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Project identification

1. Defra Project code: PS2513

2. Project title:
   QuEChERS (Optimisation and Implementation of Low Cost Generic Extraction Procedures for Pesticide Residues in Food).

3. Contractor organisation(s):
   Central Science Laboratory
   Sand Hutton
   York
   North Yorkshire
   YO41 1LZ

4. Total Defra project costs (agreed fixed price): £ £179,730.55

5. Project: start date ..... 01 April 2004

   end date ..... 30 June 2006

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Executive Summary

7. The executive summary must not exceed 2 sides in total of A4 and should be understandable to the intelligent non-scientist. It should cover the main objectives, methods and findings of the research, together with any other significant events and options for new work.

1. Background and Project Aims

The determination of pesticide residues by chemical analysis is both costly and time consuming. A reduction in analytical costs could permit an increased level of testing for more samples and/or analytes, within existing budgets. This would ultimately be of benefit in conducting risk assessments and in protecting the consumer.

Due to the diverse chemical characteristics of pesticides, it is currently necessary to use several different extraction procedures in combination with Liquid Chromatography-Mass Spectrometry/Mass Spectrometry (LC-MS/MS) and Gas Chromatography-Mass Spectrometry (GC-MS) based analyses. The recent development and implementation of a technique called "QuEChERS" (*Quick, Easy, Cheap, Effective, Rugged and Safe*) has resulted in significant cost savings for the analysis of pesticide residues using LC-MS/MS. However, due to the use of acetonitrile as the extraction solvent, the QuEChERS method has proved more difficult to implement for GC-MS analysis. To overcome this limitation this project had the following aim:

- To modify the QuEChERS procedure to allow the addition of GC amenable pesticide compounds into a generic extraction procedure. It was also proposed to expand the scope of the method by increasing the number of pesticides included in the LC-MS/MS multi-residue method.

These improvement would support the necessary ongoing development of the UK pesticides monitoring programme by providing the Pesticide Residues Committee with robust, rapid and lower cost methods for the analysis of pesticide residues in foods.

2. Key findings

To extend the range of pesticides analysed by QuEChERS using LC-MS/MS quantification/identification.

A large number of target pesticides (*circa* 130) were assessed using the QuEChERS method followed by LC-MS/MS quantification and confirmation. At a spiking concentration of 0.05 mg/kg, 102 (83 %) of these pesticides in lettuce and 95 (71 %) in pears met the validation criteria set out in the European Union Guidelines for the Analytical Quality Control of Pesticides [SANCO/10232/2006]. Validation data from experiments with a lower spiking concentration of 0.01 mg/kg showed more variability in terms of method repeatability. In this case 43 % of the pesticides sought in pears and 58 % in lettuce met the EU criteria. Nevertheless a number of the pesticides that gave unsatisfactory results using LC-MS/MS were satisfactorily analysed during the GC-MS validation (see below).

To develop and validate a QuEChERS based method for GC-MS quantification/identification of pesticides

Ethyl acetate, a commonly used extraction solvent for pesticides that are analysed by GC-MS, was assessed as an alternative extraction solvent to acetonitrile using the QuEChERS technique. For 45 of the 48 pesticides investigated the mean recoveries were within the range of 75 – 110 %. However significant losses were observed for dichlofluanid, chlozolinate and captan. Whilst the results of using ethyl acetate were promising the use of this alternative approach had a two main disadvantages; firstly, it required each sample to undergo two separate extractions (one for GC-MS analysis and one for LC-MS/MS) as opposed to a single acetonitrile extraction; secondly, ethyl acetate extracted more sample matrix components compared to acetonitrile. These extra matrix components were shown to affect the reliability of the method. For this reason it was decided to focus on the use of acetonitrile as an extraction solvent for GC-MS.

Further experiments with acetonitrile extraction showed that a “dispersive” sample clean-up using both primary secondary amine and carbon was the most applicable. Whilst the use of carbon was necessary to provide adequate clean-up for samples containing high concentrations of plant pigments (e.g. chlorophyll) this technique had the disadvantage of adsorbing some target pesticides. However, the recovery of some of these pesticides was improved by adding toluene to the sample extract.

