Know-how for Horticulture™

Reducing pesticide residue screening costs for the Australian vegetable industry through the development of multi-pesticide residue screening protocols

Dr. Neil Rothnie
Chemistry Centre (WA)

Project Number: VG00001

VG00001

This report is published by Horticulture Australia Ltd to pass on information concerning horticultural research and development undertaken for the vegetable industry.

The research contained in this report was funded by Horticulture Australia Ltd with the financial support of the vegetable industry.

ISBN 0 7341 0702 1

Published and distributed by:
Horticultural Australia Ltd
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Horticulture Australia

HORTICULTURAL RESEARCH & DEVELOPMENT CORPORATION

Final Report

PROJECT TITLE

Reducing pesticide residue screening costs for the Australian vegetable industry through the development of multi-pesticide residue screening protocols

HRDC Project No: VG00001 (10 July 2003)

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Department of Industry and Resources

HORTICULTURAL RESEARCH & DEVELOPMENT CORPORATION

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Reducing pesticide residue screening costs for the Australian vegetable industry through the development of multi-pesticide residue screening protocols

HRDC Project No: VG00001

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Purpose of Report:

This is the final report for the above project and provides both a plain english summary (media statement) and technical summary describing the successful development of a multi-pesticide residue screening assay and generic sample preparation procedure applicable to the screening of vegetables for pesticide residues. A copy of the method is provided as an attachment. Accreditation for the assay is being sought from the National Association of Testing Authority (NATA) with the approval of Horticultural Australia.

We gratefully acknowledge the support of Horticulture Australia and the Vegetable Research & Development levy payers in funding the project 'Reducing pesticide residue screening costs for the Australian vegetable industry through the development of multi-pesticide residue screening protocols'.

Report Date: 10 July 2003

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Media Summary

Pesticides are a permanent and necessary feature in modern agricultural production systems. Over 400 herbicides, fungicides and insecticides are registered for use throughout the world. Regulatory authorities throughout the world are increasingly concerned with pesticide residues and have established very stringent maximum residue levels (MRL). The world-wide trend is towards ever lower MRL's and in some instances zero tolerance.

Faced with these challenges the Australian horticultural industry has developed various "Quality Assurance Programs" that aim to reduce the potential for violative chemical residue levels and to maintain the industries reputation for "Clean Vegetables".

Pesticide residue analysis charges are very expensive and the reason for this is twofold. In the first instance a comprehensive pesticide screen requires a diverse range of expensive analytical instrumentation and sample preparation techniques. The second reason is a consequence of the large number of pesticide residues and vegetable types that are encountered. To reduce costs laboratories need to have access to analytical instrumentation and generic sample preparation techniques to replace the wide range of techniques that are currently used and must be supported by the laboratory.

This project aimed to develop generic and automated sample preparation techniques to reduce the cost of sample preparation prior to analysis and Gas Chromatography – Mass Spectrometry (GC-MS) screening procedures with true multi-pesticide residue screening capability. These objectives have largely been achieved, especially the development of generic sample preparation procedures.

The GC-MS procedure is better suited for use as a screening tool and in some instances, for example organochlorine pesticides, the use of which has now been discontinued, is not as sensitive as some other Gas Chromatographic techniques. The GC-MS procedure is however well suited to multi-pesticide residue screening and as such can be used to identify those vegetable samples containing violative pesticide residue levels. The new assay has been validated against established techniques and is being forwarded to the National Association of Testing Authorities (NATA) for accreditation.

The new assay will be made available to other government and private laboratories throughout Australia involved in pesticide residue analysis.

Technical Summary

Pesticide residue analysis charges are very high because of the diverse range of expensive analytical instrumentation and sample preparation techniques and the large number of pesticide residues and vegetable types that are encountered.

This project aimed to develop generic and automated sample preparation techniques to reduce the cost of sample preparation prior to analysis and a single Gas Chromatography – Mass Spectrometry (GC-MS) screening procedure with true multi-pesticide residue capability.

These objectives have largely been achieved, especially the development of generic sample preparation procedures. Sample preparation for this project involved the Accelerated Solvent Extraction of the vegetables with acetone/hexane (10:90). Accelerated Solvent Extraction involves extraction of the matrix with an organic solvent at a temperature above the boiling

point of the solvent mixture and under a high pressure in order to keep the solvent a liquid. The technique affords superior solvent penetration of the sample matrix and extraction efficiencies comparable with soxhlet systems but with solvent volumes of 40 mL and extraction times of 15 minutes.

Clean up of the extracts was achieved using two solid phase extraction (SPE) columns (containing Envi-carb and LC-NH_2 adsorbents) with a specific solvent system A relatively "clean" extract is obtained that only contains the analytes of interest with minimal matrix interferences.

Samples are then analysed by GC/Ion-Trap Mass Spectrometry (ITMS), in full scan mode. The Ion Trap allows sufficient sensitivity in full scan mode. In this way each analyte could be identified by retention time on the chromatographic column as well as by mass spectral data. Partially overlapping chromatographic peaks could be deconvoluted by monitoring ions specific to individual pesticides.

The method which was developed is able to screen for 77 different agricultural chemicals which represent a large range of different chemical groups consisting of insecticides, herbicides, fungicides and pesticide synergists.

The use of Accelerated Solvent Extraction has significantly reduced the analysis time for pesticides in fruit and vegetable matrices. The most significant gains will be realised by laboratories with a high sample turnover. Gas Chromatography with Ion Trap Mass Spectrometric detection in the full scan mode provides for positive identification of detected pesticides below the MRL for most analytes.

Further work is being undertaken to extend the number of pesticide residues covered by the method. The expanded procedure will include additional representatives of the major pesticide classes.

