COMMISSION RECOMMENDATION

of 3 March 1999

concerning a coordinated Community monitoring programme for 1999 to ensure compliance with maximum levels of pesticide residues in and on cereals and certain products of plant origin, including fruit and vegetables

(notified under document number C(1999) 478)

(Text with EEA relevance)

(1999/333/EC)

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Community,

Having regard to Council Directive 86/362/EEC of 24 July 1986 on the fixing of maximum levels for pesticide residues in and on cereals [1], as last amended by Directive 97/71/EC [2], and in particular Article 7(2)(b) thereof,

Having regard to Council Directive 90/642/EEC of 27 November 1990 on the fixing of maximum levels for pesticide residues in and on certain products of plant origin, including fruit and vegetables [3], as last amended by Directive 97/71/EC, and in particular Article 4(2)(b) thereof,

Whereas Article 7(2)(b) of Directive 86/362/EEC and Article 4(2)(b) of Directive 90/642/EEC require the Commission to submit to the Standing Committee on plant health by 30 September each year a recommendation setting out a coordinated Community monitoring programme to ensure compliance for maximum levels of pesticide residues set out in the Annexes II to the said Directives;

Whereas the Commission should recommend a monitoring programme each year; whereas experience gained by the Commission and the Member States in establishing, carrying out and reporting on the three previous annual coordinated monitoring programmes indicates that multiannual programmes appear to be most effective and practical; whereas it appears appropriate to indicate in this recommendation the framework of future programmes;

Whereas the Commission should progressively work towards a system which would permit the estimation of actual pesticide dietary exposure, as provided for in the second paragraph of Article 7(3) of Directive 86/362/EEC and the second paragraph of Article 4(3) of Directive 90/642/EEC; whereas to facilitate examination of the feasibility of such estimations, data concerning the monitoring of residues of pesticides in a number of food products which constitute major components of European diets should be available; whereas in view of the resources available at national level for pesticide residue monitoring, Member States are only able to analyse samples of four products each year within a coordinated monitoring programme; whereas each pesticide should generally be monitored in 20 food products over a series of five-year cycles;

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[1] OJ L 221, 7.8.1986, p. 37.
[2] OJ L 347, 18.12.1997, p. 97.
[3] OJ L 350, 14.12.1990, p. 71.

Whereas the residues recommended to be monitored in 1999 and 2000 will allow examination of the feasibility of using the data concerning the pesticides acephate, the benomyl group, chlorpyriphos, iprodione and methamidophos as these compounds (identified as Group A in Annex IA) have already been monitored between 1996 and 1998 for estimation of actual dietary exposure;

Whereas the residues recommended to be monitored in 1999, 2000 and 2001 will allow examination of the feasibility of using the data concerning the pesticides diazinon, metalaxyl, methidathion, thiabendazole and triazophos as these compounds (identified as Group B in Annex IA) have already been monitored between 1997 and 1998 for estimation of actual dietary exposure;

Whereas the residues recommended to be monitored in 1999, 2000, 2001 and 2002 will allow examination of the feasibility of using the data concerning the pesticides chlorpyriphos-methyl, deltamethrin, endosulfan, imazalil, lambda-cyhalothrin, the maneb group, mecarbam, permethrin, pirimiphos-methyl and vinclozolin as these compounds (identified as Group C in Annex IA) have already been monitored in 1998 for estimation of actual dietary exposure;

Whereas a systematic statistical approach to numbers of samples to be taken in the specific coordinated exercise is necessary; whereas such an approach has been set out by the commission of the Codex Alimentarius [1]; based on a binomial probability distribution it can be calculated that examination of a total sample number of 459 gives a 99 % confidence of detecting one sample containing pesticide residues above the LOD if it is anticipated that 1 % of products of plant origin will contain residues above the LOD; whereas the total number of samples to be taken by each Member State should be apportioned on the basis of population and consumer numbers, with a minimum of 12 samples per product and per year, and indicated in Annex IB;

Whereas draft guidelines concerning quality control procedures for pesticide residue analysis, published in Annex II [2] have been discussed by the experts of the Member States at Oreias, Portugal on 15 and 16 September 1997 and discussed and taken note of in the subgroup pesticide residues of the working group on plant health on 20 and 21 November 1997; whereas it is agreed that these draft guidelines should be implemented as far as possible by the analytical laboratories of the Member States and should be reviewed in the light of this experience;

Whereas Article 4(2)(a) of Directive 90/642/EEC requires Member States to specify the criteria applied in drawing up their national inspection programmes when sending to the Commission information on their implementation during the previous year; whereas such information should include the criteria applied in determining the numbers of samples to be taken and analyses to be carried out and the reporting levels applied and the criteria by which the reporting levels have been fixed; whereas details of accreditation under Council Directive 93/99/EEC of 29 October 1993 on the subject of additional measures concerning the official control of foodstuffs [3] of the laboratories carrying out analyses should be indicated;

Whereas information on the results of monitoring programmes is particularly appropriate for treatment, storage and transmission by electronic/informatic methods; whereas formats have been developed for supply in diskette form to the Member States by the Commission; whereas Member States should therefore be able to send their reports to the Commission in the standard format; whereas the further development of such a standard format is most effectively undertaken by the development of guidelines by the Commission;

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[1] Codex Alimentarius, Pesticide Residues in Foodstuffs, Rome 1994, ISBN 92-5-203271-1; Vol. 2, page 372.
[2] Previously published as Commission document VI/7826/97.
[3] OJ L 290, 24.11.1993, p. 14.

Whereas the measures provided for in this recommendation are in accordance with the opinion of the Standing Committee on Plant Health,

HEREBY RECOMMENDS THE MEMBER STATES TO:

1. sample and analyse for the product/pesticide residue combinations set out in Annex IA, on the basis of the number of samples of each product allocated to each Member State in Annex IB, reflecting as appropriate, national, Community and third country share of the Member State's market; for at least one pesticide possibly posing an acute risk, one of the products will be subjected to individual analysis of the items in the composite sample; two samples of an appropriate number of items will be taken, where possible the produce of a single producer; if in the first, composite sample a detectable level of the pesticide is found, the items of the second sample will be analysed individually; in 1999 this will include the combination peppers and methamidophos;

2. by 31 August 2000 report the results for the part of the specific exercise allocated for 1999 in Annex IA, together with the analytical methods used and reporting levels achieved, in accordance with the quality control procedures set out in Annex II, in a format as set out in Annex III [1];

3. by 31 August 1999, send to the Commission and to the Member States all the information as required by Article 7(3) of Directive 86/362/EEC and Article 4(3) of Directive 90/642/EEC concerning the 1998 monitoring exercise to ensure, at least by check sampling, compliance with maximum pesticide residue levels including:

   3.1. the results of their national programmes concerning pesticides listed in the Annexes II of Directives 86/362/EEC and 90/642/EEC, in relation to harmonised levels and, where these have not yet been fixed at Community level, in relation to the national levels in force;

   3.2. information on their laboratories' quality control procedures and, in particular, information concerning aspects of the guidelines concerning quality control procedures for pesticide residue analysis (Annex II) which they have not been able to apply or have had difficulty in applying;

   3.3. information on accreditation in accordance with the provisions of Article 3 of Directive 93/99/EEC (including type of accreditation, accreditation body and copy of accreditation certificate) of the laboratories carrying out the analyses.

This recommendation is addressed to the Member States.

Done at Brussels, 3 March 1999.

For the Commission
Franz FISCHLER
Member of the Commission

[1] Previously published as Commission document VI/1609/97.