The developed QuEChERS GC-MS method was assessed for 94 pesticides spiked at 0.05 mg/kg and 0.01 mg/kg in lettuce and pears. In lettuce, the recoveries for 83 (88 %) of the pesticides were in the range 70-110 % with CV’s $\leq$ 20 % at both 0.01 and 0.05 mg/kg. In pears, the recoveries for 77 (82 %) of the pesticides were in the range 70-110 % with CV’s $\leq$ 20 % at 0.01 mg/kg, and 82 compounds (87 %) at 0.05 mg/kg. Thus the vast majority of pesticides tested met the validation criteria set out in the European Union Guidelines for the Analytical Quality Control of Pesticides [SANCO/10232/2006]. Captan, chlorothalonil, dichlofluanid, dicofol, folpet and tolylfluanid could not be successfully validated (in terms of analyte recovery/repeatability). These compounds are particularly difficult to analyse but it is likely that further minor modifications to the QuEChERS extraction could address this issue.

Comparison of “old” and “new” GC-MS methods

Fifty samples of both pear and lettuce known to contain residues (previously analysed in the 2004 & 2005 Pesticide Residue Committee (PRC) monitoring programmes were extracted and reanalysed by the new acetonitrile-based QuEChERS GC-MS method. These experiments showed that data obtained by the new QuEChERS GC-MS method is comparable to the techniques currently employed in the PRC surveillance programmes. Data for folpet in lettuce indicated a negative bias for the QuEChERS extraction. This may be due to degradation of folpet during storage (up to 2 years at –20 ºC) or degradation during the extraction. However, further experiments would be required to investigate the true cause of this difference. This same bias was not apparent for folpet in pears. Due to reduced analyte recovery the new QuEChERS GC-MS method determined a lower residue concentration for pyrimethanil,

chlorothalonil and cyprodinil in the test samples. Nevertheless the procedure could be considered satisfactory for screening these analytes, as adequate sensitivity is available. Pyrimethanil and cyprodinil could alternatively be included in the LC-MS/MS suite. Any sample found to contain chlorothalonil would require repeat extraction using another method, which is comparable with current procedures.

3. Recommendations for future work

- For those unstable problematic compounds like folpet, tolylfluanid, dichlofluanid and captan the addition of sodium citrate to improve buffering should be further investigated. The addition of analyte protectants to minimise the matrix effects could also be evaluated.

- The developed acetonitrile-based QuEChERS GC-MS method should form the basis of the methods to be used within the complementary project on Rapid Low Cost Screening methods (PS2519). This work should also include an assessment of the techniques reliability for matrices that contain high concentrations of (a) acid, (b) water and (c) protein.

4. Conclusions

A single acetonitrile based QuEChERS extraction followed by a combination of GC-MS and LC-MS/MS can be used to determine *ca* 230 pesticides in lettuce and pears. Data obtained by this method is comparable to the techniques currently employed in the PRC monitoring programmes. Further experiments are required to improve the robustness of the method for a few selected pesticides and to assess its applicability to other matrices. The principles of this method should be employed in the PSD funded project (PS2519) to investigate whether a much larger number of pesticides can be screened by GC-MS.

Project Report to Defra

8. As a guide this report should be no longer than 20 sides of A4. This report is to provide Defra with details of the outputs of the research project for internal purposes; to meet the terms of the contract; and to allow Defra to publish details of the outputs to meet Environmental Information Regulation or Freedom of Information obligations. This short report to Defra does not preclude contractors from also seeking to publish a full, formal scientific report/paper in an appropriate scientific or other journal/publication. Indeed, Defra actively encourages such publications as part of the contract terms. The report to Defra should include:

- the scientific objectives as set out in the contract;
- the extent to which the objectives set out in the contract have been met;
- details of methods used and the results obtained, including statistical analysis (if appropriate);
- a discussion of the results and their reliability;
- the main implications of the findings;
- possible future work; and
- any action resulting from the research (e.g. IP, Knowledge Transfer).

Project Objectives:

To develop and validate an analytical strategy (including parallel GC-MS and LC-MS analyses) for cost effective, reliable and comprehensive screening of pesticides in fruits and vegetables.

The approach to developing a strategy consisted of the following stages:

A. Optimisation of the current LC-MS method involved;

- Further development of the LC-MS/MS method to combine all of the pesticides validated in recent R&D projects into a single multi-residue method for approximately 100 - 150 pesticides.

- An initial evaluation on the possibility of using short HPLC columns or alternative technology to decrease LC-MS analysis times.

- Validation of the developed LC-MS method for the target pesticides in pears and lettuce.