Introduction

Pesticides are a permanent and ubiquitous feature of modern horticultural production systems. Over 400 herbicides, fungicides and insecticides are registered for use throughout the world. Regulatory authorities throughout the world are increasingly concerned with pesticide residues and through CODEX have established either stringent maximum residue levels (MRL) or zero tolerance for the detection of pesticide residues not approved for use in their country. The USA, Japan and European countries have been particularly stringent in their regulations. Australia has an excellent reputation as a supplier of 'Clean Vegetables'. The challenge for the Australian horticultural industry is to maintain this image. The horticultural industry has responded to this challenge through the establishment of Quality Assurance Programs, one such program is "Safe Quality Food 2000" (SQF2000). These programs include a provision for pesticide residue screening to ensure that the measures and documented procedures put in place to minimise pesticide residues are effective. However the cost of pesticide screening is very high. The reasons for these high costs are essentially twofold. In the first instance a comprehensive pesticide screen requires a multiplicity of instrumental techniques, including several liquid (LC) and Gas Chromatographic (GC) systems equipped with ECD, FPD, NPD and Mass Spectrometric detection (MS). The second reason is a consequence of the large number of pesticide and vegetable types that must be screened. Because of this, laboratories tend to use a wide range of sample preparation and

clean up procedures for individual pesticides (or classes of pesticides) rather than generic sample clean up and detection systems.

In response to these challenges, large well-equipped overseas laboratories have developed multi-residue screening protocols utilising either GC-MS-MS instruments or a combination of GC-MS and GC with Atomic Emission Detection (AED). These instrumental techniques are complemented by low cost generic sample preparation techniques. It is this combination of multi-pesticide residue and generic sample preparation techniques that reduces screening costs.

In addition the various sample extraction techniques use various solvent systems and generate significant waste solvent disposal problems. Recently, new automated extraction systems have become commercially available which show extraction efficiencies approaching that of Soxhlet systems but able to perform the extraction in 15 minutes instead of overnight runs. These systems significantly use only 20-40 ml of solvent. One such system is the Accelerated Solvent Extractor (ASE) which uses a combination of high temperature and pressure to allow penetration of the sample matrix by solvent. These systems have the advantage not only of excellent extraction efficiency but can also be automated thus reducing labour costs and method bias owing to poor extraction..

Specific multi component detection systems such as MS, when used in combination with these automated sample preparation techniques, are capable of analysing most pesticide residue combinations in two runs.

To ensure that the methodologies developed in this project are suitable for the analysis of new pesticides and pesticides of concern to other countries, even though they may not be approved for use in Australia, advice has been sought from:

- state agriculture departments
- industry horticultural development officers
- the National Residue Survey (NRS)
- CODEX and FAO guidelines and
- Infopest

The new multi-pesticide residue screening techniques developed in this project will be used to reduce compliance costs associated with Quality Assurance Programs and safeguard the industry's reputation for high quality. They will also be made available to other Australian laboratories without restriction.

Milestones

Milestone	Due	Description	Status
No. 1	**1/10/00**	HRDC Research, Development and Commercialisation Agreement signed and voluntary contribution received (if relevant). Intellectual Property arrangements in place.	**Completed**
No. 2	**31/3/01**	Chromatographic conditions for the GC-MS-MS, and GC-AED determination of a range of registered Australian pesticide standards will have been established.	**Completed**
No. 3	**30/09/01**	Establish chromatographic conditions and sample extraction protocols for the determination of pesticides in spiked vegetable samples	**Completed**
No. 4	**31/03/02**	Optimisation of generic sample clean-up procedures and residue detection limits	**Completed**
No. 5	**30/08/02**	Validation of preferred analytical methodologies	**Completed**
No.6	**30/10/02**	Final report received by due date and all previous milestones achieved. Final report was delayed due to staff resignation and need to generate more method validation data consistent with the requirements of the National Association of Testing Authorities (NATA)	**Completed**

Materials and Methods

Sample preparation for this project involved the Accelerated Solvent Extraction of the vegetables with acetone/hexane (10:90). Accelerated Solvent Extraction involves extraction of the matrix with an organic solvent at a temperature above the boiling point of the solvent mixture and under a high pressure. Using this system a better extraction efficiency is observed.

Although a larger amount of analytes are recovered a correspondingly large amount of interferences are also obtained. The extract is loaded onto two solid phase extraction (SPE) columns (containing Envi-carb and LC-NH_2 adsorbents) using a specific solvent system. The adsorbents are then washed with solvents of varying polarity to extract out the components of interest without removing the trapped interferences. Consequently a "clean" extract is obtained that only contains the analytes of interest without matrix interferences.

Samples are then analysed by GC/Ion-Trap Mass Spectrometry (ITMS), in full scan mode. Each analyte was identified by retention time on the chromatographic column as well as by mass spectral data. These parameters are given in the table below (Table 1).

Table 1.

Analyte	Minutes	Quantitation Ion m/z
Methomyl	9.68	88
Dichlorvos	11.18	185
Bendiocarb	11.33	166
Carbofuran	11.57	164
Methamidophos	11.70	94
Diuron	11.73	187
5-Dichlorobenzonitrile	12.67	171
Pebulate	12.87	128
Mevinphos	13.19	127
Methiocarb	14.60	168
Trifluralin	14.69	306
Benfluralin	14.79	292
Propachlor	15.45	120
Ethoprophos	15.50	158
Chlorpropham	15.62	127
Pencyuron	15.83	180
Phorate	16.26	75
Hexachlorobenzene	16.48	284
Bendiocarb	16.77	151
Terbufos	16.99	231
Propyzamide	17.07	173
Atrazine	17.30	200
Quintozene	17.47	295
Disulfoton	17.71	88
Dimethoate	17.87	87
Pirimicarb	18.61	166
Terbacil	18.69	161
Prometrin	19.19	241
Metalaxyl M	19.36	206
Methyl parathion	19.43	109
Metribuzin	19.53	198
Metolachlor	19.69	162
Chlorpyrifos	19.86	314
Ethofumesate	19.87	207
Dichlofluanid	20.12	123
Bioallethrin	20.20	123
Fipronil	20.35	368
Bromacil	20.63	207
Pendimethalin	20.69	252
Pyrethrum	20.96	123
Penconazole	21.00	248
Triadimenol	21.18	112
Procymidone	21.32	96
cis-Chlordane	21.43	373
Trans-Chlordane	21.68	373
Pyrefinox	21.78	262
Prothiophos	21.94	309

