d.	0·27	0·23	0·15	0·07	0·44
Rice extract					
Range	12·9–13·3	12·8–14·5	12·7–13·5	13·5–14·4	14·4–15·4
Mean	13·09	13·57	13·06	13·91	14·79
s.d.	0·13	0·55	0·28	0·34	0·37
Pig ration					
Range	5·3–6·0	5·1–5·9	5·2–5·6	5·6–5·9	6·0–6·3
Mean	5·57	5·45	5·37	5·72	6·20
s.d.	0·29	0·39	0·16	0·11	0·10
Poultry ration					
Range	4·6–6·4	5·3–6·2	5·2–5·6	5·6–5·9	5·4–6·7
Mean	5·93	5·82	5·37	5·72	6·10
s.d.	0·50	0·35	0·16	0·11	0·54
Cattle feed 1					
Range	5·3–6·1	5·0–6·2	5·4–5·9	5·5–6·1	6·1–6·7
Mean	5·79	5·66	5·52	5·95	6·40
s.d.	0·21	0·46	0·17	0·28	0·25
Cattle feed 2					
Range	4·0–4·7	4·1–4·9	3·7–4·0	3·8–4·3	4·1–4·8
Mean	4·25	4·44	3·82	4·13	4·39
s.d.	0·22	0·30	0·14	0·18	0·34

* Results obtained using semi-automatic apparatus.

manual or automatic techniques (Table V). Where this ratio is greater than 1/100, significantly higher results are obtained due to inadequate digestion whereas lower S/R ratios lead to slightly lower fibre contents.

4. FAT CONTENT OF SAMPLES

High fat content in feeds could produce erroneously high results for crude fibre caused by poor penetration of the digestion medium or premature consumption of reagent by reaction with the fat. This is not a major problem for most feed samples where the fat content is usually below 5%, but in cases where the fat content of the feed is thought to exceed this figure, its removal is advised prior to digestion[17].

5. FILTRATION TECHNIQUES

Of the alternative systems to filter paper that have been employed over the years, the use of sand, cloth and centrifugation amongst other systems, has not proved universally acceptable. More recently, sintered glass crucibles and fine

stainless steel gauzes of similar mesh size have been tested as alternatives to filter paper in conjunction with filtration under reduced pressure. The former have the dual advantages of easier handling during filtration and use as a container for the sample at all stages of the method, thereby avoiding transference losses. The latter system is actually a more rapid filtering device, but otherwise has limited use and great care must be taken when transferring samples from the gauze to another container.

Both filters perform better with filter aids such as asbestos (now no longer available), celite, macerated cellulose or glass fibre filter paper, or ceramic fibre, studies having been made on the last two in recent years[18,19]. Even then, filtration becomes extremely difficult, and in some cases impossible, using crucibles or gauzes finer than that corresponding to porosity 2 (approximately 100 μm diameter pore size).

The advantages and drawbacks of these filter aids may be summarised as follows:

a. Asbestos, originally recommended in the UK legislation Regulation Method, is considered a health hazard and must not be used.
b. Most types of filter paper (including glass fibre) aid filtration but, when wet, hinder attempts to remove and transfer sample residues, resulting in transference losses.
c. Celite is probably the best filter aid for use with the automatic Tecator machine, where back pressure may be applied to the sinter to free any clogging of sinter pores. However, this facility is not usually available when using manual apparatus so that when the Celite beds down, further filtration is prevented. Also, unlike other filter aids, the material needs heat treatment prior to use to remove residual organic matter.
d. Macerated glass fibre filter paper was found to be slightly better than Celite for manual use with sintered crucibles but problems still arise from bedding down during filtration.
e. Ceramic fibre appears to be the most satisfactory filter aid for a manual method, not only assisting rapid filtration of all samples tested, but also acting as a very good anti-bumping medium during digestion. This observation supports the work of Holst[19], who made comparisons with an official AOAC method.