B. Optimisation of the GC-MS method involved an evaluation of:

- Large volume PTV (programmable thermal vaporisation) injection method, enabling larger quantities of acetonitrile extract to be introduced to the GC-MS system which if successful would facilitate the use of the same extracts for LC and GC analysis.

- A modification of the extraction method to include a solvent exchange into a more suitable solvent for GC analysis, enabling a standard hot, splitless injection to be employed. Thus same extracts would be shared for LC and GC analysis, but an extra step would have to be included at the end of the extraction procedure to allow the solvent exchange prior to GC analysis.

- An assessment of the QuEChERS approach using a solvent more suitable for GC analysis (i.e. ethyl acetate). Although this would require two separate extractions for GC and LC analysis, it is possible that the use of dual extraction procedures could still be more efficient than the use of solvent exchange steps.

Once developed the most appropriate QuEChERS based GC-MS method was to be validated for the target pesticides in pears and lettuce

C. Finally the new QuEChERS based GC-MS method was to be compared to the existing multi-residue approaches by analysing samples obtained from the 2004/2005 PRC surveillance programme for lettuce and pears. This comparison would allow a reliable assessment of (a) the robustness and (b) the cost-effectiveness of the new methodology.

The progress against individual individual milestones is shown below:

1. Development and validation of an LC-MS/MS method for 100-150 target pesticides

1.1 Optimisation of the current LC-MS method for 100-150 target pesticides

The QuEChERS method followed by LC-MS/MS quantification/identification was evaluated for 133 target pesticides in pears and lettuce. Analysis was undertaken using a Sciex API 2000 triple quadrupole (Applied Biosystems) mass spectrometer with a turboionspray source in the positive mode and with reversed-phase chromatography.

1.2 Evaluation on the possibility of using short columns to decrease LC-MS/MS analysis times

Current multi-residue LC-MS/MS (40-50 analytes) run times are typically 40 minutes. The possibilities of using short HPLC columns (HyPURITY C_{18} analytical column, Waters Atlantis dC18 and Waters Sunfire) to reduce chromatographic run times and increase sample throughput were evaluated. A method was developed that allowed separation of 57 compounds in less than 15 minutes. However, the short retention times of early eluting pesticides prevented the use of a divert valve (used to prevent early eluting matrix contaminants from entering the mass spectrometer). In practice the use of short columns is not suitable for the analysis of large numbers of pesticides in crude ('non-cleaned') acetonitrile extracts of fruits and vegetables. It was considered unacceptable to include the necessary clean-up steps (time consuming and expensive) and /or reducing the scope of the analysis as the use of a divert valve (to remove matrix-components) would also eliminate some of the pesticides of interest. Therefore, since no clean up is necessary for most samples extracted by the QuEChERS acetonitrile method, conventional HPLC columns were used for method validation (see 1.3).

1.3 Validation (recovery, repeatability) of the developed LC-MS/MS method for the agreed target analytes for pears and lettuce

The optimised QuEChERS acetonitrile LC-MS/MS method (see 1.1 above) was validated for lettuce and pears. Data from these matrix experiments are shown in Tables 1 and 2, respectively. After spiking at 0.05 mg/kg, 102 compounds (83 %) in lettuce and 95 compounds (71 %) in pears met the validation criteria (recovery 70 – 110 % recovery and CV's ≤ 20 %) set out in the European Union Guidelines for the Analytical Quality Control of Pesticides [SANCO/10232/2006]. Results at the lower spiking concentration of 0.01 mg/kg showed more variability. In this case 43 % of the pesticides sought in pears and 58 % in lettuce met the EU criteria (recovery 70 – 110 % and CV's ≤ 30 %). A number of the compounds that gave unsatisfactory results using LC-MS/MS were satisfactorily analysed in the GC-MS validation (see below).

2. Development and validation of a QuEChERS based GC-MS method for 100-150 target pesticides

2.1 Evaluation of the use of LVI-GC-MS on QuEChERS acetonitrile extracts

Gas Chromatography Mass Selective Detectors (GC-MSD) can be operated in Selective Ion Monitoring (SIM) or Full Scan mode. In SIM, the system is programmed to analyse a limited number of pre-selected pesticides (targeted analysis) at relatively high sensitivity. Full Scan monitoring allows all GC-amenable pesticides to be screened in a single analysis but with low sensitivity compared to SIM. To be able to detect the pesticides at the limits (0.01-0.05 mg/kg) required for the Pesticide Residues Committee programme a higher level of analyte loading onto the column is required for Full Scan mode compared to SIM. This can be achieved by offline manual concentration of the extract or on-line Large Volume Injection (LVI) which is automated, more cost effective and more reproducible.