ANNEX IA

Pesticide/product combinations to be monitored in the specific exercise set out in point 1 of the recommendation

Pesticide residue to be analysed for	Years (1)			
	1999	2000	2001 (2)	2002 (3)
GROUP A				
Acephate	(a)	(b)		
Benomyl group	(a)	(b)		
Chlorpyriphos	(a)	(b)		
Iprodione	(a)	(b)		
Methamidophos	(a)	(b)		
GROUP B				
Diazinon	(a)	(b)	(c)	
Metalaxyl	(a)	(b)	(c)	
Methidathion	(a)	(b)	(c)	
Thiabendazol	(a)	(b)	(c)	
Triazophos	(a)	(b)	(c)	
GROUP C				
Chlorpyriphos-methyl	(a)	(b)	(c)	(d)
Deltamethrin	(a)	(b)	(c)	(d)
Endosulfan	(a)	(b)	(c)	(d)
Imazalil	(a)	(b)	(c)	(d)
Lambda-cyhalothrin	(a)	(b)	(c)	(d)
Maneb group	(a)	(b)	(c)	(d)
Mecarbam	(a)	(b)	(c)	(d)
Permethrin	(a)	(b)	(c)	(d)
Pirimiphos-methyl	(a)	(b)	(c)	(d)
Vinclozolin	(a)	(b)	(c)	(d)

(1) Indicative for 2000, 2001 and 2002, subject to programmes which will be recommended for these years.
(2) Group D to be specified later.
(3) Groups D and E to be specified later.
(a) cauliflower (fresh or frozen), pepper, wheat (grain), melon (not squash or watermelon)
(b) rice (husked or polished), cucumber, head cabbage, peas (frozen or fresh, analysed without pods)
(c) apples, barley, tomatoes, lettuce
(d) pears, bananas, beans (fresh or frozen), potatoes.

ANNEX IB

Number of samples of each product to be taken by each Member State, in the coordinated Community monitoring programme for 1999

B	DK	D	EL	E	F	IRL	I	L	NL	A	P	FIN	S	UK	Total
12	12	93	12	45	66	12	65	12	17	12	12	12	12	66	460

ANNEX II

Quality control procedures for pesticide residues analysis

Introduction

1. Data on pesticide residues may be used for checking compliance with maximum residue limits (MRLs), to support enforcement actions, or to assess consumer exposure to pesticides. Analysis of residues is challenging and appropriate quality control procedures are essential to demonstrate the validity of results, without incurring unnecessary costs. Pesticide residues must be identified correctly in order to be quantified. Where knowledge of the quantity of the residue detected is important, the more stringent of the requirements in this document will apply. Less stringent alternatives are provided if the exact level of residues is relatively unimportant – for example, where it is sufficient to know that the residues comply with MRLs. A glossary of terms is appended.

Operating principles

2. Laboratory operations should meet the requirements of a recognised accreditation scheme, which complies with EN45001 or good laboratory practice (GLP).

3. The laboratory must participate in appropriate proficiency testing schemes, such as those organised by the European Commission, FAPAS and CHEK. Where unacceptable z-scores are achieved, the problems should be rectified before proceeding with further analyses for the pesticides involved.

4. For quantitative results, critical weights and volumes must be measured using equipment of accuracy within ± 2 %, preferably within ± 1 %. Weighing and volumetric equipment must be calibrated, maintained and used according to the manufacturer's instructions. A similar approach should be adopted for spectrometric equipment requiring calibration for wavelength, mass/charge ratio, etc. As far as practicable, analyses should encompass the components defined by MRLs.

Sampling, transport, processing and storage of samples

Sampling

5. Samples should be taken in accordance with Council Directive 79/700/EEC [1], or superseding legislation. Where it is impractical to take primary samples randomly within a lot, the method of sampling must be recorded.

Sample transportation

6. Samples must be transported to the laboratory in clean containers and robust packaging. Polythene bags, ventilated if appropriate, are acceptable for most samples but low-permeability bags (e.g. nylon-film) must be used for samples to be analysed for residues of fumigants. Samples of commodities pre-packed for retail sale should not be removed from their packaging before transport. Very fragile or perishable products (e.g. ripe raspberries) may have to be frozen to avoid spoilage and then transported in 'dry ice' or similar, to avoid thawing in transit. Similarly,

[1] OJ L 207, 15.8.1979, p. 26.

samples which are frozen at the time of collection must be transported without thawing. Samples which may be damaged by chilling (e.g. bananas) must be protected from both high and low temperatures. Samples must be identified clearly and indelibly, using labels which cannot be detached inadvertently. The use of marker pens containing organic solvents should be avoided for labelling bags containing samples to be analysed for fumigant residues. Rapid transmission to the laboratory, preferably within one day, is essential for most samples. Perishable, fragile or heavy samples, which are likely to deteriorate and/or be damaged in transit, require special care in packing. The condition of samples delivered to the laboratory should approximate to that acceptable to a discerning purchaser, otherwise samples should normally be considered unfit for analysis.

Sample processing for analysis

7. On receipt, each sample must be allocated a unique reference code by the laboratory.

8. Sample processing and sub-sampling must take place before visible deterioration of the sample occurs. Canned, dried or similarly processed samples must be analysed within the shelf-life, unless stored in deep freeze.

9. Sample processing and storage procedures should be demonstrated to have no significant affect on measured residues. Samples should be homogenised, comminuted and/or mixed before withdrawing portions for analysis. Where labile residues could otherwise be lost in this process, samples may be comminuted frozen (i.e. in the presence of 'dry ice' or similar). Where comminution, etc. is known to affect residues (e.g. of dithiocarbamates or fumigants) and practical alternative procedures are not available, the analytical portion may consist of whole units of the commodity, or segments removed from whole units. If the analytical portion thus consists of few units or segments, it is unlikely to be representative of the analytical sample and replicate portions must be analysed from the outset, to provide a better indication of the mean value. All analyses should be undertaken within the shortest time practicable, to minimise the need for sample storage. Analyses for residues of very labile or volatile pesticides may have to be completed on the day of sample receipt.

Pesticide standards, calibration solutions, etc.

Identity and purity of standards

10. Reference standards (including pesticides, their metabolites, derivatives or degradation products) and internal standards should be of known purity, where possible. On receipt, they must be dated, given a unique reference, and allocated an expiry date. The expiry date allocated may differ from that given by the supplier of the reference standard, if it is known to be appropriate to the pesticide under the storage conditions employed. Certified standards should, and uncertified standards must, be checked for identity and (approximate) purity by chromatography, infrared spectrophotometry, mass spectrometry (MS) or nuclear magnetic resonance spectrometry. As far as practicable, the reference spectrum used for this purpose should have been, or should be, rationalised as compatible with the chemical structure of analyte. After the allocated expiry date, reference standards may be retained if the purity is shown to remain acceptable but a new expiry date must be allocated. Otherwise they must be replaced. The relative purity of new and old reference standards of the same pesticide may be determined by comparing the detector responses obtained from concurrent, freshly-prepared dilutions of the old and new materials (see also point 15). Differences between old and new reference standards that are not attributable to differences in quoted purity should be investigated and the length and/or conditions of storage revised, as appropriate.

11. The chromatographic response, etc., obtained from the standard must be demonstrated as attributable to the analyte, prior to analysis of samples and preferably by MS. Where the detected species is a pyrolysis product which is also a metabolite of the pesticide [1], an alternative detection system must be used if the metabolite is not included in the definition of the MRL.

Storage of standards

12 Reference standards may be stored in their original containers, if suitable, but the caps must not be of rubber materials. If a standard changes visibly during storage it must not be used without checking the purity, unless this is due to simple freezing and melting. Standards of pesticides should be stored according to manufacturers' instructions (where given), to minimise degradation. Generally, storage at low temperature (refrigerator or freezer) in the dark is satisfactory. The containers must be sealed to avoid entry of water, which is especially likely during equilibration to room temperature.

Preparation, use and storage of analyte standard solutions, suspensions, etc.

13. Preparation of pesticide solutions (or solid dilutions) requires careful attention to detail. The identity and mass (or volume, for highly volatile compounds) of the reference standard, the identity of the solvent (or other diluent) employed, and the calibrated volumes of flasks and pipettes used, must be recorded. Amorphous solid compounds should be homogenised before removing a portion for weighing. Initial (stock) and subsequent (working) dilutions should be uniquely identified, permanently labelled and the concentrations corrected for the purity of the reference standard (where this is known with certainty). Individual aliquots of solutions used for calibration need not be uniquely identified but their origin and method of preparation must be recorded.

14. The pesticide must not react with, and should have adequate solubility in the solvents used to prepare solutions. The solvents must be appropriate to the method of analysis and be compatible with the determination system used. Adsorption onto containers, particularly of ionic pesticides, must be avoided by addition of acid, silanisation of glassware, or use of plastic containers, as appropriate, but such measures must not lead to interference with the subsequent detection of the pesticide. Not less than about 10 mg of the pesticide reference standard should be weighed, directly into a volumetric flask if practicable. Alternatively, the pesticide may be weighed into a pre-weighed (or tared) vessel and quantitatively transferred by rinsing with solvent to a volumetric flask. Volatile liquid pesticides should be dispensed by weight or volume (if the density is known) directly into a less volatile solvent in a volumetric flask. Gaseous fumigants may be dispensed by bubbling into solvent and weighing the mass transferred, or by preparing gaseous dilutions (e.g. with a gas-tight syringe). In the latter case, the mixture must not contact reactive metals.