Analyte	Minutes	Quantitation Ion m/z
Hexaconazole	22.13	214
p,p-DDE	22.24	318
Buprofezin	22.31	105
Napropamide	22.34	271
Methidathion	22.36	145
Dieldrin	22.51	79
Buprimate	22.60	273
Endosulfan II	23.03	241
Myclobutanil	23.06	179
Endrin	23.31	81
Cyproconazole	23.37	222
Carboxin	23.56	143
p,p-DDT	23.66	235
Sulprofos	23.97	322
Benalaxyl	24.29	148
Propargite	24.42	135
Bifenthrin	24.59	182
Tebuconazole	24.81	250
Norflurazon	24.97	303
Endosulfan sulfate	25.02	272
Methoxychlor	25.11	227
Hexazinone	25.78	171
Fenoxycarb	25.92	116
Methoxychlor	26.01	227
Furathiocarb	26.06	163
Tetradifon	26.75	356
Pyrazophos	27.19	374
Permethrin1	27.56	163
Fenarimol	27.62	139
Permethrin2	27.75	163
Bitertanol	27.78	170
Cyfluthrin I	28.24	163
Cyfluthrin II	28.50	163
Cyfluthrin III	28.49	163
Cypermethrin I	28.87	163
Cypermethrin II	29.02	163
Cypermethrin III	29.15	163
Fluvalinate	29.95	248
Fluvalinate II	29.99	248
Deltamethrin I	30.75	225
Deltamethrin II	31.16	225

A copy of the analytical method is attached.

A series of experiments were performed to establish the validity of the method. One of the best indications for the robustness of the method is the repeated analysis of a number of vegetables spiked with the analytes at the Limit of Quantitation (0.02 mg/Kg). These were determined from a minimum of nine spikes of five different vegetable matrices (Table 2).

One matrix (carrot) was done at a higher spiking level to determine variability in the recoveries at a higher incidence of ions within the ion trap mass spectrometer. The matrices were chosen to represent the higher consumption vegetables as well as a good range of family types to demonstrate the robustness of the method to varied matrices.

Table 2.

Matrix	Type	Botanical Name	Family
Carrot	Root	*Daucus carota*	Apiaceae - Parsley
Celery	Stalk/Leaf	*Apium graveolens*	Apiaceae - Parsley
Potato	Tuber	*Solanum tuberosum*	Solanaceae - Potato
Asparagus	Shoot	*Asparagus officinalis*	Liliaceae - Lily
Cucumber	Cucurbit	*Cucumis sativus*	Cucurbitaceae - Gourd

All experiments showed good recoveries with some matrix enhancement effects apparent. The full set of validation results can be found in the appendices of the method.

Discussion

Original objectives:
To develop a practical and low-cost multi-pesticide residue screening procedure that can be used to reduce quality assurance compliance costs associated with multi-pesticide residue screening, defined pesticide suites as described in the grower SQF2000 plan and, in most instances, single pesticide residue screens.

This output will be complemented through the development of low-cost generic sample extraction and cleanup procedures.

The method developed is able to screen for 77 agricultural chemicals. These chemicals were chosen to represent a large range of different chemical groups consisting of insecticides, herbicides, fungicides and pesticide synergists.

The following groups are represented:

- organochlorine insecticide
- synthetic pyrethroid insecticide
- organophosphorous insecticide
- phenylpyrazole herbicide
- thiocarbamate herbicide
- dinitroaniline herbicide
- chloroacetamide herbicide
- benzamide herbicide
- triazine herbicide
- urea herbicide
- uracil herbicide
- benzofuran herbicide
- triazinone herbicide
- benzonitrile herbicide
- a range of fungicides

Further work is in progress to extend the number of pesticide residues covered by the method. The expanded procedure will include additional representatives of the major pesticide classes.

The evidence indicates that the extraction and clean-up methods that were developed for this method are suitable for a wide range of analytes with widely varying chemical structures. Accelerated solvent extraction (ASE) gives almost quantitative extraction and thus lower uncertainties owing to a smaller bias within the method. With further improvements to the solvent evaporation systems a faster and more efficient procedure could be used for higher throughput.

There is the potential to expand the method to include quantitation of analytes in non-compliant samples detected using the screening method. This would use other sensitive detectors such as electron-capture and nitrogen-phosphorous detection, which would, possibly, allow quantitation at even lower quantitation levels. The method can also be extended to other similar food matrices such as fruit.

Analytical laboratories will be able to utilise this method to screen for 77 agricultural chemicals and to use the technologies involved to easily adapt the procedure, with minimal effort, to many other agricultural chemicals in vegetables.

Since much of the information is already acquired, laboratories utilising this method need only perform basic validation procedures to provide evidence that they are capable of using the method, instead of the extensive validation procedures required for a new method.

Any extension to the method will need additional validation to demonstrate that the laboratory and the method are capable for the extension proposed.

Technology Transfer

The technology developed as a result of this project consists of an analytical chemistry method of analysis for screening pesticide residues in fruit and vegetables. This method has been validated and NATA accreditation is currently being sought.

The method will be made available to any Australian NATA accredited laboratory free of encumbrance.

Recommendations

Further work on the automated extraction of pesticides is planned. The critical point is the evaporation of the ASE extracts. Some automated evaporation systems have been tested and others are in the process of being investigated.

ADMINISTRATION OF THE PROJECT/PROGRAM

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CERTIFICATION

This proposal has been seen and endorsed by your organisation and any collaborators involved.

Signature of Project/Program Leader **Date**

Name **Organisation**

Signature of Organisation's Administration Contact **Date**

Name **Organisation**

Title: **Multi-Residue Screening in Vegetables**

Screening Method for Multiple pesticide Residues in vegetables by GC/Ion-Trap MS.