6. ASHING CONDITIONS

The recommended ashing temperature of 500°C for several hours was found to be satisfactory although higher temperatures (up to 900°C) for shorter times give equally good results (Table VI). However, higher temperatures require the use of more robust apparatus (e.g. Pyrex). Even then, crucibles have a limited useful life, and deterioration, which is not always predictable, can be accompanied by unacceptably large "blank" values. Also, changes in temperature should be gradual when working with sintered crucibles to avoid breakage caused by thermal shock, as well as to prolong their useful working life. Above 500°C, the sinter melts.

TABLE VI

COMPARISON OF FIBRE CONTENTS USING DIFFERENT ASHING TECHNIQUES

	Fibre content (*per cent.*)	
Ashing Conditions	550°C (6 h)	900°C (30 min)
Pig Feed	6·05	6·18
	5·90	5·98
	5·89	5·86
	5·81	5·85
	5·77	5·83
Mean	5·88	5·94
s.d.	0·11	0·15

Comparison of Automatic and Manual Techniques

The Tecator system has the advantages of speed of operation and good precision whilst avoiding losses by transfer. On the other hand attainment of boiling temperature is often not as rapid as desired nor as uniform between individual distillation columns. This may lead to fibre figures slightly higher than those obtained by a manual method (Table V).

As a result of the foregoing considerations, this laboratory has developed two separate manual methods using simple inexpensive apparatus with comparable repeatability. One method is a directly comparable double filtration technique using a sinter with filter aid, the other avoids filtration after the acid digestion stage by the addition of excess alkali to neutralise unused acid and to complete the second digestion stage. After completing the alkali digestion and filtration an acid wash is incorporated to remove alkali-insoluble material. The new proposed single filtration version of the LGC method not only has the advantage of being much quicker than double filtration methods but also avoids some losses by transfer. Apart from the differences shown in the ration feeds, which are probably due to a combination of experimental factors as well as feed constituents, the results (Table VII) indicate reasonable agreement between single and double filtration methods.

During the development of the single filtration method it was thought prudent to compare the nature of the residues after digestion with those obtained using the double filtration method. For this purpose, two samples were taken through the proposed methods and the respective residues were examined chromatographically by the method of Englyst[13]. The profiles of the residues were almost identical (Fig. 2) confirming that the residues from both methods comprised similar substances. The proposed methods are given in the Appendix.

Acknowledgement

The work on which this paper is based was done on behalf of and fully funded by the Ministry of Agriculture, Fisheries and Food.

TABLE VII

PERCENTAGE OF CRUDE FIBRE IN ANIMAL FEEDING STUFFS. COMPARISON OF FIBRE RESULTS OBTAINED BY SINGLE AND DOUBLE FILTRATION METHODS

	Filtration			
	Double	Single	Double	Single
	Wheat		*Maize gluten*	
Range	2·7–3·6	2·8–3·5	7·5–7·9	7·8–9·4
Mean	3·04	3·08	7·60	8·61
s.d.	0·28	0·26	0·18	0·54
	Viton NIS		*Supersoy*	
Range	40·5–45·6	38·3–43·3	8·0–11·6	8·0–12·6
Mean	42·4	40·9	9·59	9·67
s.d	2.0	1·9	0·27	1·75
	Rice bran		*Ration 109*	
Range	19·7–22·8	21·1–22·3	12·5–13·8	13·4–14·4
Mean	21·5	21·6	13·2	14·0
s.d.	1·2	0·4	0·4	0·4
	Layers ration		*Ration 101*	
Range	7·1–8·0	8·9–9·8	9·6–10·3	9·9–13·8
Mean	7·44	9·29	9·87	11·9
s.d.	0·30	0·31	0·25	1·3
	Cattle Feed (Low Fibre)		*Cattle Feed (High Fibre)*	
Range	3·9–4·2	4·2·5·1	9·2–10·8	9·1–10·6
Mean	4·01	4·63	9·89	10·1
s.d.	0·11	0·32	0·48	0·49