15. Pesticide solutions (or solid phase dilutions) must be allocated an expiry date, after which they should normally be discarded. Newly prepared stock solutions should be diluted (in a matrix extract, if appropriate) and compared with those to be discarded. If the mean response of the detector to the new solution differs by more than ± 5 % from the old one [2], the new solution should be checked for accuracy against a further newly prepared one. The number of determinations required for this comparison is dependent upon the precision of the detection system used. If the response from the old stock standard is confirmed as > 5 % lower than the new standard, the storage period for solutions must be shortened or the storage conditions improved. If the responses from old and the new stock standards do not differ significantly, a longer storage period may be considered. Aqueous suspensions of dithiocarbamates and solutions

[1] For example, 4,4′-dichlorobenzophenone from dicofol, tetrahydrophthalimide from captan and captafol, phthalimide from folpet, 2-chlorobenzonitrile from clofentezine.

[2] Alternatively, a t-test of the means should not show a significant difference at the 5 % level.

(or gaseous dilutions) of highly volatile fumigant pesticides must be prepared freshly and comparison of new and old standards is inappropriate. The validity of such a standard may be checked by comparison with one that is freshly, and independently, prepared.

16. The response of some detection systems (e.g. GC, LC-MS, ELISA) to certain pesticides may be affected by the presence of co-extractives from the sample. These 'matrix effects' may be observed as increased or decreased responses, compared with those produced by simple solvent solutions of the analyte. Partition in headspace analyses and SPME is also frequently affected by components present in the samples. GC enhancement or suppression effects may reflect increased or decreased transmission efficiency of the pesticide through the injector, compared with that in solvent only. Effects on MS response may be produced by co-eluting matrix components influencing the efficiency of ionisation or ion collection. The presence, or absence, of such effects may be demonstrated by comparing detector response to the analyte in a simple solvent solution with that obtained from the matrix-matched equivalent. Matrix effects can be very variable and unpredictable in occurrence and an initial demonstration of a measurable effect, or none, does not indicate that this situation will not change subsequently. More reliable calibration may be obtained in such cases if the calibration solutions are matrix-matched. The 'matrix concentration' employed should be consistent for all analyses in a batch. Samples known not to contain detectable residues or interfering compounds (i.e. 'blanks') may be used to prepare extracts for matrix-matched calibration solutions, etc. The blank extracts required for this may be prepared most conveniently during the extraction of batches of samples. These blank extracts may also be analysed without addition of pesticides, to demonstrate whether contamination has occurred during extraction and clean-up, and whether detector responses to matrix components interfere with analyte determination. Calibration solutions that are matrix-matched and/or that are of mixed pesticides may be less stable than solutions of individual pesticides in pure solvent.

17. Solutions should not be exposed to direct sunlight and should be stored at low temperature in the dark, in a refrigerator or freezer, sealed to avoid loss of solvent or entry of water. Solutions removed from low temperature storage should be equilibrated to room temperature and remixed before use.

18. Unless calibration solutions and extracts are internally standardised, unmeasured losses of the solvent by evaporation are unacceptable. Solvent losses from small volumes are difficult to monitor and, in the absence of an internal standard, great care is required to avoid evaporation. Where an internal standard is used, evaporation losses should also be minimised, to avoid influencing matrix effects (see point 16). Septum closures are particularly prone to evaporation losses (in addition to being a source of contamination) and should be replaced as soon as practicable after piercing, if extracts in vials are to be retained.

Extraction and concentration

Extraction conditions and efficiency

19. Analytical portions should be disintegrated thoroughly before or during extraction, to maximise extraction efficiency, except where it has been demonstrated that the nature of the process (e.g. supercritical fluid extraction, SFE, of certain sample types) renders disintegration unnecessary. Over-heating during extraction must be avoided to minimise solvent or pesticide losses. Temperature, pH, etc. must be controlled if they are known to affect extraction efficiency and/or pesticide stability.

20. Where total extraction of the residue from the analytical portion is not intended, with only an aliquot of the extract removed from the extraction mixture, the volume of solvent added initially should be measured to within ± 1 %. Solvent evaporation prior to removing the aliquot must be avoided or measured (by weight or by internal standard addition). Where solvent loss exceeding 1 % may occur with this type of extraction, the loss should be measured routinely.

Extract concentration and dilution to volume

21. Great care is required where extracts are to be evaporated to dryness, as trace quantities of many pesticides may be lost from surfaces in this way. A small quantity of a high boiling point solvent may be used as a 'keeper' and the evaporation temperature should be as low as practical. Frothing and vigorous boiling of extracts, or dispersion of droplets, must be avoided. A stream of dry nitrogen or centrifugal evaporation is generally preferable to the use of an air stream for small-scale evaporation, as air is more likely to lead to oxidation or to introduce water and other contaminants.

22. Where extracts are to be made up to a specified volume, accurately calibrated vessels of not less than 1 ml capacity should be used. Where dried extracts are dissolved in a fixed volume of solvent delivered from a syringe, or similar, the solvent should have a boiling point high enough to avoid further evaporation. Where the final solvent volume is not measured directly, a fixed mass of internal standard should be added to enable measurement of the volume, particularly for volumes less than 1 ml.

23. The stability of pesticides in extracts can vary greatly according to the pesticide and the nature of the extract. Although storage of extracts in a refrigerator or freezer may be helpful, the loss during a day at the temperature of an autosampler rack mounted on a GC may equal that occurring during a month's storage in deep freeze. Pesticide stability in extracts should be investigated during method validation.

Contamination and interference

Contamination

24. Samples must be separated from each other, and from other sources of potential contamination, during transit to, and storage at the laboratory. This is particularly important with surface or dusty residues, or with volatile pesticides, and samples which could bear such residues should be doubly-sealed in polythene or nylon bags and transported and processed separately. Pest control measures taken in or near the laboratory, if essential, must be limited to the use of products which will not be sought as residues.

25. Solvents (including water), reagents, filter aids, etc. should be checked for possible interference problems. Solvents used for fumigant residues analysis may be particularly problematic because solvent impurities and the pesticide may have similar volatilities and could be chemically identical to the residues.

26. Equipment and containers used for residues analysis must be free from significant interfering contaminants. Reusable volumetric equipment, such as flasks, pipettes and syringes, must be cleaned scrupulously. Separate glassware, etc. should be allocated to calibration standards and to sample extracts. Rubber and plastic items (e.g. seals, protective gloves, wash bottles), polishes and lubricants are potential sources of analytical interference. Contamination by dithiocarbamates, ethylenethiourea and diphenylamine from rubber articles or some lubricating oils is particularly problematic, because it is indistinguishable from pesticide residues.

27. Vial seals should be PTFE-lined. Extracts should be kept out of contact with seals, especially after piercing, by keeping vials upright. Vial seals must be replaced quickly after piercing, if re-analysis of the extracts is necessary. Disposable vials should not be reused.

28. Where an internal standard is used, unintended contamination of extracts or pesticide solutions with the internal standard, or vice versa, must be avoided.

Interference

29. Interference from natural constituents of samples, co-extracted during residues analysis, is frequent and must be recognised. Where the analyte occurs naturally in, or is produced from, the sample (e.g. inorganic bromide in all commodities; sulfur in soil; or carbon disulfide produced from the *Cruciferaceae*), low-level residues from pesticide use cannot be distinguished from natural levels. Natural occurrence of these analytes must be taken into account in planning analyses and in the interpretation of results. Not all interference produces simple, positive detector responses. Suppression or enhancement effects on gas chromatographic transmission, or on ion generation/collection efficiency in MS, may be produced by co-eluting pesticides or sample matrix components. Wherever this could occur, the response of the detection system to pesticides should be assessed, individually and with other pesticides, in pure solvent and in relevant 'blank' extracts. Reagent blanks (procedural blanks) should be analysed at method validation, and at any time thereafter that it is necessary to distinguish interference due to the matrix from that which could be introduced during analysis.