SAFETY CONSIDERATIONS

WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION. IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY

Acetonitrile: Acetonitrile is highly flammable. It is toxic by inhalation, contact with skin and ingestion. Keep away from sources of ignition, oxidising agents, acids, conc. sulfuric acid and cyanide complexes.

Acetone: Acetone is highly flammable. Keep away from sources of ignition and take precautionary measures against static discharges.

Hexane: Acetone is highly flammable. Keep away from sources of ignition and take precautionary measures against static discharges

Toluene: Toluene is highly flammable. It is harmful by inhalation and highly flammable.

Pesticides: All pesticides are Schedule 5.3. They are harmful by inhalation, ingestion and may be absorbed through the skin.

1. SCOPE

This method enables detection of a range of pesticides (77 analytes) including organochlorine, organophosphorous, synthetic pyrethroids and carbamate pesticides, a variety of herbicides, and some fungicides in vegetables at levels below their respective maximum residue levels (MRL's), except where indicated in Table 1.

This method is a screening method only and cannot quatitate those pesticides higher than the limit of quantitation. For quantiation of analytes, further validation is required for that matrix.

Table 1. Analytes and Limits of Reporting for Vegetables and Limitations Based on the Reported MRLs (reference 10.1)

Analyte	**LOQ**	**MRL Carrot**	**MRL Celery**	**MRL Potato**	**MRL Asparagus**	**MRL Cucumber**
Organochlorine-Insecticide						
a-Chlordane	0.02	0.02	0.02	0.02	0.02	0.05
b-Chlordane	0.02	0.02	0.02	0.02	0.02	0.05
pp-DDT	0.02	1	1	1	1	1
pp-DDE	0.02	1	1	1	1	1
Dieldrin	0.02	0.1		0.1	0.1	0.1
b-Endosulfan	0.02	2		2	2	2
Endosulfan Sulfate	0.02					
Endrin	0.02					
HCB – Hexachlorobenzene	0.02					
Methoxychlor	0.02					
Procymidone	0.02	1		0.1		

Title: **Multi-Residue Screening in Vegetables**

Analyte	**LOQ**	**MRL Carrot**	**MRL Celery**	**MRL Potato**	**MRL Asparagus**	**MRL Cucumber**
Cypermethrin	0.1	**0.01**	**0.01**	**0.01**	0.5	**0.01**
	0.02 mg/Kg LOQ for Asparagus					
Permethrin	0.02		5	0.05		0.2
Bifenthrin	0.02					
Cyfluthrin	0.1					
	0.02 mg/Kg LOQ for Asparagus and Cucumber					
Fluvalinate	0.1				0.2	
	0.02 mg/Kg LOQ for Asparagus and Cucumber					
Bioallethrin	0.02					
Pyrethrins (Pyrethrum)	0.1	1	1	1	1	1
Deltamethrin	0.1					
	0.02 mg/Kg LOQ for Asparagus					
Organophosphorous-Insecticide						
Chlorpyrifos	0.02	**0.01**	5	0.05	0.5	**0.01**
Dichlorvos	0.02	0.5	0.5	0.5	0.5	0.5
Dimethoate	0.02	2	2	2	2	2
Methamidophos	0.1		2	0.25		0.5
Methidathion	0.02	**0.01**	0.1	**0.01**	0.1	0.1
Mevinphos	0.02					
Parathion- Methyl	0.02	0.5	3	0.05		
Phorate	0.02	0.5	0.5	0.5	0.5	0.5
Pyrazoaphos	0.02					0.2
Ethoprophos	0.02			0.02		
Terbufos	0.02					
Disulfoton	0.02	0.5	0.5	0.5	0.5	0.5
Prothiofos	0.02					
Sulprofos	0.02					
Methiocarb	0.02	0.1	0.1	0.1	0.1	0.1
Methomyl	0.1					0.2
Pirimicarb	0.02	1	1	1	1	1
Chlorpropham	0.02			30		
Bendiocarb	0.02					
Furathiocarb	0.02					
Carbofuran	0.02 for Cucumber, 0.1 for Carrot					
Phenylpyrazole-Herbicide						
Fipronil	0.02			**0.01**	0.5	
ThioCarbamate – Herbicides						
Pebulate	0.02					
Dinitroaniline - Herbicide						
Trifluralin	0.02	0.5	0.05	0.05	0.05	0.05

Title: **Multi-Residue Screening in Vegetables**

Analyte	**LOQ**	**MRL Carrot**	**MRL Celery**	**MRL Potato**	**MRL Asparagus**	**MRL Cucumber**
Benfluralin	0.02					
Pendimethalin	0.02	0.05		0.05		
Chloroacetamide - Herbicide						
Propachlor	0.02					
Metolachlor	0.02					0.05
Benzamide - Herbicide						
Propyzamide	0.02					
Triazine - Herbicide						
Atrazine	0.02			**0.01**		
Prometryn	0.02	0.1	0.1	0.1	0.1	0.1
Ureas - Herbicides						
Diuron	0.02				2	
Uracil - Herbicide						
Terbacil	0.02				0.04	
Bromacil	0.02					
Benzofuran - Herbicide						
Ethofumesate	0.02					
Triazinone - Herbicide						
Metribuzin	0.02			0.05	0.2	
Hexazinone	0.02					
Benzonitrile -Herbicide						
3,5-Dichlorobenzonitrile	0.02					
Other Insecticides						
Buprofezin	0.02					
Fenoxycarb	0.02					
Other Herbicides						
Napropamide	0.02					
Norflurazon	0.02				0.05	

Title: **Multi-Residue Screening in Vegetables**

Analyte	**LOQ**	**MRL Carrot**	**MRL Celery**	**MRL Potato**	**MRL Asparagus**	**MRL Cucumber**
General						
Buprimate	0.02					
Propargite	0.02	3	3	3	3	3
Tetradifon	0.02	5	5	5	5	5
Fungicide						
Pencycuron	0.02			0.05		
Quintozene	0.02		0.3	0.2		
Metalaxyl-M	0.02	0.1	0.1	0.1	0.1	0.1
Dichlofluanid	0.1					
Penconazole	0.02					
Triadimenol	0.02					0.5
Pyrifenox	0.02					
Hexaconazole	0.02					
Myclobutanil	0.02				0.02	
Cyproconazole	0.02			0.02		
Carboxin	0.02					
Benalaxyl	0.02					0.2
Tebuconazole	0.02					
Fenarimol	0.02					0.2
Bitertanol	0.02					

Numbers in bold indicate LOQ>MRL.