References

1. Stanogias, G. and Pearce G. R., *Brit. J. Nutr.*, 1985, **53**, 513.
2. "The Feeding Stuffs Regulations 1988", S.I. 1988, No. 396, H.M.S.O., London.
3. Van Soest, P. J., *Proc. Nutr. Soc.*, 1973, **32**, 123.
4. Norman, A. G., *J. of Agri. Soc.*, 1935, **25**, 529.
5. Southgate, D. A. T., *J. Plant Foods*, 1978, **3**, 9.
6. Southgate, D. A. T., and Faulks R. M., Food Laboratory News Letter, January 1988, 15, Swedish National Food Administration, Uppsala, 1988.
7. Holt, K. E., *J. Assoc. Off. Analyt. Chem.*, 1962, **45**, 578.
8. Van Soest, P. J., and Wine, R. H., *J. Assoc. Off. Agric. Chem.*, 1967, **50**, 50.
9. Van Soest, P. J., *J. Assoc. Off. Analyt. Chem.*, 1973, **56**, 781.
10. Asp, N. G., Johansson, C. G., Hallmer, H., and Siljestrom, M., *J. Agric. Fd. Chem.*, 1983, **31**, 476.
11. Robertson, J. B. and Van Soest, P. J., (Ref. 6). "Carbohydrate Health", in Proceedings of Symposium on "Analytical Problems of Fibre", Institute of Food Technologists, 1976, 69.
12. Schaller, D. R., *Food Production Dev.*, 1977, **11**, 70.
13. Mongeau, R., and Brassard, R. J., *Food Sci.*, 1986, **51**, 1333.
14. Englyst, H. N., and Cummings, J. H., *Analyst*, 1984, **109, 937**.
15. Hallab, A. H., and Epps, E. A., *J. Assoc. Off. Agric. Chem.*, 1963, **46**, 1006.
16. "Automatic Methods of Analysis using Tecator products", Tecator Company Ltd., Thornbury, Bristol.
17. "The Feeding Stuffs (Sampling & Analysis) Regulations 1982", S.I. 1982, No. 1144, H.M.S.O., London.
18. Craddick, R. C., and Hatfield, L., *J. Assoc. Off. Analyt. Chem.*, 1981, **64**, 1275.
19. Holst, D. O., *J. Assoc. Off. Analyt. Chem.*, 1982, **65**, 265.