During this project an LVI method that allowed 10 µl injections of acetonitrile extracts was optimised. The method provided adequate limits of detection for most pesticides when used in conjunction with SIM analysis. However the chromatographic peak shapes were not as good in acetonitrile compared to other solvents and the sensitivity is not sufficient in Full Scan mode. In order to achieve a reporting limit of 0.005 mg kg^{-1} (to allow accurate quantitation at 0.01 mg kg^{-1}) using QuEChERS extracts (1 g ml^{-1} crop concentration), a 30 µl injection would be required. Since this is problematic other options including solvent exchange prior to GC-MS analysis and use of an alternative extraction solvent (ethyl acetate) were also evaluated.

2.2 Evaluation of the use of an acetonitrile QuEChERS extraction followed by a solvent exchange into an alternative solvent prior to GC-MS analysis.

In these experiments acetonitrile sample extracts (of a known volume) were concentrated to near dryness and made back up to the initial volume with a more suitable GC solvent such as iso-octane or toluene.

Standard mixes of pesticides were made up at the same concentrations in acetonitrile, iso-octane and toluene. For each of the solvents, the injection parameters and GC oven temperature settings were optimised (based on the peak shapes and intensities for each pesticide over a range of concentrations). As the pesticides have very different physico-chemical properties, it is impossible to optimise the injection conditions for each individual pesticide in one analysis, so a compromise had to be made. Spiked acetonitrile extracts were solvent exchanged into each of the alternative solvents prior to GC-MS analysis using 1 µl splitless injection. A volumetric ‘syringe’ standard was added after the solvent exchange to ensure any variation in injection volume was taken into account when comparing response. Solvent exchange into iso-octane (immiscible with acetonitrile) was impractical, whereas solvent exchange into toluene was feasible but time consuming. Chromatographic performance in toluene was not as good as with ethyl acetate. The solvent exchange step had a number of disadvantages as the sample preparation time is increased and there was potential for volatile pesticides to be lost during the concentration process. Therefore other approaches were explored (see below).

2.3 Evaluation of a QuEChERS-type extraction using ethyl acetate as the extraction solvent, followed by GC-MS analysis.

Ethyl acetate, a commonly used extraction solvent for pesticides that are analysed by GC, was assessed as an alternative extraction solvent to acetonitrile in a QuEChERS-type extraction. For 45 of the 48 pesticides studied, mean recoveries were within the range of 75 – 110 %, but there were significant losses for dichlofluanid, chlozolinate and captan.

The assessment of ethyl acetate was also performed using different combinations of extraction salts: anhydrous sodium hydrogen carbonate and anhydrous sodium sulfate; and anhydrous magnesium sulfate and sodium acetate were used. Mean recoveries were between 75 and 112 % including dichlofluanid, chlozolinate and captan. This procedure was then applied to the analysis of a further 24 organophosphorus pesticides. Mean recoveries were generally excellent, all were within the range 70 – 110 % except for methamidophos, acephate and omethoate, which had mean recoveries of 18, 10 and 25 % respectively. Control of the extraction temperature (30 ℃) for at least 20 min utes after solvent and salt addition increased recoveries of methamidophos, acephate and omethoate (32, 21 and 43 % respectively using sodium hydrogen carbonate and sodium sulphate; and 44, 28 and 52 % using magnesium sulfate and sodium acetate) but not to an acceptable level. These three pesticides (all polar organophosphorus pesticides) can be analysed successfully by LC-MS/MS, and it has previously been demonstrated that a QuEChERS extraction using acetonitrile yields acceptable recoveries for these compounds. Although this should be possible, the LC-MS/MS conditions need to be optimised to allow the inclusion of polar organophosphorus pesticides into the proposed multi-residue list.