2. DEFINITIONS

SPE: Solid phase extraction
OPs: Organophosphorus pesticides
OCs: Organochlorine and other halogenated pesticides
Pyr's: Pyrethroid pesticides
ASE: Accelerated Solvent Extraction

3. PRINCIPLE

Due to the large variety of pesticides in use, a multiresidue method is required for routine analysis. This involves the Accelerated Solvent Extraction of the vegetables with acetone/hexane (10:90). Interferences are removed from the extract by passing though two solid phase extraction (SPE) columns (Envi-carb and LC-NH_2). The adsorbent is then washed with solvents of varying polarity to remove the components of interest.

Samples are analysed by GC/Ion-Trap Mass Spectrometry (ITMS).

Title: **Multi-Residue Screening in Vegetables**

4. REAGENTS

4.1 Acetonitrile: nanograde

4.2 Toluene: nanograde

4.3 Anhydrous sodium sulphate

4.4 Envi-Carb SPE tube: solid phase extraction cartridge 3mL (250mg of carbon) Supelco. In any batch of analysis the SPE cartridges must all belong to a single lot number.

4.5 LC-NH_2 SPE tube: solid phase extraction cartridge 3mL (500mg) Supelco. In any batch of analysis the SPE cartridges must all belong to a single lot number.

4.6 Acetone, nanograde

4.7 Hexane, nanograde

4.8 Methanol: HPLC grade.

4.9 Standards

All primary standards must be precisely weighed and solutions entered in the "HIPPO" database. The standards must be labelled and an expiry set at 6 months for the working standards. All standards are stored in a freezer when not used.

4.9.1 Calibration Stock Solutions

These concentrated standard solutions are prepared by precisely weighing calculated masses of pure standard into volumetric flasks. The individual analyte solutions are then made up to volume in acetone. Concentrations are calculated using equation 1.

Stock standard	Approx mass of analyte (mg)	Volume of solvent (mL)	Approx standard concentration (ug/mL)
Individual Analyte	10	50	200

Equation 1:

$$Concentration(ug\ /\ mL) = \frac{weight(mg)}{volume(mL)} \times 1000$$

Where,
Concentration (µg/mL) = concentration of stock solution for that analyte
Weight (mg) = The mass of analyte added to the volumetric flask
Volume (mL) = The volume of the final solution

4.9.2 Mixed Standard Solution

A mixed OC standard (approx. 2 µg/mL) is prepared from the individual stock solutions (4.9.1). 2 mL (using a calibrated glass pipette) of each stock standard is added to a single volumetric flask and made up to 200mL in acetone. Concentrations are calculated using equation 2.

Equation 2:

$$Concentration_{\text{int}ermed} = \frac{Concentration_{Stockso\ln} \times Vol_{Aliquot}}{Volume_{Total}}$$

Where,
$Concentration_{intermed}$ = conc of analyte in the intermediate mixed std solution (4.9.2) (µg/mL)
$Concentration_{stocksoln}$ = concentration of analyte in the individual stock solution (4.9.1) (µg/mL)
$Vol_{Aliquot}$ = Volume of stock solution (4.9.1) added (mL)
$Volume_{total}$ = The volume of the final solution (4.9.2) (mL)

4.9.3 Calibration (Working) Standard

A dilution of the mixed standard solution (4.9.2) is prepared for one calibration standard at approx 0.2 ug/mL. 2 mL (using a calibrated glass pipette) of the mixed standard solution (4.9.2) is added to a 20 mL volumetric flask and made to volume in acetone. Concentrations are calculated using equation 3.

Equation 3:

$$Concentration_{workingstd} = \frac{Concentration_{intermed} \times Vol_{Aliquot}}{Volume_{Total}}$$

Where,

$Concentration_{workingstd}$ = concentration of analyte in the working std solution (4.9.3) (µg/mL)
$Concentration_{intermed}$ = concentration of analyte in the intermediate mixed std solution (4.9.2) (µg/mL)
$Vol_{Aliquot}$ = Volume of mixed std solution (4.9.2) added (mL)
$Volume_{total}$ = The volume of the final solution (4.9.3) (mL)

4.9.4 Matrix Matched (MM) Calibration (Working) Standard

A MM calibration standard is prepared at approx 0.2 ug/mL from the mixed standard solution (4.9.2). A blank matrix extract is prepared by preparing a blank matrix through the procedure from 7.1 to 7.18. 100 ul of the mixed std solution (4.9.2) is then added to the blank matrix extract to obtain a final concentration of 0.2 ug/mL.

4.10 Stock Internal Standard Solution

Approximately 10 mg of triphenyl phosphate is precisely into a 100 mL volumetric flasks. The solution is then made up to volume in acetone. Concentrations are calculated using equation 1.

4.11 Working Internal Standard Solution

A working internal standard solution (approx. 2 µg/mL) is prepared from the stock solution (4.10). 1 mL (using a calibrated glass pipette) of the stock standard is added to a 50mL volumetric flask and made up in acetone. Concentrations are calculated using equation 2.