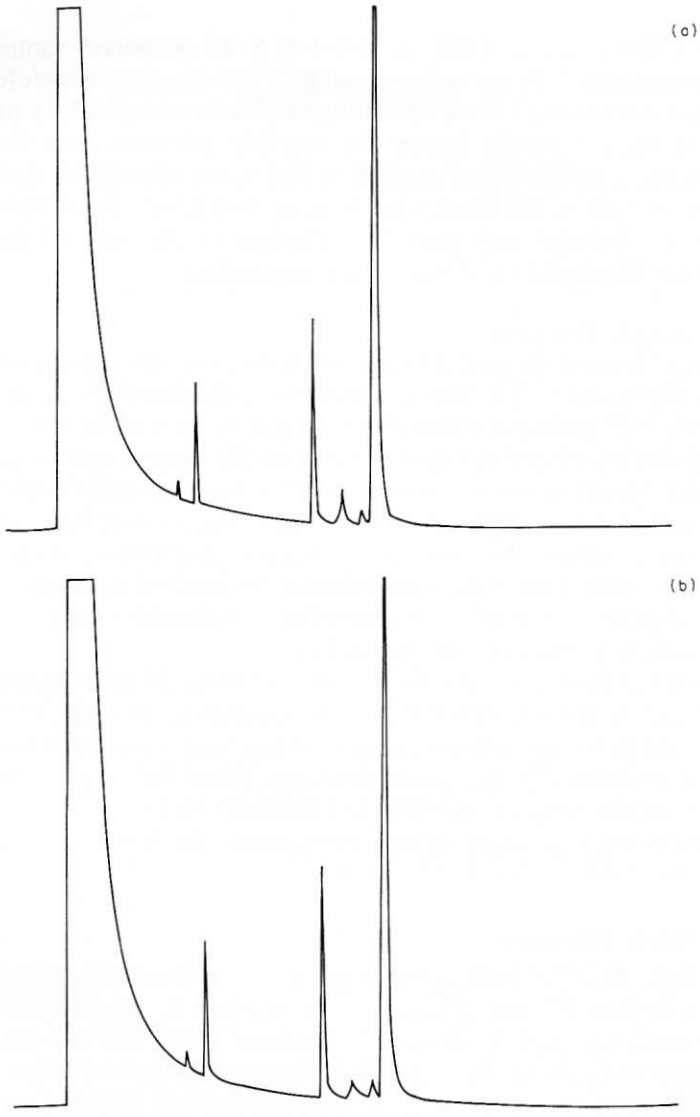

Fig. 2. Gas chromatogram obtained from digestion of residues of cattle feed (low fibre) after (a) single filtration and (b) double filtration.

Appendix: LGC Modified Methods For The Determination Of Crude Fibre In Animal Feeding stuffs

REAGENTS

1. *Sulphuric acid solution, 0·13* M.
2. *Potassium hydroxide solution, 0·23* M.
3. *Potassium hydroxide solution, 1·0* M.
4. *Acetone*.

PROCEDURE

Weigh, to the nearest 0·001 g, 0·9–1·1 g of prepared sample into a pre-weighed porosity 2 Pyrex sinter crucible. Pour the sample carefully into a 600 ml beaker containing 150 ml of boiling sulphuric acid (0·13 M) and 0·5 g of ceramic fibre then carefully lower the crucible sideways into the beaker. Immediately place a round-bottom flask of cold water over the beaker, to act as a condenser, and allow the beaker contents to boil gently for 30 min, swirling occasionally to dislodge any particles adhering to the side of the beaker. Continue using Method 1 or Method 2 as appropriate.

Method 1—Double Filtration

Using tongs, remove the crucible and wash its external surfaces with boiling water into the beaker. Fit the crucible to a Buchner flask, and spread approximately 0·25 g of fresh ceramic fibre over the sinter surface. With forceps, carefully lift out the boiled ceramic fibre from the beaker and place over the fresh material. Start the suction and filter the sample, washing with two 30 ml portions of boiling water. After filtration, remove the ceramic fibre, place it and the crucible in a sideways position in the beaker, and add carefully 150 ml of boiling 0·23 M potassium hydroxide solution. Immediately fit the condenser flask, and boil gently for 30 min, again swirling occasionally to dislodge particles which may adhere to the sides of the beaker.

Filter exactly as before, but this time wash with three 30 ml portions of boiling water, cool and then wash with three 25 ml portions of acetone.

Dry the crucible to constant weight in a drying oven set at 100°C, cooling the crucible in a desiccator before each weighing. Place the crucible in a muffle furnace and ash the contents at 500°C to constant weight.

Carry out a blank test, omitting only the sample. The loss in weight resulting from ashing must not exceed 4 mg.

Method 2—Single Filtration

Add carefully 80 ml of boiling 1·0 M potassium hydroxide solution and boil gently for a further 30 min. Exactly as in Method 1, remove the crucible, washing its outer surfaces, fit it on to a Buchner flask, and use the filtration technique described above after the acid digestion. After the water washings have passed through the sinter, stop the vacuum and add 25 ml of boiling 0·5 M sulphuric acid. Allow to stand for 1 min, then reapply the vacuum. Repeat by the addition of a further 25 ml of boiling 0·5 M sulphuric acid, following by three 30 ml water washings, then three 30 ml acetone washings.

Dry the crucible to constant weight and proceed as before.

J. Assoc. Publ. Analysts, 1989, **27**, 69–70

Book Reviews

LABORATORY MANUAL FOR THE EXAMINATION OF WATER, WASTE WATER AND SOIL. By H. RUMP and H. KRIST. VCH: Weinheim. 1988. Price DM 58 (£20.25). 202 pp.