Analytical calibration and chromatographic integration

Basic requirements for acceptable calibration

30. In a batch of determinations, the calibration should derive from two or more replicate measurements of detector response at each level. In all cases, the detector responses used to quantify residue levels must be within the dynamic range of the detection system.

31. In determining the presence or absence of measurable residues in samples, residues below the lowest calibrated level (LCL, corresponding to the intended reporting limit) should be reported as '< [LCL] mg/kg', whether or not a response to the analyte is evident. Where it is considered necessary to report measurable residues that are below the LCL initially used, further determinations must be performed using a new and lower LCL.

32. Where an analysis batch includes samples with residues about, or below, the LCL, the detector response to the analyte must be qualitatively distinguishable and measurable at the LCL. Where the response to the intended LCL is inadequate, a higher calibration level which meets the criteria must be adopted as the LCL. In general, a minimum signal/noise ratio (S/N) of 3:1 is acceptable for the LCL, although this may apply to summed signals, for example with MS data. Although S/N is often expressed in terms of 'electronic' or 'detector' noise, 'chemical noise' from co-eluting interfering compounds must also be taken into account.

33. Calibration by interpolation between two levels is acceptable where the mean response factors for each level indicate linearity of response (i.e. the lower being not less than 90 % of the higher response factor). Where three or more levels are utilised, an appropriate calibration line may be fitted. The calibration line should not normally be forced through the origin. Where calculations are computerised, the fit of the calibration must be inspected visually, avoiding reliance on correlation coefficients, to ensure that the fit is satisfactory in the region relevant to the residues detected. Where the difference between calibration levels is large and interpolation appears questionable, the individual levels may be used as single-point calibrations.

34. Calculation of residues or recovery data by extrapolation from the calibrated levels may introduce inaccuracies related to the degree of extrapolation. Calculation from a single calibration point is most likely to involve extrapolation and assumes a linear response, with the

intercept at the origin. Extrapolation is acceptable for calculation of results exceeding the LCL, if the sample response is within ± 10 % of the calibration response where the MRL is exceeded, or is within ± 50 % where the MRL is not exceeded. Where the level of addition for recovery corresponds to the LCL, recovery < 100 % may be calculated by extrapolation, although the estimate may be inaccurate.

35. Calibration at two or more levels, with, for example, additional calibration at two times the target LCL, provides a back-up LCL if the target level is not measurable and usually allows a wider range of residue levels to be estimated more accurately. Single-level calibration may be used in screening to determine whether or not the calibration level is exceeded by residues or, alternatively, to quantify residues that are at, or close to, the calibration level. The latter application may provide more accurate results than multi-level calibration where the detector response is variable.

36. Extracts containing high-level residues may be diluted to bring them within the calibrated range but it may be necessary to adjust the 'concentration of matrix' in the calibration solutions, because the matrix effects on the response may be diminished by dilution of the matrix components present in sample extracts, etc.

Calibration in batches of determinations

37. In a sequence of determinations (e.g. chromatography), the calibration determinations must bracket the samples. That is, each sequence must begin and end with calibration. Intermediate calibrations may be required if the response of the detection system is too variable. In parallel determinations (e.g. ELISA using 96-well plates), the calibrations should be distributed to detect differences in response due to position.

38. In general, batch sizes for determination should be adjusted so that detector responses to replicate bracketing calibrations do not differ by more than 20 %. Where the response differs by more than 20 %, the determinations should be repeated in smaller batches. Repeat of determinations is not necessary for samples which contain residues < LCL, if the LCL response remains measurable throughout the batch.

39. Residues to be quantified accurately must be accompanied by appropriate calibration. Wherever practicable, the detection system should be calibrated for all analytes sought, in every batch of analyses. Where, for multi-residue screening, this would require a disproportionately large number of calibration determinations in each batch (for example, where many analytes must be determined in separate solutions, because they would otherwise interfere with one another), the detection system must be calibrated for 'reference' pesticides, as a minimum, in each batch of sample analyses. 'Reference' pesticides are defined in sub/paragraphs 39.1 and 39.2 below. The 'reference' pesticides may be combined in a single solution. The minimum acceptable frequency of calibration during screening analysis is given in Table 1. Where a particular pesticide is not calibrated in a batch of determinations, the results for that pesticide must be considered tentative.

39.1. In the following cases, *all* analytes sought must be considered as 'reference' analytes:

(i) where an MRL has been exceeded;

(ii) where for any other reason, the analytes sought must be quantified with demonstrable accuracy;

(iii) where single-residue methods are employed.

39.2. In all other cases, the 'reference' analytes must include those listed below:

(i) the pesticides likely to be detected in the samples analysed *and*

(ii) two or more pesticides most likely to give poor or variable response or recovery *and*

(iii) one pesticide expected to give repeatably good response and recovery.

Category (i) may incorporate the requirements of categories (ii) and (iii).

Table 1

Minimum frequencies for calibration and recovery determination

	'Reference'pesticides	Pesticides infrequently found in the commodities analysed	Pesticides not previously found, or no longer found, in the commodities analysed
Calibration	Two levels, two bracketing injections (etc.) of all analytes, in every batch of determinations. Batch size should be adjusted so that bracketing calibration responses do not differ by > 20 %	A rolling programme, to include all such pesticides once per 10 determination batches or three months. Two levels, two injections of each, bracketing the batch of determinations	Once per year or survey. Two levels, two injections of each, bracketing the batch of determinations
Recovery	One for each pesticide in every batch of analyses/extractions	One for each pesticide, synchronised with the corresponding calibration series, as above	One for each pesticide, synchronised with the corresponding calibration series, as above

Observations:

(a) 'Reference'pesticides are defined in subparagraphs 39.1 and 39.2 above.

(b) Where additional pesticides are intended to be encompassed in analyses, the reference pesticides must be chosen with great care, to ensure that detector responses to the reference pesticides show that residues of the other pesticides will be detected with the claimed sensitivity.

(c) Where calibration and recovery of a particular pesticide are not conducted in the batches, there is a risk that subsequent measurements may show that the results for the pesticide are not valid for the batches.

Matrix-matched calibration

40. Chromatographic transmission, detector response, or partition in headspace analysis, may be altered by components from the sample matrix or solvents, etc. (see point 16). In general, pesticide calibration standards should be prepared freshly in a matrix extract which provides accurate calibration (i.e.'matrix-matched'). The blank commodity used for matrix-matching may, or may not, have to be identical to the samples but the variable and unpredictable nature of matrix effects require that the use of a non-identical matrix should be re-validated at intervals. For any particular pesticide and sample, the validity of the matrix used for preparation of calibration solutions may be checked by addition of a known quantity of the pesticide to the sample extract (etc.) and comparing the increase in analyte response produced with the response produced by the supposedly equivalent matrix-matched calibration standard.

41. Care is required where the material used to prepare matrix-matched calibrations either contains the analyte or produces a detector signal which interferes with the determination of the analyte. There are several cases and each is likely to create additional uncertainty about the final result.

41.1. Where the analyte is naturally present in all samples and only levels much higher than those occurring naturally are important. For example, inorganic bromide in celery. A 'zero' level must be included in the calibration and the blank material should be chosen for its low level of analyte. The analyte concentration in the blank is determined from the slope and intercept ('zero' level) of the calibration curve and this value must be added to the nominal calibration levels. The blank value must not be subtracted from the level found in the samples. The 'zero' becomes equivalent to the level in the blank material and this is thus the LCL. The blank material should be made homogeneous, to ensure that the LCL remains similar from batch to batch. Results below the 'zero' level should be expressed as in point 31.

41.2. Where the analyte is of natural origin and detectable in all or most samples but the level is close to, or above the target LCL. For example, carbon disulfide produced from brassicas. A more specific method (for dithiocarbamates in this case) may be used; or the target LCL may be set at a substantially higher level and the results interpreted with caution.

41.3. Where (i) the analyte is detectable in all samples but is not naturally present. For example imazalil in certain citrus. Following rigorous confirmation that measurable residues are truly present in high frequency, a sample containing a particularly low level of the analyte should be utilised for calibration, as described in point 41.1.