Title: **Multi-Residue Screening in Vegetables**

5. APPARATUS

5.1 Homogeniser: Roboblixer (if required) and a Heidolf homogeniser
5.2 Graduated tubes (10mL)
5.3 Graduated centrifuge tubes (15mL)
5.4 Rotary evaporator
5.5 SPE vacuum manifold
5.6 SPE reservoirs (>15mL)
5.7 Reservoir adaptors
5.8 Teflon needles for vacuum manifolds (Alltech)
5.9 Dionex Accelerated Solvent Extractor (ASE) #200

5.9.1 *Analytical Conditions*

Solvent: Hexane:Acetone (90:10)
Temperature : 100°C
Pressure : 1500psi
Heat up time : 5 min

Static Time : 5 min

Flush Volume : 60%
Purge Time : 100s
Static Cycles : 1-2

5.10 ASE cell. All ASE cells must be thoroughly clean and dry before use. To prepare an ASE cell, remove the end of the cell furthest from the dionex mark. Add to the cell a small disc of glass fibre filter paper cut to the same diameter as the inside of the cell. Push the filter paper gently to the bottom of the cell ensuring that it is flush with the bottom of the cell. Add a small amount (1 to 2 g) of hydromatrix to the bottom of the cell just before use.

5.11 Gas Chromatograph/ Mass spectrometer

5.11.1 Gas Chromatograph/ Mass spectrometer
Varian 3800 Gas Chromatograph / Saturn 2000 Ion Trap Mass Spectrometer.
The GC column used is a J&W DB-35MS 30m x 0.25mm x 0.25um
Analytical conditions

Injector	Programmed split/splitless 35°C (4min) to 280°C (10mins) @ 100°/min. With split ratio at 100:1 for 1min, splitless for 1min, then returning to split.
Detector	Varian Saturn Ion Trap MS, full scan 50-550 Source temp 250°C
Column	35°C for 4mins 20°C/min to 160°C 8°C/min to 280°C, hold for 10 mins

5.11.2 GC/MS method to be used: hrdcINJTRIAL.mth
5.11.3 See Varian instrument manuals for specific details on the operation of the gas chromatographs and/or data systems.

Title: **Multi-Residue Screening in Vegetables**

6. SAMPLING and SAMPLE PREPARATION

The samples must be of merchantable quality. The samples are registered on receipt and placed in a chest freezer at –20^{o}C. The portion of the fruit or vegetable to be analysed is subsampled according to the requirements of the NRA guidelines (reference 10.2 and 10.3). The samples are stored in the freezer until analysed.

Samples are collected according to the following guidelines

Sample Size	A minimum of two items per sample and a minimum of 1 Kg per sample.
Transport	***Place samples in separate clean bags (paper or foil if possible). Transport bags in esky or other container that will protect food from sunlight and physical damage.*** Do not wash or clean samples.

Quarantine Note: If the samples are from interstate or overseas, label with a rectangular orange quarantine sticker and place them into the **quarantine** freezer and record the sample detail.

7. PROCEDURE

If sample extracts are to be left overnight the solutions must be stored in a freezer in 15 mL graduated screw-top centrifuge tubes.

7.1 Precisely weigh 10g of the sample into a small wide-necked beaker or watch glass containing an equivalent amount of hydromatrix. The hydromatrix is present to remove any water.

7.2 Transfer the mixture to a clean mortar making sure that all of the sample is transferred. Add more small amounts of hydromatrix if some sample remains in the glass beaker or watch glass.

7.3 Add a small amount of clean sand to the mortar and grind the sample carefully into the hydromatrix. Make sure that the pestle does not contact the wet sample directly until it is thoroughly dry.

7.4 When the sample mixture is dry and homogenised with the hydromatrix, add the mixture to a pre-prepared ASE cell. Add only a small amount of mixture at a time and tap the cell gently to ensure an even packing. Fill the cell to the top, if there is not enough mixture to do so then fill the remaining space with hydromatrix. If there is too much mixture and it will not fit into the cell then discard and repeat the steps 7.1 to 7.4.

7.5 Add 100 uL of the spike solution to the tope of the hydromatrix for the matrix spike and control samples.

7.6 Screw on the top end of the cell and tighten. Make sure that the cell is completely sealed and the ends are tight before extraction.

7.7 Put the cells into the ASE instrument and extract using the ASE conditions given in ?.?.?.

7.8 Take the collected extract and transfer quantitatively to a round bottom flask through a funnel containing approx 5 g of sodium sulphate to remove residual water. Rinse with a small volume (5 mL) of acetonitrile.

7.9 Concentrate the eluant to a low volume using a rotary evaporator set at 35°C. Exchange with acetonitrile by adding 20 mL acetonitrile and concentrating to a low volume (approx 5 mL) after the addition. Do not allow to go to dryness.

7.10 Transfer the concentrated extract to a graduated test tube and evaporate under nitrogen to approx 1 mL.

7.11 Place clean glass tubes in the vacuum manifold.

7.12 Connect teflon needles to each adaptor on the vacuum manifold.

7.13 Condition the SPE tubes with 2 mL of acetonitrile. Discard these solutions.

7.14 Fit a L-NH_2 SPE column to each teflon needle.

7.15 Fit an ENVI-Carb tube in series with the LC-NH_2 SPE column using a reservoir adaptor as in figure 1.

7.15 Quantitatively transfer the solutions from 7.10 to each ENVI-Carb tube using an acetonitrile / toluene (1:1) solution (~5mL). Ensure all material on the tube sides have been re-dissolved and transferred using 2 x 1 mL aliquots of acetonitrile/toluene (1:1). Add aliquots to SPE cartridges.

7.16 Elute the analytes with 4 mL of acetoniltrile / toluene followed by 6 mL of 100% acetoinitrile. Allow the SPE tubs to elute under gravity.