The results of using ethyl acetate as the extraction solvent and employing either anhydrous sodium sulfate and anhydrous sodium hydrogen carbonate or magnesium sulfate and sodium acetate appeared promising. However, using an alternative extraction solvent had disadvantages. Firstly, it would require each sample to undergo two separate extractions (one for GC-MS analysis and one for LC-MS) as opposed to a single acetonitrile extraction; secondly, ethyl acetate extracted more sample matrix components compared to acetonitrile. This leads to increased maintenance of the GC instruments and to more problems when interpreting the analytical data. To overcome this issue the use of simple, rapid clean-up methods using different solid phase extraction materials in dispersive and cartridge modes were evaluated. Envi-carb (de-activated carbon) provided more efficient clean-up of fruit and vegetables compared to PSA (primary secondary amine) material, but decreased the recovery of some chlorinated pesticides.

2.4 Evaluation of the use of an acetonitrile QuEChERS extraction

Several different clean up procedures (alternative solid phase extraction materials in dispersive, plunger and cartridge modes) were evaluated for acetonitrile extracts. The quantification of the pesticide concentrations in the cleaned-up extracts was made using a GC single quadrupole MS system and using a 10 µl injection. After reviewing preliminary results (data not shown) PSD considered that acetonitrile extraction with dispersive clean-up using both primary secondary amine and carbon was the most appropriate method for application to the annual monitoring programme. The use of carbon was necessary to provide adequate clean-up for samples containing high concentrations of plant pigments (e.g. chlorophyll) but had the disadvantage of adsorbing some pesticides. The addition of toluene (20% by volume of the final extract) was found to improve the recovery of some of these pesticides. A schematic of the final method is shown in Flow Diagram A.

2.5 Validation of the QuEChERS-type GC-MS method.

The aim of this part of the project was to validate the PSD agreed method (as shown in Flow Diagram A) in terms of recovery, repeatability and relative extraction efficiency for a target list of analytes in pears and lettuce.

The final method was assessed for 94 pesticides at 0.05 mg/kg and 0.01 mg/kg in lettuce and pears using GC-MS. The results for the validation of lettuce and pears are shown in Tables 3 and 4 respectively.

In lettuce, the recoveries for 83 (88 %) of the pesticides were in the range 70-110 % with CV's $\leq$ 20 % at both 0.01 and 0.05 mg/kg. In pears, the recoveries for 77 (82 %) of the pesticides were in the range 70-110 % with CV's $\leq$ 20 % at 0.01 mg/kg, and 82 compounds (87 %) at 0.05 mg/kg.

Captan, chlorothalonil, dichlofluanid, dicofol, folpet and tolylfluanid could not be successfully validated. These compounds are particularly difficult to analyse but recently available information suggets that this issue may be resolved with the addition of sodium citrate during the QuEChERS extraction.

2.6 *Analysis of 50 samples (using typical PRC Quality Control) of both lettuce and pear from the 2005 PRC programme by the validated GC-MS based QuEChERS-type extraction methods. Comparison of data obtained from the surveillance programme using the non QuEChERS based methods*.

Fifty samples of both pear and lettuce known to contain residues (previously analysed in the 2004 & 2005 PRC programmes) were extracted by the new method and analysed for 94 pesticides. These analyses were performed in batch sizes similar to those employed for previous surveys, thus enabling a direct comparison of the efficiency of the new approach compared to the existing surveillance method (i.e. ethyl acetate extraction with gel permeation chromatography clean-up and GC-MSD analysis, as shown in Flow Diagram A) to be made.

A comparison of the previously acquired surveillance data with the results obtained using the new QuEChERS GC-MS method is shown for lettuce and pear samples in Tables 5 and 6, respectively. Associated Quality Control data from the QuEChERS GC-MS method is shown in Tables 7 and 8.

For each pesticide/commodity combination where >5 samples contained residues, these data are also presented graphically in Figures 1 – 11. Two formats have been used for this presentation. In the "(a)" version of the figures the data from the original surveillance method is plotted against the data obtained by new method based on QuEChERS GC-MS. A 'line of equality' has been drawn to indicate where the data points would fall if the concentrations obtained were exactly equal. Where appropriate the associated MRL's have been included in this graph. This is to help demonstrate whether analysis by either method would lead to the same decision regarding compliance or non-compliance. The "(b)" figure displays the same data as a histogram but includes information on the CSL sample number for reference. From these data the methods can be considered to be broadly comparable and samples containing non-compliant residues are correctly identified by the new method.

The determination of folpet in lettuce (Figure 3a) indicates a negative bias for the QuEChERS extraction, which may be due to degradation during storage (up to 2 years at –20 ºC) or degradation during the extraction. Further work would be required to determine the reason for

the difference observed. A recent modification to the QuEChERS method, which uses sodium citrate instead of sodium acetate, is reported to improve the stability and recovery of a number of pesticides including folpet. The negative bias observed for folpet in lettuce is not apparent for folpet in pears (Figure 8a) indicating that losses are matrix dependent.