The authors of this (240 mm × 165 mm page size) book have crammed an almost unbelievable amount of information into its 202 pages.

The book starts with a section (nowadays seemingly obligatory) on laboratory safety, which goes further than the bland regurgitation usually found, and includes a table of substances which should be isolated from one another, details of chemical storage requirements, and simple first aid (including chemical burns).

The second section deals with quality control, and includes a discussion of the calculation of mean standard deviation, the use of Dixons test, the "F" test, "t" test & control charts. The section ends with an outline of the use of a correlation matrix for use when a large number of samples are taken from one sampling point.

The third and fourth sections cover the purpose of analysis and what determinations are relevant to the achievement of that purpose. Tables list normal concentration ranges of a number of parameters in ground water, surface waters, wastes etc. The text continues with a discussion of sampling plans and methods of sampling, measurement of water flow, and preservation of samples.

So far as analytical chemists are concerned, the meat of the book is to be found in sections five and six, which cover analytical techniques. Analytical methods are presented for the determination of some 32 chemical or physical parameters (in some cases alternatives are given) plus details of a limited range of microbiological tests. The text also includes details of a technique for concentration of parasite eggs. The chemical methods are all "wet" chemistry, and no reference is made to techniques such as the various types of chromatography nor A.A. spectroscopy. To be fair to the authors and publishers, the preface does state "Methods involving complex apparatus have been deliberately omitted", but the average person probably does not read a preface before purchasing. All the methods are well set out and include notes on interferences and suggestions for eliminating these. Most methods will be well known to practising chemists of more than 15 years experience, but the determination of ammonia by use of sodium dichloro*iso*cyanurate is new to this reviewer.

All the methods relate to water analysis, for despite its title this is really what the book covers, with only very brief details being given of digestion of waste waters and extraction of soils.

The text ends with a section on interpretation of results, which lists various E.E.C., W.H.O. and Federal German Republic standards, together with other tables covering recommended standards for water to be used for concrete, water likely to be aggressive to concrete, salinity of irrigation water, limits for effluents from various industries etc. This section is followed by appendices consisting of statistical tables and three computer programmes in BASIC (although there is no indication of which variety) for the calculation of mean, standard deviation, ion balance & regression analysis. The index does not correlate with the text; most items appear to be indexed as actual page minus 1, thus the method for zinc is listed in the contents as page 134, in the index as page 133, and is actually situated on page 134.

Had this review been written 20 years ago, there would have been no hesitation in saying that Rump & Krist was an essential requirement for every laboratory undertaking water analysis. However, as noted above, the book does not cover the instrumental techniques which have replaced many of the methods here detailed. Nonetheless, the book will still be a valuable addition, and the introductory sections and the section on interpretation would make valuable reading for a person just taking up water analysis.

D. DUNN

ATLAS OF POLYMER AND PLASTICS ANALYSIS. SECOND EDITION. VOLUME 2 PART B, PLASTICS, FIBRES, RUBBERS, RESINS, STARTING AND AUXILIARY MATERIALS, DEGRADATION PRODUCTS. By D. O. HUMMELL and F. SCHOLL. VCH: Weinheim. 1988. Price DM 580. 577 pp.

This volume is one of three. Volume 1 is entitled "Polymers Structures and Spectra", and Volume 3 "Additives and Processing Aids". This is Volume 2, and it deals with analytical methods, including spectroscopy and characteristic absorptions and descriptions of compound classes. At a price equivalent to approximately £240, I expected a "state of the art" work. I found this to be the case.

Synthetic and natural polymers and plastics form the subject matter. Analytical techniques include classical chemical, physical, pyrolytic, spectroscopic and chromatographic methods. As is to be expected from the nature of the subject the spectroscopic techniques, in particular the ones based on infra-red spectroscopy, form a major part of the volume. The brief mention of techniques based on analytical microscopy will disappoint many public analysts. However the depth of cover of the other techniques is such that this volume should quickly establish itself as a standard reference source, and certainly should be included in the library of the larger laboratory in the not too distant future.

P. CLARE