7.17 Evaporate to less than 0.5 mL under nitrogen. Make to a final volume of 0.9 mL with acetone.

7.18 Add 100 uL of the internal standard solution (4.11) to the collected SPE eluant.

7.19 Analyse the standards and the samples by Gas chromatography.

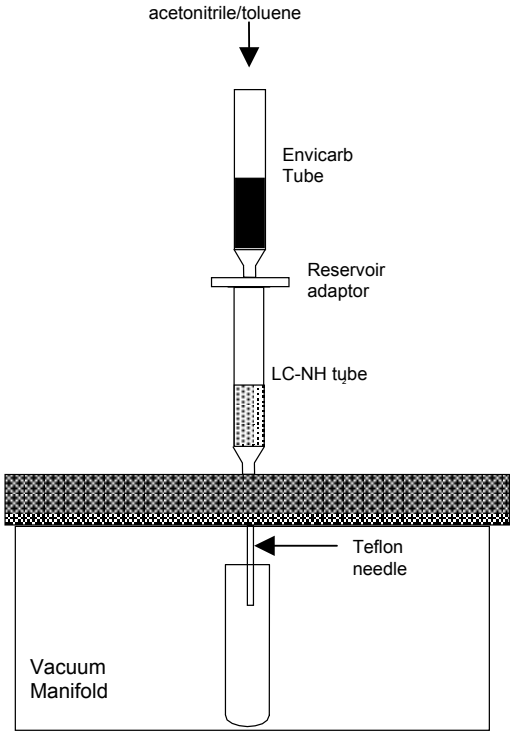

Figure1.

8 CALCULATION, INTERPRETATION AND REPORTING OF RESULTS

8.1 GC Interpretation of analytes

8.1.1 See Appendix A for specific retention times.

8.1.2 Each matrix matched standard must be run at the beginning and at the end of each batch of samples.

8.1.3 Analytes are identified by retention time within a retention time window and by quantitation ion (see appendix A).

8.2 Calculation of Analyte concentrations:

Owing to the highly variable response of the Ion-Trap mass spectrometer to the matrix a single point calibration against a matrix matched standard is used to determine if an analyte is present. If the Response Factor (RF) of the analyte in the sample is greater than the RFof the analyte in the Matrix Matched calibration standard (4.9.4) then it is considered to be present above quantitation limits. Further investigation is then required to quantitate the exact amount present in the sample. Response Factors (RF) are calculated according to Equation 5.

Equation 5.

$$RF = \frac{Signal_{Analyte}}{Signal_{IS}}$$

Where,
RF = Response Factor
$Signal_{Analyte}$ = The signal of the analyte in the solution, entered as raw data (area)
$Signal_{IS}$ = The signal of the Internal Standard (triphenyl phosphate) in the solution, entered as raw data (area).

8.4 Calculation of Analyte concentrations:

If a signal of the analyte in the sample is within 0 to 20% over the signal of the analyte in the matrix matched standard, then a tentative semi-quantitative result can be reported according to Equation 6 below. Signals in the sample below that of the standard are considered to not be present.

Equation 6.

$$\mathrm{Re}sult(mg/Kg) = \frac{RF_{sam}}{\mathrm{RF}_{std}} \times Conc_{Std} \times \frac{Vol_{final}}{Wt_{sam}} \times 1000$$

Where,
Result (mg/Kg) = The concentration of the analyte in the sample in mg/Kg
RF_{sam} = Response Factor of the analyte in the sample
RF_{std} = Response Factor of the analyte in the standard
$Conc_{std}$ = Concentration of the analyte in the standard (4.9.4)
Vol_{final} = Volume of final extract (7.18)
Wt_{Sam} = Weight of initial sample in g (7.1)

8.5 Reporting of Results

All positive results are reported as “Trace”. All quantitative results are reported to 2 significant figures.

9. QUALITY ASSURANCE

The quality control procedures set out in the Residue Chemistry Section SOP QA-02 must be followed.

The reproducibility of the instrument and the validity of the method must be checked, therefore, a blank, a procedural blank and a recovery sample must be run with every batch of samples. The retention times and ratio of the peaks on the chromatograms for the sample must be similar to the ratio of the peaks for the standards.

9.1 The blank is prepared by following this method using a control fruit/vegetable. The blank fruit/vegetable must be extracted and analysed in the same manner as the samples (*i.e.* an internal standard and a surrogate are added to the sample). The result for the blank sample should not interfere with the quantitation of the lower reporting levels for each analyte (see section 8).

9.2 Surrogates must be added to every sample, recovery and procedural blank, and the recovery determined.

9.3 The recovery is prepared by adding 100 uL of a 2ug/mL recovery solution to 10 g of sample. The recovery sample is then extracted and analysed in the same manner as the samples (with surrogates and internal standards added).

9.4 A duplicate of a sample must be performed and the result must match to the original sample. For screening purposes this means that both samples must be negative or both positive.

10. REFERENCES

10.1 The Maximum Residues Limits, National Residues Authority. Table 1. Maximum residue limits of agricultural and veterinary chemicals and associated substances in food commodities. August 2002. For updates see http://www.nra.gov.au

10.2 The Maximum Residues Limits, National Residues Authority. Table 2. Portion of the commodity to which the maximum residue limit applies (and which is analysed) For updates see http://www.nra.gov.au

10.3 The Maximum Residues Limits, National Residues Authority. Table 3. Residue definition For updates see http://www.nra.gov.au

Title: **Multi-Residue Screening in Vegetables**

11. APPENDICES

Appendix	Content
A	Pesticide Retention Times and *m/z* values for Ion-Trap MS
B	Recovery Data
C	Retention Time Variability
D	Repeatability of analysis – Instrumentation Variation
E	Matrix–Matched Standard and solvent prepared standards
F	Repeatability of the preparation of Matrix-Matched Standards
G	Analysis of Variance (ANOVA) of variability of recoveries

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Appendix A: Average Pesticide Retention Times and *m/z* values for Ion-Trap MS

NB: These times are indicative only. As the column becomes degraded and sections at the front of the column are removed, the absolute retention time will change.

Table 2.

