Pure & Appl. Chem., Vol. 70, No. 12, pp. 2309–2312, 1998.
Printed in Great Britain.

Laboratory proficiency testing programmes

John Gilbert and Alan L Patey

Ministry of Agriculture, Fisheries and Food, CSL Food Science Laboratory, Norwich Research Park, Colney, Norwich NR4 7UQ (UK).

Formal accreditation, operation of effective internal quality control procedures together with participation in laboratory proficiency testing schemes are key elements in ensuring the quality of results generated by analytical laboratories. A large number of commercial proficiency testing schemes are now in operation covering almost all sectors of analytical chemistry. In the UK a proficiency testing scheme for food analysis called FAPAS® has been operating since 1990, and covers a wide range of analytes. This scheme is used to exemplify the principles and approaches to laboratory proficiency testing.

INTRODUCTION

It is now widely accepted that there are three essential elements to laboratory quality assurance which assist the process of facilitating mutual recognition of results. These elements are:-

- Accreditation to EN45000 (involving third party auditing)
- Use of validated analytical methods
- Participation in laboratory proficiency testing

Formal adoption of these principles in the European Union in the sector of food testing is mandated in the Food Control Directive - Additional Measures (1) and more widely the principles are being accepted for laboratories involved in Import/Export Controls (2).

This paper concentrates on the latter aspect, that of proficiency testing, accreditation and validated methods being covered elsewhere (3, 4). The requirements for developing and operating proficiency testing schemes are outlined in an International Harmonised Protocol (5) together with ISO Guide 43 (6). There are a large number of proficiency testing schemes which operate world-wide and cover all sectors of chemical and biological measurement. For example in the UK alone there are schemes such as 'CONTEST' run by the Laboratory of the Government Chemist covering toxic contaminants in soil, 'AQUACHECK' run by WRC (Medmenham) covering water, soil, sludge and wastewaters, and 'Laboratory Environmental Analysis Proficiency Scheme' run by Yorkshire Environmental covering waters and industrial effluent. In the food sector the largest and most comprehensive proficiency testing scheme is run by CSL Food Science Laboratory in the UK and is called 'FAPAS®'. This scheme which covers a wide range of analytes including pesticides, nitrate and toxic elements is used in this paper to exemplify more generally the organisation and benefits of laboratory proficiency testing.

PARTICIPATION

Although some proficiency testing schemes are 'closed', meaning they are available only to specified laboratories, most schemes are 'open', require payment to participate and encompass international involvement. There are cost benefits to reasonably large population sizes (50 laboratories plus) taking part in each round of proficiency testing, as well as statistical benefits to data handing. During 1997/98 some 553 laboratories took part in FAPAS® originating from Africa (7), N.America (13), S. America (13), Asia (21), Australasia (10), Mid-Pacific (1) and Europe (488).

In proficiency testing each laboratory is free to use its method of analysis of choice. Useful correlations between methods and performance can be obtained from the proficiency testing reports, although the

*Lecture presented at the XI CHEMRAWN Meeting on Environmental Chemistry: Latin American Symposium on Environmental Analytical Chemistry, Montevideo, Uruguay, 15–20 March 1998.
Other presentations are published in this issue, pp. 2259–2336.

organisers are not judgmental and participants are left to draw their own conclusions about the relative merits of different methodologies. The identities of laboratories taking part in proficiency testing at all times remain confidential unless disclosure is authorised.

TEST MATERIALS AND ANALYTES

Since 1990, during the first seven year period of operation of FAPAS® some 17 different series of test materials were available, these being increased to 19 in 1988/99. Test materials must be as identical as possible to the normal sample that would be received for analysis. Some contaminants such as mycotoxins and veterinary drugs must be naturally incurred rather than spiked, although spiking is acceptable where the absence of matrix binding can be demonstrated. Some typical matrices for FAPAS® have included canned meat, sheep liver, peanut butter, wine, vegetable purée and apple juice. Analytes have included trace elements, veterinary drug residues, mycotoxins, nitrate, pesticides and food additives.