The lower concentrations obtained for pyrimethanil (samples 54302 and 53923, Table 5), chlorothalonil (sample 53920, Table 5), and cyprodinil (samples 53920 and 47807, Table 5) using the QuEChERS GC-MS method is probably due to losses resulting from the use of carbon in the dispersive clean-up stage.

The confirmation of identity and quantification of captan at low concentrations is notoriously difficult. Tables 5 and 6 show that the concentration of captan residues determined in the surveillance samples by both the original and new procedures are generally comparable. However, the results obtained using the new QuEChERS GC-MS procedure are only considered to be qualitative, as the ion ratios often did not meet the confirmation criteria. Confirmation of captan in the presence of high concentrations of co-eluting tolyfluanid was not possible because of common ions (e.g. pears samples 56592 and 56595, Table 6). Therefore suspected residues of captan will still require confirmation by ECD (as is the case with current procedures) or the use of a more selective technique such as GC-TOF-MS.

Table 7 and 8 show the batch (spiking) recoveries obtained by the QuEChERS GC-MS method during the evaluation of lettuce and pear samples from the 2005 PRC programme. The majority of analytes tested had acceptable recoveries according to EU guidelines (Section 65 of SANCO/10232/2006 on acceptability of analytical performance for routine recoveries states that “Acceptable limits for single recovery should be in the range 60 - 140 %”). Although some batch recoveries for the QuEChERS GC-MS method were in the range 25 to 50% (as highlighted in Table 7 and 8) these analytes could be considered satisfactory for screening purposes due to the high signal/noise ratios obtained (data not shown). Alternatively pyrimethanil and cyprodinil could be included in the LC-MS/MS suite. Any sample found to contain chlorothalonil would require repeat extraction using another method, as is the case with the existing procedure.

Overall the GC-MS results obtained during this exercise indicate that, with a few exceptions, the extraction efficiency of QuEChERS acetonitrile method is essentially equivalent to the existing method based on ethyl acetate extraction with gel permeation chromatography clean-up.

3. Proposal for further R&D to integrate the GC and LC multi-residue approaches.

Table 9 summarises the applicability of the newly integrated QuEChERS LC-MS/MS and GC-MS procedure. This Table uses validation data from Tables 1 - 4 to indicate which technique (LC or GC) is appropriate for each analyte-matrix combination at different concentrations. The results demonstrate that the combination of LC-MS/MS and GC methods provide good analyte coverage. However, minor modifications in the methodology may need to be considered to overcome low recoveries for some analytes. Proposals for future R&D include:

- *Improvements to sample extraction/clean-up*
  For those unstable problematic compounds like folpet, tolylfluanid, dichlofluanid and captan, the addition of sodium citrate to improve buffering should be assessed.

  A reduction in the quantity of carbon used in the clean-up, which may eliminate the need for toluene, could also be evaluated.

The addition of analyte protectants to minimise the matrix effects could be investigated.

- *Improvements to GC-MS*
  The use of Siltek treated sintered liners in place of carbofrit could also be evaluated. Although carbofrit inserts have been used successfully there have been reports that the carbofrit can retain certain OP pesticides. Siltek treated liners which are reported to be a more inert alternative are now available, although this option is likely to be more costly compared to the use of carbofrit in the liner.

  The use of GC-MS/MS in place of GC-MS would provide greater selectivity for analytes that suffered from chemical interference.