41.4. Where the 'background' is not due to the analyte but due to an interfering natural or synthetic chemical, present in some or all samples. A more efficient clean-up or a more specific detection system should be used. Where this is not practicable and the maximum level found in 'blank' material is below the target LCL, an approach similar to that in point 41.1 may be adopted. In this case, results must be interpreted with caution and residues >LCL should be confirmed rigorously.

42. In GC analysis, both matrix-matching of calibration solutions and column/injector 'priming' are normally required. The priming effect resembles a long-lasting matrix effect but is rarely permanent and rarely eliminates matrix effects. Where required, priming should be performed immediately prior to the first series of calibration determinations in a batch of analyses.

Effects of pesticide mixtures on calibration

43. Calibration and recovery using mixed standards of pesticides is acceptable but the detection system should be checked for similarity of response to the matrix-matched pesticides, individually and in mixture. In the unusual cases where these responses differ significantly, residues of single pesticides must be quantified using individual calibration standards. In exceptional cases, multiple residues may require a specially-prepared calibration standard.

Calibration for pesticides which are mixtures of isomers, etc.

44. Where a pesticide calibration standard is a mixture of isomers, etc. detector response generally may be assumed to be similar, on a molar basis, for each component. However, enzyme assays (e.g. cholinesterase) and immuno-assays may give calibration errors if the component ratio of the standard differs significantly from that of the measured residue. An alternative detection system should be used to quantify such residues.

Calibration using derivatives or degradation products

45. Where the pesticide is detected as a degradation product or derivative, the calibration solutions should be prepared from a reference standard of that degradation product or derivative, if available.

46. Determination of pesticides as unstable derivatives (e.g. some Schiff bases), which cannot be prepared as pure standards, should be avoided.

Chromatographic integration

47. All chromatograms must be scrutinised and the baseline checked and adjusted, as required, by the analyst. Where interfering peaks are present, a consistent approach to the positioning of the baseline must be adopted for all analyses, although such peaks cannot be integrated 'correctly'. A similarly consistent approach must be adopted for the integration of tailing peaks. Peak height or peak area data may be used, whichever yields the more accurate and repeatable results (as assessed from recovery and calibration data).

48. Calibration by mixed isomer (or similar) standards may utilise summed peak areas, summed peak heights, or measurement of a single component, whichever is demonstrated to be the more accurate.

Analytical methods

Acceptability of analytical methods

49. Adequate validation of an analytical method provides guidance on its suitability for the intended purpose, although good performance in practice usually remains dependent upon the analyst. Validation information, used to support the selection of a method, should relate to an appropriate range of pesticides and sample matrices and may include: (i) the accuracy and precision (reproducibility or repeatability) achieved, preferably over an appropriate range of concentrations; (ii) the sensitivity achieved; (iii) evidence of the specificity; (iv) a test of robustness or ruggedness.

50. The analytical method normally should be capable of providing repeatable recovery (for pesticides added at levels greater than approximately five times their limits of determination) within the range 70 % to 110 %, for all compounds sought by the method, ideally with a mean recovery for each compound between 80 % to 100 %. Where the difficulty of the analysis does not permit this accuracy and precision and there is no satisfactory alternative method, this issue must be considered before taking enforcement action. Before adopting it for monitoring, the analyst's performance of the method should be assessed by means of two or more recovery determinations from each appropriate sample matrix. Where a residue is to be determined as a moiety derived from two or more components of the residue, method performance should be assessed for all components.

Methods for determination of fat or dry weight content

51. Where results are expressed on the basis of dry weight or fat content, the method used to determine the dry weight or fat content must be consistent. Ideally it should be validated against a recognised standard method.

Recovery determinations

Samples, spiking levels, inclusion in analysis batches

52. Residues to be quantified accurately must be accompanied by concurrent recovery determinations. Where practicable, recovery of all analytes sought should be determined with each batch of analyses. However, where this would require a disproportionately large number of

recovery analyses, for example where a very large number of analytes is sought using selective detectors (e.g. ECD, NPD), the minimum acceptable frequency recovery determinations for various classes of pesticides is given in Table 1. Analysis of a reference material may provide an alternative to recovery determination, providing the material contains the relevant analytes at appropriate levels and that the residues are stable in storage.

53. Pesticide recovery should be determined by addition (spiking) of the analytes to a sample of 'blank' matrix, similar to that under study. The spiking level may be 1 to 10 times the LCL, at the MRL, or at some other level relevant to the particular samples. The blank material chosen should preferably be known not to contain measurable levels of the analytes. Where the blank material contains the analyte at detectable levels (e.g. inorganic bromide) or an interfering compound, the spiking level for recovery should be ≥ 5 times the level present in the blank material. The analyte (or apparent analyte) concentration in such a blank matrix should be determined by multiple analysis. The signal from the blank should be confirmed as due to the analyte, or otherwise, as the case may be.

54. As far as practicable, the recovery of all components defined by the MRL should be determined. Where a residue is determined as a common moiety, routine recovery (see Table 1) may be determined for the component which either normally predominates in residues or is likely to provide the lowest recovery.

Acceptability of analytical performance

55. Irrespective of the levels of addition, routine recovery data may be more variable than indicated by repeatability data from validation of the method. Recovery should be monitored and corrective action must be taken when either a significant drift in the mean recovery, or an unacceptable result occurs. Care must be taken in assessing recovery at the LCL for this purpose. Recoveries which differ from the routine mean by more than two standard deviations should, and those differing by more than three standard deviations must be investigated. Although this does not automatically mean that such recoveries are unacceptable, the batch should normally be re-analysed. Generally, routine recovery within the range 60 % to 140 % may be considered acceptable (great care may be required in the interpretation of recovery where the spiking level is at or about the LOD or at the LCL). Where the mean for routine recovery approaches an extreme of this range and a recovery result is significantly beyond it, results for the batch of samples must be considered cautiously. Exceptionally, where recovery is low but consistent and the basis for this is well established (e.g. due to pesticide distribution in partition), a mean recovery below 60 % may be acceptable. However, wherever practicable, a more accurate method should be used. Where recovery for the batch is unacceptable, either acceptable recovery should be re-established and all samples in the batch re-analysed, or the results must be considered to be no more than semi-quantitative.

56. Where recovery for a pesticide is outside 70 % to 110 % for the batch, samples found to contain violative residues of that pesticide should re-analysed, to provide accurate results supported by recovery data within the 70 % to 110 % range. If recovery within this range cannot be achieved, decisions on the action to be taken must acknowledge that the residue level may not be known with good accuracy.

57. In certain cases, determination of recovery may not be possible: for example, in direct analysis of liquid samples and various SPME or headspace analyses. In direct analysis of liquids, accuracy and precision are determined by the calibration, assuming that losses of the pesticide (e.g. by adsorption) do not occur between sampling and analysis. In SPME and headspace analysis, accuracy and precision may be a function of the extent to which the analyte is equilibrated within and between the phases and, where practical, this should be demonstrated.

Proficiency testing and analysis of reference materials

58. As indicated in point 3, regular participation in relevant proficiency tests is essential, with appropriate action taken to remedy problems that become evident. In addition, previously characterised and homogeneous in-house reference materials may be analysed to help provide continuing evidence of the quality of analytical performance, if the residues present are known to be stable in storage.

Confirmation of results

Principles of confirmation

59. It is impossible to prove the complete absence of residues but results which are below the LCL, and therefore not to be reported as absolute numbers, are considered confirmed if the recovery and LCL data for the batch are acceptable. Adoption of a 'reporting limit' at the LCL avoids the high and unjustifiable cost of proving the presence, or absence, of residues at such low levels that the data are not meaningful. Where a batch of analyses did not include calibration or recovery of the particular pesticides, the corresponding data for the reference pesticides provide only indirect evidence of a satisfactory analysis. Such results cannot be considered confirmed, although the data may be adequate for some purposes.

60. Results at or above the LCL require additional support in order to be considered confirmed. Where the batch of analyses was performed without calibration for the particular pesticide, the results must be regarded as very tentative and confirmation is essential. In this case, the minimum requirement is re-analysis of the extracts, with appropriate calibration for the pesticides detected. As the pesticides involved should be detected infrequently (see Table 1) and may therefore be unusual, re-analysis of the sample with concurrent recovery determination is to be preferred.