For example a typical test material which has been prepared was a purée of grapes containing 6 pesticide residues. In this case 12 kg of grapes (tested free of residues) were made into a purée and spiked with a solution of pesticides in acetone. The acetone was allowed to evaporate and the purée thoroughly mixed in a blender. The test material was divided into weighed aliquots (60-65 g) in sequentially numbered screw-capped jars and stored at -20°C prior to homogeneity testing and distribution.

HOMOGENEITY ANALYSIS

The underlying basis of successful proficiency testing is that each participant receives an identical test material. The International Protocol (5) requires that each test material is tested for homogeneity by a prescribed procedure and can only be issued for assessment of a particular analyte if either of two statistical tests is passed. The tests are the F-test or the s_s/σ test, where s_s is the square route of the sampling variance and σ is the target value for standard deviation (5). The latter test is passed if the numerical result is less that 0.3, this figure being derived by perception. If neither of these tests is passed then the test material cannot be issued and over the time period that FAPAS® has been in operation about 5% of candidate test materials have failed homogeneity and have been discarded. Overall 20% of test materials have analytes which fail the F-test, but do pass the s_s/σ test, and so it is still possible to issue these test materials.

PERFORMANCE MARKINGS

The International Protocol (5) recommends that performance marking of a laboratory's performance is given by z-score which is defined as:

$$z = (x-\hat{X})/\sigma$$

Where x is the measurement of analyte concentration in the test material.

$\hat{X}$ is the assigned value, the best estimate of the "true" concentration of the analyte.

and σ is the target value for standard deviation.

$\hat{X}$, the assigned value is usually obtained from the robust mean (7) of the entire data population for the analyte in question or exceptionally from results from a group of datum (i.e. specialist) laboratories. In FAPAS® a datum laboratory is defined as a laboratory having satisfactory performance in at least four out of the preceding five Rounds of testing for the group of analytes in question. Datum laboratories are used in areas of analytical difficulty such as trace element analysis, or where the participant population is too small. Target values for standard deviation (σ) are obtained from collaborative trial data (where available), or from the use of the Horwitz equation (8).

PROFICIENCY REPORTS

At the end of a round, which is usually 8 weeks after a test material is distributed, proficiency reports for individual participants are prepared and z-score markings are shown in both tabular and ordered histogram form. A typical example of the histogram presentation is shown in Figure 1 which shows the z-score data for 62 laboratories that analysed for the pesticide procymidone in grape puree test material. In this example 51 laboratories were in the z-score range between +2 and -2 which is deemed as being satisfactory (5, 7).

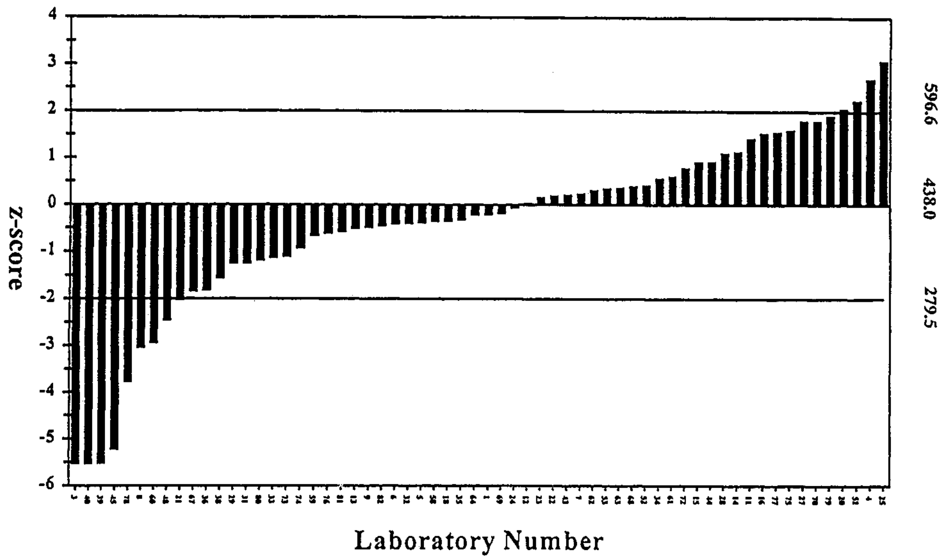

Fig 1 Typical histogram presentation of z-scores for FAPAS exercise (December 1997) for the determination of procymidone in grape puree test material.