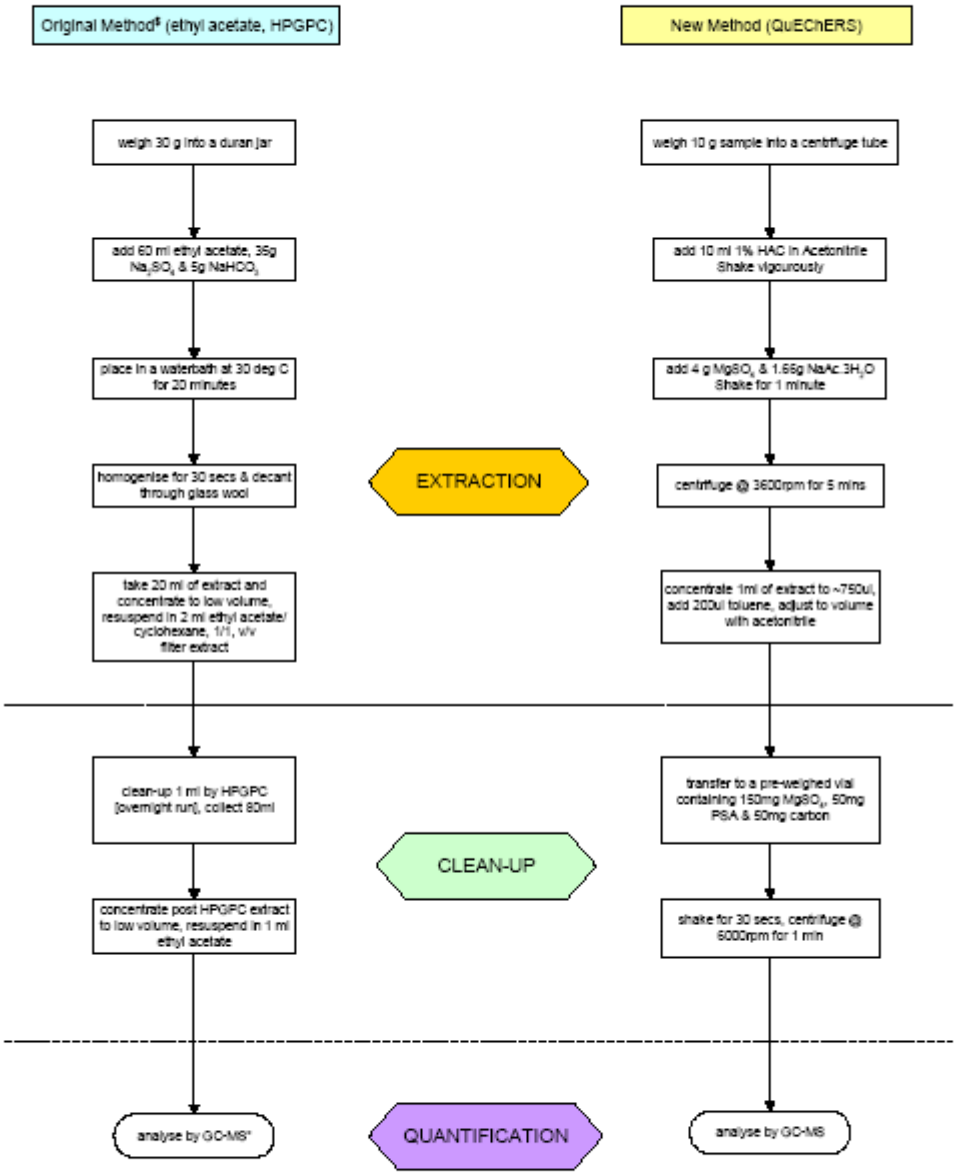
  The acetonitrile-based QuEChERS GC-MS method developed in this project will be employed in a complementary project for the development Rapid Low Cost Screening methods (PS2519). This will include an assessment of of response in full scan mode for matrices that contain high concentrations of (a) acid, (b) water and (c) protein.

- *Improvements to LC-MS/MS*
  Improved LC-MS/MS repeatability (and detection limits if required) could be achieved transferring the method from the existing API 2000 instrument to the newer API 4000 (or equivalent).

4. Conclusion

A single acetonitrile based QuEChERS extraction followed by a combination of GC-MS and LC-MS/MS can be used to determine *ca.* 230 pesticides in lettuce and pears. Data obtained by this method is comparable to the techniques currently employed in the PRC monitoring programmes. Further experiments are required to improve the robustness of the method for a few selected pesticides and to assess its applicability to other matrices. The principles of this method should be employed in the PSD funded project (PS2519) to investigate whether a much larger number of pesticides can be screened by GC-MS.

Flow Diagram A: Comparison of GC-MS methods for pesticides



$ this is the primary screening method used for pear and lettuce PRC surveys, a secondary extraction using an SPE clean-up is frequently required
*quantification may consist of 1 or 2 separate runs

Figures as .pdf files (double click to open)

"PS2513 Figures 1-5 021106.pdf"

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References to published material

9. This section should be used to record links (hypertext links where possible) or references to other published material generated by, or relating to this project.

None