61. Where enforcement action will be taken, or other important decisions made, on the basis of results exceeding the LCL, acceptable concurrent calibration and recovery data are essential, supported by further confirmation. The nature and extent of the further confirmation required depends upon the relative importance of the particular result and the frequency with which similar residues are found. Quality control procedures for confirmatory analysis must be rigorous.

Approaches to confirmation

62. Confirmation of the analyte detected should be quantitative and qualitative.

63. Assays based on immunochemistry, colorimetry, thin-layer chromatography or electron-capture detectors tend to require the most confirmatory support, because of their lack of specificity. Where 'selective' detectors are used with GC or LC, a second chromatographic column of significantly different polarity (or a second 'specific' detection system) provides only limited confirmatory evidence. This may be acceptable for frequent, low-level residues where a proportion of the residues is also confirmed by a more definitive technique but the use throughout of the more definitive technique is preferable.

64. Where a residue exceeds the MRL or where it should not be present in the sample, the result must be confirmed by the least equivocal method available *and* by analysis of one or more additional analytical portions. Residues in replicate portions may be quantified by either the

screening or the confirmatory technique. The number of replicate portions to be analysed should be determined by the variation in results obtained.

Confirmation by mass spectrometry

65. MS is capable of providing almost unequivocal confirmation of residues of most pesticides but the confirmatory data must comply with certain minimum requirements. Matrix-matched calibration standards should normally be used for confirmation of quantity but the reference mass spectrum should derive from the reference standard, or a solution of it in pure solvent. To avoid distortion of ion ratios, the quantity of material used for the reference spectrum must not overload the detector. Confirmation of high-level residues may be straightforward but results close to the limit of MS determination must be considered on a case-by-case basis.

66. Chromatograms of relevant ions should have peaks (minimum three scans, minimum summed S/N 3:1) with similar retention time, peak shape and response ratio as those obtained from a calibration standard, analysed in the same batch. Where chromatograms of notionally unrelated ions include peaks with a similar retention time and shape, or where this information is not available (e.g. from 'limited scanning' or selected ion monitoring), additional confirmation may be required. Where an ion-chromatogram shows evidence of significant chromatographic interference, that ion must not be relied upon to quantify or identify residues.

67. Spectra should be background-subtracted, if appropriate, but the background must be selected with care to avoid distortion of the data. Where ions unrelated to the analyte in a peak-averaged 'full-scan' spectrum (i.e. from m/z 50 to 50 mass units greater than the 'molecular ion') do not exceed a quarter of base peak intensity in electron-impact ionisation spectra, or one-tenth for all other ionisation methods, the spectrum may be accepted as sufficient evidence of identity. Where these limits are exceeded and the unrelated ions derive from chromatographically overlapping species, an alternative background may be subtracted, and/or additional evidence may be sought. Intensity ratios for principal ions should be within 80 % to 120 % of those obtained from the standard. Where an ion-chromatogram shows significant chromatographic interference that ion should not be used to determine an intensity ratio and additional supporting evidence may be required. The most abundant ion that shows no evidence of chromatographic interference should be used to quantify a residue. With electron-impact ionisation, in particular, the absence of interfering ions may be used to support identification where the analyte spectrum is very simple.

68. Ionisation by electron-impact, or by further fragmentation of selected ions (MS/MS), coupled with acquisition of full-scan spectra, generally provides the most definitive evidence of identity and quantity. Mass spectra produced by less energetic processes (e.g. chemical ionisation, atmospheric pressure ionisation) may be too simple to confirm identity without further evidence. Unless the isotope ratio of the ion(s) or the chromatographic profile of isomers of the analyte is highly characteristic, additional supporting evidence is likely to be required. This may be provided by: (i) a different chromatographic separation system; (ii) a different ionisation technique; (iii) MS/MS; (iv) the use of medium-high resolution MS; or (v) altering fragmentation by changing the 'cone voltage' in LC-MS. In using medium-high resolution MS or MS/MS, wherever possible the ions selected should be characteristic of the pesticide rather than common to many organic compounds.

69. Full-scan spectra provide the most convincing identification but sensitivity may be improved by scanning a limited mass range or by selected ion monitoring. With these techniques, the minimum requirement is for data from two ions of m/z > 200; or three ions of m/z > 100. Additional supporting evidence (see point 68) may be required in some cases and must be provided where the analyte spectrum does not permit these requirements to be met.

Confirmation in an independent laboratory

70. Where important residues cannot be confirmed locally, the confirmation may be carried out in another laboratory, if practicable.

Reporting of results

Expression of results

71. Results should normally be expressed as defined by the MRL and in mg/kg. Samples in which residues are lower than the LCL should be reported as < (LCL) mg/kg.

Calculation of results

72. In general, residue data should not be corrected for recovery. Routine recovery enables analytical performance to be monitored and provides general guidance as to the accuracy of results. It does not necessarily establish the accuracy and uncertainty (see point 77) achieved for a particular sample. Results must not be corrected for blank values where these are due to the analyte (see point 41).

73. Where confirmed data are derived from a single analytical portion (i.e. the residue is not violative or unusual), the reported result should be that derived from the detection technique considered to be the most accurate. Generally this will be the technique providing the best specificity. Where results are obtained by two or more equally accurate techniques, the mean value may be reported.

74. Where two or more analytical portions have been analysed, the arithmetic mean of the most accurate results obtained from each portion should be reported. Where good comminution and/or mixing of samples is undertaken, the RSD of results between analytical portions should not exceed 30 % if the residue measured is significantly greater than the LOD. Close to the LOD, the variation in results may be much higher and this should be taken into account in deciding what action should be taken.

75. Where the definition of an MRL includes two or more compounds, one component often predominates in residues. Where the components are detected separately (rather than as a common moiety), the overall reporting limit for the pesticide should be the LCL of the component producing the lowest response on a molar basis. For example, if the LCL for endosulfan isomers is 0,05 mg/kg and that of the sulphate metabolite is 0,1 mg/kg, then the overall reporting limit for endosulfan should be quoted as 0,1 mg/kg. Where the reference standard contains two or more components producing similar molar responses but which differ in concentration, for example chlorfenvinphos mixed isomers, the reporting limit may apply to the component producing the largest absolute response. If this approach is adopted, the lack of a characteristic component profile supporting the identification of residues at or about the reporting limit may require the use of a more rigorous confirmation technique.

Rounding of data

76. When reporting results < 0,1 mg/kg, data should be rounded to one significant figure; results ≥ 0,1 mg/kg but < 10 mg/kg should be rounded to two significant figures; results ≥ 10 mg/kg

may be rounded to three significant figures or to a whole number. These requirements do not necessarily reflect the uncertainty associated with the data.

Quantifying the uncertainty of results

77. Measurement uncertainty is a useful quantitative indicator of the confidence that can be placed on results. Uncertainty data do not replace the need for confirmation and they are required primarily to support very important results. ISO rules for evaluating and expressing uncertainty in measurement [1] require identification of the potential sources of uncertainty that influence the result. This formal approach may be adopted, if required, but a simpler method may be employed, such as the use of the standard deviation of either repeatability or internal reproducibility. These values may be derived from recovery data or the analysis of reference materials. However, the uncertainty data must relate to the specific pesticide and should have been generated from the relevant matrix, at a level approximating that in the sample. It may therefore be necessary to produce uncertainty data from recoveries over a range of concentrations. Ideally, uncertainty data should be derived from replicate analysis of 5 to 10 portions of the sample and thus embrace the uncertainties of both sub-sampling and analysis. the uncertainty may be expressed as the 95 % confidence interval for the result.

Compliance decisions

78. A decision on whether or not results indicate that a residue exceeds an MRL should take into account the concentration found and the validity of measurement indicated by the corresponding quality control data. Decisions on the consequent action should be made on a case-by-case basis.

79. Where residues measured in the sample(s) taken from a lot do not exceed the MRL(s), the lot is compliant with the MRL(s).

80. Where results for the laboratory sample(s) taken from a lot exceed the MRL, a decision that the lot is non-compliant must take into account: (i) the range of results obtained from replicate laboratory samples and/or replicate analytical portions, as applicable; and (ii) the accuracy and uncertainty of analysis. In general, a non-compliance decision will require acceptable calibration, concurrent recovery determination and confirmatory data. Where the presence of a pesticide is unacceptable regardless of level, the lot is non-compliant if the residue is at or above the LCL and its identity is confirmed.