PERFORMANCE TRENDS

Organochlorine pesticide analysis

During the period 1990-6 the overall satisfactory performance of organochlorine pesticide analyses carried out has progressively increased from a level of mid 60% to over 80%. The analytical performance for the individual pesticides present in the 15 test materials (bovine or vegetable oils) circulated during that time ranged from 64% being satisfactory for the determination of β-HCH to 86% satisfactory for 4,4-DDE. The levels of pesticides present in the oils varied with each test material with the lowest being at 15 µg/kg and the highest 1.08 mg/kg.

Trace element analysis

In 1991-5, 137 laboratories analysed the lead content (40 µg/kg - 2 mg/kg) of a range of test materials such as vegetable powders. Almost 1000 results were obtained with the overall performance of the set relatively stable at 75% satisfactory. Superficially it appeared that little improvement in analytical proficiency was occurring. However, when sub-sets of laboratories that had taken part in all the rounds were considered the picture was different. Looking at a sub-set of 22 similar UK laboratories which took part in nine rounds of testing at regular intervals, in the first four rounds 66% of the results were satisfactory for accuracy, but in the last four rounds 94% were satisfactory. In the UK at that time, 87 laboratories had taken part in at least two rounds of lead analysis. Only 44% of laboratories were satisfactory at their first participation, but this rose to 71% after continued participation.

Proficiency in analysis for mercury in foodstuffs revealed a different picture to lead where improvement in proficiency could only be demonstrated with reference to sub-sets of the population. In 1994-6, milk and vegetable powders were analysed for mercury (between 150 µg/kg and 365 µg/kg present) by 78 laboratories from 26 countries. During this period of time overall performance increased slowly, but regularly from an initial 80% satisfactory to 87% of the total population at the end of the period.

Improvement in performance

Some of the unsatisfactory performance markings for laboratories are due to simple reporting errors. However, on occasion the use of inappropriate methodology can be detected. As an example of this in a round of veterinary drug residue testing the laboratories that used immunological techniques grossly overestimated the level of drug present in contrast to the results from those laboratories that used a range of other methods. With this latter purpose in mind the final reports of FAPAS® rounds contain a section which describes in summary form the methods of analysis used. Thus participants can see the methods used by satisfactory, questionable and unsatisfactory performers alike and so may decide to change aspects of their own methods in the future.

CONCLUSION

Unquestionably participation in proficiency testing is an essential element in quality assurance for laboratories involved in chemical measurement. As participation increases so more specialised schemes will be developed to match the needs of laboratories in terms of testing measurement of specific analytes in varied matrices.

REFERENCES

1. European Community. Council Directive 93/99EEC on the Subject of Additional Measures Concerning the Official Control of Foodstuffs, Official Journal of the European Communities L290 of 24th November 1993.
2. Report of the 21st Session of Codex Committee on Methods of Analysis & sampling, FAO, Rome, 1997, ALINORM97/23A.
3. Food & Drink Laboratory Accreditation - a Practical Approach by S Wilson & G Weir, Published by Chapman & Hall, London, 1995
4. M. Thompson, R. Wood, Pure Appl. Chem., 67, 649-666, (1995)
5. M. Thompson, R.Wood, JAOAC International 76, 926-940 (1993).
6. International Organisation of Standardisation, *Development and Operation of Laboratory Proficiency Testing*, ISO Guide 43, Geneva, Switzerland (1984).
7. UK Ministry of Agriculture, Fisheries and Food, Protocol for the Food Analysis Performance Assessment Scheme, Organisation and Analysis of Data, (1990).
8. W. Horwitz, Anal. Chem., 54, 67A-76A (1982).