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Preliminary Estimates of the Between-Laboratory Variability from Rounds 1 - 4 of the IWTO Wool Residue Interlaboratory Proficiency Program 1999 - 2001

By

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SUMMARY

An initial IWTO wool residue interlaboratory proficiency program was conducted by the Australian National Residue Survey (NRS) from March 1999 to March 2001. As the program operated for only five rounds of testing, and as participation progressively declined, the statistical data to estimate the between-laboratory uncertainty are limited.
However, when the available data are examined, values for the between-laboratory uncertainty are consistent with the empirical Horwitz function that summarises the results from around 10,000 other interlaboratory chemical analysis data sets obtained for matrices from geological to agricultural, and for analytes from metals to pesticides to biological materials. The Horwitz function suggests that analytical uncertainty increases as the concentration of the analyte decreases and it has been shown to be relatively independent of the analyte, matrix, and analytical method.
This is a satisfactory result for the initial rounds from the IWTO wool residue proficiency program, given the difficulties presented by the extremely complex wool wax matrix.
The interlaboratory program is to be restarted in early 2005 with support from Australian Wool Innovation Ltd, again using Australia's NRS. The data from the forthcoming program will be added to the existing data to improve the estimation of the between-laboratory variabilities for the different pesticide groups.

REPORT

INTRODUCTION

Draft Test Method 59 for testing of pesticide residues on greasy wool [1] differs from most IWTO test methods in that it is non-prescriptive. This is to allow the most cost effective analytical methodology to be developed and modified as improvements in technology arise.

The test method has two main provisions,

1. that the Laboratory is shown to be proficient in an IWTO approved interlaboratory proficiency testing program and

2. that the laboratory meets the requirements of ISO/IEC 17025 for the specific method that is used to produce test certificates.

In a situation where test methods are not prescribed, a laboratory would generally need to demonstrate its proficiency by successful participation in an interlaboratory proficiency program to demonstrate the technical proficiency required by ISO/IEC 17025. The IWTO Interlaboratory Proficiency Program is therefore of central importance if IWTO is to establish a pesticide residue test method.

RESULTS FOR PROFICIENCY ROUNDS 1 – 4

An IWTO initial interlaboratory residue test program was conducted by the Australian National Residue Survey (NRS), and operated between March 1999 and March 2001 with five reports being produced [2-6]. The program ceased in 2001 when, for a number of reasons, participation declined and funding support was withdrawn.

Because this interlaboratory program only operated for a short period and with limited participation, it was not possible to accurately calculate the between-laboratory variability for individual analytes, and it is only possible to approximately estimate the variability for groups of analytes, for organophosphates, synthetic pyrethroids and for analytes that had separate programs (cyromazine, dicyclanil, triflumuron and diflubenzuron). There were too few laboratories to allow meaningful statistics for the organochlorines. Only the first four rounds are included in this analysis as participation in Round 5 was too small.

The accompanying report [7] indicates that the interlaboratory program will be re-started with support from Australian Wool Innovation Limited (AWI) and, as more data are obtained, it will be possible to generate more robust figures. This will also depend on having enough laboratories participating in all chemical classes so that an improved statistical evaluation of the data can be undertaken.

From the initial interlaboratory program, an examination of the variability of the median values generated by all laboratories for all of the analytes (other than organochlorines) from Rounds 1 - 4 provided the following initial estimates of between-laboratory variability and expanded uncertainty (Table 1).

Table 1. Between-laboratory CV(%) and expanded uncertainties estimated from proficiency test data.

Analyte(s)	**Between Lab Uncertainty (% CV of median)**	**Expanded Uncertainty (95 % Confidence estimates)***	**Concentration Range (mg/kg)**
organophosphates	16	32	0.6 – 8
synthetic pyrethroids	18	36	0.7 – 5
dicyclanil	22	44	1.6 – 12.8
cyromazine	28	56	1 – 9
triflumuron	11	22	1.7 – 27
diflubenzuron	17	34	2 – 12.5

 # CVs (%) for each analyte group represent the average of the robust CVs determined for each analyte of the group in Rounds 1 – 4 proficiency tests; outliers excluded

**The 95 % confidence levels are obtained by multiplying the between laboratory uncertainty by a coverage factor of 2.*

While there are no statistical data available for the organochlorines, the between-laboratory uncertainty appears to be similar to that for organophosphates and synthetic pyrethroids (i.e. around 15 %).

While the concentration range for the pesticides on wool is very narrow and the data are very limited, the figures are similar to those generated by the empirical Horwitz function [8,9] and those outlined by others for this concentration range [10].

HORWITZ FUNCTION

Horwitz derived a simple empirical exponential function from examination of almost 10,000 interlaboratory data sets obtained between 1915 and 1995 from collaborative trials (i.e. method performance studies for which analytical methods were prescribed), at concentrations from ng/kg (10^{-12}) to 100% pure, for matrices from geological to agricultural, and for analytes from metals to pesticides to biological materials. The Horwitz function is relatively independent of the analyte, matrix, and measurement method and suggests that analytical uncertainty increases as the concentration of the analyte decreases. Empirically the uncertainty doubles for each decrease in concentration by a factor of 100.

A recent study by Alder *et al.* [10] specifically examined interlaboratory proficiency tests performed with pesticides in fatty matrices. The between-laboratory uncertainty (expressed as a percentage of the concentration was 16% at a concentration of 1 mg/kg and 23% at 0.1 mg/kg, values consistent with the Horwitz function, and, importantly, with the results in Table 1.

In general the results from these initial rounds of the first interlaboratory testing are regarded as satisfactory given that:

1. this was the first interlaboratory program performed with this particularly difficult matrix,
2. a variety of sample extraction and analysis techniques were used,
3. some of the samples were spiked at near to the limits of reporting (1 mg/kg) for some of the analytes, and
4. these proficiency test results also include an uncertainty component due to the fact that analytical methods were not prescribed which was not the case for the data used to derive the Horwitz function.

The analytical uncertainty is expected to exceed the Horwitz predictions as the limits of reporting are approached. At the limits of detection, the response from the analyte becomes indistinguishable from the response from the matrix.

It is interesting to note that the analytes that gave the highest between-laboratory variability were cyromazine and dicyclanil. This higher observed between-laboratory variability may reflect the fact that these polar compounds have different physical and chemical characteristics to the fat-soluble pesticides and consequently are more difficult to analyse in this matrix (different extraction/cleanup procedures required) and/or the fact that the chemicals appear to be more associated with the wool fibre than the wool grease. Alder *et al* [10] noted that measurement uncertainty in relation to pesticide residues increased in non-fatty matrices compared with fatty matrices. Additional wool proficiency test data may help clarify this issue.

CONCLUSION

Most IWTO test methods are based on physical measurements using prescribed equipment and standardized methodologies. Most operate over quite narrow ranges, where the highest and lowest results may vary by less than an order of magnitude. In contrast, residues of pesticides in wool samples may vary by four orders of magnitude.

More importantly, a demonstration of laboratory proficiency depends not only on reliably estimating the concentration of each analyte, but also on not reporting false positive results and false negative results in the very complex wool wax matrix [7].

The measure used to assess the quality of the initial IWTO interlaboratory chemical residue testing program should be the same measure used to assess other interlaboratory chemical residue testing programs. On that basis this preliminary analysis indicates that the initial rounds of the IWTO interlaboratory program are consistent with the vast history of other chemical analysis proficiency programs.

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