81. Where the presence of a low level of a pesticide is to initiate enforcement action, the possibility of cross-contamination having occurred before, during or after sampling must be considered.

Retention of information

82. Sample data records, laboratory notebooks, chromatograms, tables of results, disks or tapes bearing chromatographic or spectral data, etc., must be retained for scrutiny. Following submission of the report, data should be retained for five years for violative samples, or two years for non-violative samples.

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[1] Anonymous (1993), 'Guide to the expression of uncertainty in measurement' (ISBN 92-67-10188-9). ISO, Geneva, Switzerland.

Glossary

Batch	For extraction, clean-up and similar processes, a batch is a series of samples dealt with by an analyst (or team of analysts) in parallel, usually in one day, and should incorporate at least one recovery determination. For the detection procedure, a batch is a series of determinations undertaken without a significant time break and which incorporates all relevant calibration determinations. Batches of determinations may also be referred to as 'analysis runs', 'run sequences', 'chromatography runs', etc., but with formats such as 96-well plates, a plate will form a batch. A determination batch may incorporate more than one extraction batch
Blank	(i) A sample known not to contain detectable levels of the analytes sought. An extract (or equivalent) of such a sample may be known as a matrix blank (ii) A complete analysis conducted using the solvents and reagents only, in the absence of any sample (in certain cases it may be necessary to substitute water for the sample in order to make the analysis realistic). Also known as a reagent blank or procedural blank
Bracketing	Organisation of a batch of determinations such that the detection system is calibrated immediately before and after the analysis of the samples. For example, calibrant 1, calibrant 2, sample 1 … sample *n*, calibrant 1, calibrant 2
Calibration	Determination of the response produced from the analyte by the detection system, over the range of concentrations to be reported and at the time the samples are analysed. The solutions, etc. used for this purpose may be termed calibration solutions, calibration standards or calibration extracts. Calibration of detector response is wholly distinct from calibration of weighing and volumetric equipment, from mass calibration of mass spectrometers, and so on
CHEK	A proficiency testing scheme organised by the Inspectorate for Health Protection, Groningen, The Netherlands
ECD	Electron-capture detector
ELISA	Enzyme-linked immuno-sorbent assay
EU	European Union
FAPAS	Food analysis performance assessment scheme, a proficiency testing scheme organised by the Ministry of Agriculture, Fisheries and Food, Norwich, UK
FPD	Flame-photometric detector (may be specific to sulphur or phosphorus detection)
GC	Gas chromatography (gas-liquid chromatography)
Internal reproducibility	The repeatability of recovery of an analyte, achieved within a laboratory using the same method on several or many occasions
LC	Liquid chromatography (primarily high performance liquid chromatography, HPLC)
LCL	Lowest calibrated level. The lowest concentration of analyte with which the detection system is calibrated, in seeking to determine the presence or absence of measurable residues. It will normally form the reporting limit
Level	Usually refers to concentration (e.g. mg/kg, μg/ml) but may refer to quantity (e.g. np, pg)
LOD	Limit of determination (or limit of quantitation)

Matrix blank	See blank
Matrix-matched calibration	See also'calibration'. The use of calibration solutions, or headspace partitions, or SPME fibres, etc., in which all constituents (other than the analyte) are similar to, or produce the same effect on analytical response as, the equivalent solutions (etc.) produced from the samples to be analysed. The matrix blank (see 'blank', above) should be prepared making similar solvents, reagents, clean-up, etc., to those used for the analysis of the corresponding samples. In practice, the pesticide is added to a blank extract (or a blank sample for headspace analysis) for a matrix similar to that analysed. The objectives are: (i) to compensate for analyte response enhancement or suppression effects induced by sample co-extractives (ii)to provide a chromatogram for integration which has underlying interference comparable to that of the sample. The matrix used may differ from that of the samples if it is shown to achieve these objectives
MRL	Maximum residue limit
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry, here taken to include MS. An MS procedure in which a particular ion from the primary ionisation process is isolated, fragmented by collision or otherwise, and the product ions separated (MS/MS or MS^2). The procedure may be carried out repetitively on a sequence of product ions (MS^n), although this is not usually practical with low-level residues
NPD	Nitrogen-phosphorus detector
Priming	Preliminary deactivation of a GC column and/or injector, by injection of a suitable solution or extract immediately before starting a batch of determinations. The increase in response to the analyte, which normally occurs, is due to increased transmission. Extracts used for priming do not normally need to be from a matrix identical to that of the samples to be analysed. To avoid carry-over, it is usually preferable that priming extracts contains little or no detectable pesticide
Procedural blank	See blank
Reagent blank	See blank
Reference pesticide	A pesticide which must be incorporated into recovery and calibration determinations in each batch of analyses (paragraphs 33 to 35)
Reference material	A sample which has been characterised with respect to the content of a pesticide. Certified reference materials are normally characterised in a number of laboratories, for concentration and homogeneity of distribution of the pesticide. In-house reference materials are characterised in a single laboratory and, as far as practicable, they should be shown to be homogeneous and stable
Reference spectrum	A spectrum of absorption (e.g. UV, IR), fluorescence, ionisation products (MS), etc., derived from the analyte and which may be characteristic of it. The reference mass spectrum preferably should be produced from the reference standard (or a solution of the reference standard) by the instrument used for analysis of the samples, and similar ionisation conditions must be used
Reference standard	A relatively pure sample of an analyte (or internal standard) of known purity. Usually > 90 % purity, except for technical concentrates of certain pesticides

Reporting limit	The lowest level at which residues will be reported as absolute numbers. It may represent the practical limit of determination, or it may be above that level to limit analysis costs. It should equal the lowest calibrated level (LCL), the level below which there is no experimental evidence to prove that residues will have been detected and calibrated satisfactorily
RSD	Relative standard deviation (coefficient of variation)
SFE	Supercritical fluid extraction
Solid phase dilution	Dilution of a pesticide by distribution within a finely divided solid, such as starch powder. Normally used only for insoluble analytes such as the complex dithiocarbamates
S/N	Signal-to-noise ratio
SPME	Solid phase micro-extraction

ANNEX III

WORKING DOCUMENT

For guidance to the Member States with regard to the implementation of Commission recommendations concerning coordinated Community monitoring programmes to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables and the presentation of Member States' reports on national monitoring

INTRODUCTION

1. Commission recommendations on fruit and vegetable monitoring have been adopted and published since 1995 (listed at Annex 3).

1.2. The EFTA Surveillance Authority makes parallel recommendations and in practice Norway participates in all discussions concerning monitoring, other than the Standing Committee on Plant Health, and makes reports to the Commission.

1.3. The purpose of this work document is to indicate solutions to questions and confusing situations which have arisen. It is hoped that all Member States can implement the various changes in this version of the guidelines in the presentation of their reports on the 1997 monitoring (by 31 August 1998) and can definitively implement them for their reports on their 1998 monitoring.

DISTRIBUTION

2. Member States should send their monitoring reports to the Commission (DG VI, DG XXIV and Joint Research Centre) and to each of the other Member States (contact point list — Annex 1).

2.1. Member States should, in particular, send their reports directly by e-mail or on diskette to the Commission, following the guidance set out in this note so that the task of collating and compiling a report at Community level is facilitated.

REPORT FORMAT

3. Reports should be made in the format set out in Tables A, B, C and D of the Annex to working document VI/1609/97–rev. 5 (available on request see detailed points below).

3.1. Member States' reports should also be made in text/narrative. In particular, Member States should draft, if possible with a version in English, a one-page (400-500 word) summary of their reported monitoring activities during the year, which could be incorporated into a European report compiled by the Commission. The summary report should distinguish between the coordinated EC monitoring programme and national monitoring and should, in particular, contain the following information:

3.1.1. the summarised statistical situation, including:

— total number of samples (not analyses) of all food items (not to be itemised) examined,

— total number of samples (not analyses) in which pesticide residues which were looked for were not detected,

— total number of samples (not analyses) in which one or more residues were detected below the MRL,

— total number of samples (not analyses) in which one or more residues were detected exceeding the MRL (record total and EC MRL exceedings separately);

3.1.2. a summary statement of the total number of residues analysed or an estimate, if appropriate;

3.1.3. a list of the 10 most frequently reported pesticide residues in descending order of findings;

3.1.4. a summary of the detailed information given about sample numbers and quality assurance (see paragraph 12).

REPORT FORMAT — DISKETTE/INFORMATIC REQUIREMENTS

4.1. For the coordinated Community monitoring results the information should be compiled in Excel tables.

4.1.1. Pesticides should be listed in English alphabetical order or in the order set out in the recommendation.

REPORTS IN TABULAR FORM

5. In addition to the summary report described in paragraph 3.1, reports in the form of tables as set out in the Annex should be made:

— Table A: Summarised statistical report (all pesticide monitoring),

— Table B: Notification of the coordinated programme (specific exercise) to the European Commission,

— Table C: Notification of check sampling and monitoring to the European Commission,

— Table D: Details of confirmed residues exceeding the MRL (EC-harmonised MRL only, excluding national MRLs in open positions),

— Table E: Details of samples with multiple residues (two and more) in single samples.

EC AND NATIONAL MRLs

6. The Commission recommendations for coordinated monitoring programmes up to that for 1998 cover only MRLs established in Annex II to Directive 90/642/EEC; recommendations for 1999 onwards will also cover MRLs established in Annex II to Directive 86/362/EEC. Member States may set national MRLs for pesticides or products not covered by these Directives and may, of course, set national MRLs for pesticides and products which are covered but for which, at present, the position is 'open'.

REPORTING LEVELS

Reporting levels for each pesticide residue have been indicated by the Council when setting MRLs. In principle, the reporting level is the routinely achievable limit of quantification practical for the monitoring laboratories

7. Member States should make specific reports with supporting information on reporting level problems and/or highlight such cases for remedial action.

ROUTINE MONITORING — CHECK SAMPLING — SURVEILLANCE

8. Historically, national monitoring programmes have not been random as they have always sought to maximise the use of restricted resources by concentrating on known or suspect problem areas. Frequently national multiannual programmes will concentrate on certain products on a rolling basis and will always tend to be targeted in accordance with certain criteria

COMPLIANCE MONITORING — ENFORCEMENT — TARGETED

9. Article 4 of Directive 89/397/EEC also covers inspections where non-compliance is suspected. Compliance monitoring is clearly more than targeted routine monitoring and will normally be in reaction to an earlier finding of residues above the MRL: this may be a reaction within days or weeks of such a finding and/or during the following production/import season and the monitoring may involve the holding of consignments until analyses are completed.

9.1. It is commonly argued that compliance monitoring is likely to result in the detection of a greater number of MRL exceedings but, of course, the deterrent nature of published compliance monitoring may result a in lower number of MRL exceedings being detected.

9.2. Member States should consider what parts of their monitoring programmes constitute clearly identifiable compliance monitoring and should report these on separate Tables C and D as annexed.

EXCEEDING OF MRLs

10. Table D of the Annex requires certain information concerning each sample exceeding MRLs. In making their annual reports, Member States should clearly indicate what they have included as exceedings of MRLs. These may include:

— cases where the analytical laboratory has certified an exceeding within the application of the quality assurance applicable to the analysis,

— cases where official warnings have been issued to the holders of the products inspected and sampled,

— cases where legal or administrative consequences have followed, e.g. prosecution, the levying of penalties or fines.

MULTIPLE RESIDUES

11. Table E of the Annex covers details of samples with more than two pesticide residues detected in single samples. This table responds to current concerns about multiple residue effects in seeking data on such cases, which will be passed to experts for evaluation (both toxicologically and in relation to authorisation policies). Member States should report on residues of both harmonised and, where possible, national pesticides. It is intended to pass a comprehensive dossier of multiple residue data to the Scientific Committee on Plants for guidance on any action to be taken.

QUALITY ASSURANCE

12. Information concerning quality assurance relating to the data supplied to the Commission is an essential under-pinning of the pesticide residue monitoring work and will be included in the annual European reports.

12.1. Member States should report on national actions assuring quality of information supplied to the Commission; this should include, in particular, actions additional to those covered by the three elements where quality assurance actions are implemented at EC/EEA level; accreditation of laboratories, EC proficiency tests and quality control procedures for pesticide residue analysis — guidelines for residues monitoring in the European Union.

12.1.1. Accreditation, in accordance with the provisions of Article 3 of Directive 93/99/EEC on the subject of additional measures concerning the official control of foodstuffs: laboratories undertaking analyses of foodstuffs for pesticide residues are required to obtain the appropriate accreditation by 1 November 1998. Commission recommendations for 1997 onwards require details of accreditation; Commission recommendations for 1999 onwards specify the detail as including 'type of accreditation, accreditation body and copy of accreditation certificate'. For 1999 onwards, the Commission will not be able to accept information from Member States' laboratories which are not accredited.

12.1.2. EC proficiency tests were first conducted in 1997 and it is intended that proficiency tests will be conducted annually. Participation of laboratories in EC proficiency tests will assist them in gaining accreditation and it should be a condition of acceptability of data by Member States for submission to the Commission that the laboratory concerned has participated in such a test as well as being accredited (see 12.1.1).

12.1.3. Quality control procedures for pesticide residue analysis — guidelines for residues monitoring in the European Union. These guidelines (Doc. 7826/VI/97) were developed for and discussed at the quality control workshop, held in Oeiras, Portugal in September 1997. As agreed at the working group of the Standing Committee on Plant Health (20 and 21 November 1997), Member States and Norway would aim to implement the guidelines from 1998 onwards and would report on their implementation to the Commission, in particular where difficulties have been found. It is intended to organise further quality control workshops, within the budgetary provisions available, in principle at two-yearly intervals.

ANNEX 1

National authorities and contact points for pesticide residue monitoring

(see EC report on 1996)

ANNEX 2

Pesticides for which MRLs are established in Annex II to Directives 86/362/EEC, 86/363/EEC and 90/642/EEC

MRLs established by Directives 93/57/EEC and 93/58/EEC (35 compounds: in force 31 December 1993)

Acephate
Chlorothalonil
Chlorpyriphos
Chlorpyriphos-methyl
Cypermethrin
Deltamethrin
Fenvalerate
Glyphosate
Imazalil
Iprodione
Permethrin
Carbendazim (*Benomyl*, Carbendazim, Thiophanate-Methyl)
CS_2 (*Maneb*, Mancozeb, Metiram, Propineb, Zineb)
Methamidophos
Procymidone
Vinclozolin
DDT
Amitrole
Atrazine
Binpacryl
Bromophos-ethyl
Captafol
Dichlorprop
Dinoseb
Dioxathion
Endrin
Ethylene dibromide
Fenchlorphos
Heptachlor
Maleic hydrazide
Methyl bromide
Paraquat
TEPP
Camphechlor (toxaphene)
2,4,5-T

MRLs established by Directives 94/29/EC and 94/30/EC (12 compounds: in force 30 June 1995)

Daminozide
Lambda-cyhalothrin
Propiconazole
Carbofuran
Carbosulfan
Benfurocarb
Furathiocarb
Cyfluthrin
Metalaxyl
Benalaxyl
Fenarimol
Etephon

MRLs established by Directives 95/38/EC and 95/39/EC (6 compounds: in force 1 July 1996)

Methidathion
Methomyl (Thiodicarb)
Amitraz
Pirimiphos-methyl
Aldicarb
Thiabendazole

MRLs established by Directives 96/32/EC and 96/33/EC (13 compounds: in force 30 April 1997)

Triforine
Endosulfan
Fentin
Phorate
Dicofol
Chlormequat
Propyzamide
Propoxur
Disulfoton
Fenbutatin oxide
Triazaphos
Diazinon
Mecarbam

ANNEX 3

Commission recommendations on pesticide residue monitoring

Commission Recommendation 95/156/EC of 8 March 1995 concerning a coordinated Community monitoring programme for 1998 to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables (OJ L 103, 6.5.1995, p. 38).

Commission Recommendation 96/199/EC of 1 March 1996 concerning a coordinated Community monitoring programme for 1998 to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables (OJ L 64, 14.3.1996, p. 18).

Commission Recommendation 96/738/EC of 2 December 1996 concerning a coordinated Community monitoring programme for 1998 to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables (OJ L 355, 24.12.1996, p. 54).

Commission Recommendation 97/822/EC of 3 November 1997 concerning a coordinated Community monitoring programme for 1998 to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables (OJ L 337, 9.12.1997, p. 14).