Analyte		**Quantitation Ion**
	minutes	m/z
Methomyl	9.684	88
Dichlorvos	11.183	185
Bendiocarb	11.334	166
Carbofuran	11.574	164
Methamidophos	11.701	94
Diuron	11.728	187
5-Dichlorobenzonitrile	12.665	171
Pebulate	12.870	128
Mevinphos	13.193	127
Methiocarb	14.601	168
Trifluralin	14.691	306
Benfluralin	14.785	292
Propachlor	15.449	120
Ethoprophos	15.497	158
Chlorpropham	15.619	127
Pencyuron	15.825	180
Phorate	16.257	75
Hexachlorobenzene	16.481	284
Bendiocarb	16.770	151
Terbufos	16.990	231
Propyzamide	17.073	173
Atrazine	17.301	200
Quintozene	17.473	295
Disulfoton	17.705	88
Dimethoate	17.874	87
Pirimicarb	18.607	166
Terbacil	18.694	161
Prometrin	19.191	241
Metalaxyl M	19.363	206
Methyl parathion	19.434	109
Metribuzin	19.526	198
Metolachlor	19.685	162
Chlorpyrifos	19.857	314
Ethofumesate	19.874	207
Dichlofluanid	20.119	123
Bioallethrin	20.202	123
Fipronil	20.350	368
Bromacil	20.633	207
Pendimethalin	20.693	252
Pyrethrum	20.961	123
Penconazole	20.997	248
Triadimenol	21.183	112
Procymidone	21.323	96
cis-Chlordane	21.431	373

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Analyte		**Quantitation Ion**
	minutes	m/z
Trans-Chlordane	21.676	373
Pyrefinox	21.777	262
Prothiophos	21.940	309
Hexaconazole	22.129	214
p,p-DDE	22.238	318
Buprofezin	22.313	105
Napropamide	22.339	271
Methidathion	22.362	145
Dieldrin	22.508	79
Buprimate	22.599	273
Endosulfan II	23.031	241
Myclobutanil	23.064	179
Endrin	23.305	81
Cyproconazole	23.367	222
Carboxin	23.559	143
p,p-DDT	23.664	235
Sulprofos	23.967	322
Benalaxyl	24.293	148
Propargite	24.420	135
Bifenthrin	24.587	182
Tebuconazole	24.810	250
Norflurazon	24.967	303
Endosulfan sulfate	25.018	272
Methoxychlor	25.111	227
Hexazinone	25.782	171
Fenoxycarb	25.924	116
Methoxychlor	26.008	227
Furathiocarb	26.057	163
Tetradifon	26.746	356
Pyrazophos	27.191	374
Permethrin1	27.563	163
Fenarimol	27.622	139
Permethrin2	27.747	163
Bitertanol	27.780	170
Cyfluthrin I	28.244	163
Cyfluthrin II	28.497	163
Cyfluthrin III	28.487	163
Cypermethrin I	28.867	163
Cypermethrin II	29.021	163
Cypermethrin III	29.150	163
Fluvalinate	29.947	248
Fluvalinate II	29.992	248
Deltamethrin I	30.745	225
Deltamethrin II	31.161	225

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Appendix B: Recovery Data

Recoveries at Limit of Quantitation 0.02 mg/Kg were determined from a minimum of nine spikes of five different vegetable matrices (Table 3). One matrix (carrot) was done at a higher spiking level to determine variability in the recoveries at a higher incidence of ions within the ion trap. All initial recovery data is presented below

Table 3.

Matrix	Type	Botanical Name	Family
Carrot	Root	*Daucus carota*	Apiaceae - Parsley
Celery	Stalk/Leaf	*Apium graveolens*	Apiaceae - Parsley
Potato	Tuber	*Solanum tuberosum*	Solanaceae - Potato
Asparagus	Shoot	*Asparagus officinalis*	Liliaceae - Lily
Cucumber	Cucurbit	*Cucumis sativus*	Cucurbitaceae - Gourd

ND: Not Determined

Carrot 0.02 mg/Kg Level

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Dichlorvos	22	0	0	27	0	50	24	70	53	77	32	29	10
Methamidophos	5	4	0	18	17	0	15	0	0	0	6	8	10
Diuron	153	105	190	184	165	203	105	187	199	172	166	36	10
3,5-Dichlorobenzonitrile	21	17	38	47	38	56	35	83	93	102	53	30	10
Pebulate	24	17	43	52	34	57	33	89	90	90	53	28	10
Mevinphos	38	28	62	60	58	69	39	66	78	77	57	17	10
Methiocarb	35	21	58	49	62	59	38	78	81	73	55	20	10
Trifluralin	64	34	79	79	75	83	37	79	79	69	68	18	10
Benfluralin	63	36	83	80	79	82	39	85	85	77	71	19	10
Propachlor	55	36	81	72	75	82	43	90	91	89	71	20	10
Ethoprophos	39	28	67	63	53	64	38	81	83	93	61	21	10
Chlorpropham	62	38	83	77	72	84	45	91	88	89	73	19	10
Pencyuron	0	0	0	0	0	0	0	0	0	0	0	0	10
Phorate	42	29	59	43	58	36	34	65	61	55	48	13	10
Hexachlorobenzene	38	29	60	43	37	74	39	82	86	83	57	22	10
Bendiocarb	50	32	39	50	49	45	13	62	43	53	44	13	10
Terbufos	56	33	72	57	66	51	39	77	74	71	60	15	10
Propyzamide	80	49	101	101	106	120	52	105	111	105	93	25	10
Atrazine	73	42	100	89	93	108	54	100	101	102	86	23	10
Quintozene	60	42	85	87	89	106	48	89	107	96	81	23	10
Disulfoton	48	24	52	13	33	0	25	56	38	31	32	18	10
Dimethoate	58	27	60	48	2	3	33	91	0	0	32	32	10
Primicarb	59	38	85	77	80	84	44	93	91	87	74	20	10
Terbacil	115	86	213	180	207	219	110	221	214	207	177	53	10
Prometryn	64	41	73	83	82	0	46	91	97	96	67	31	10
Metalaxyl M	68	55	84	101	83	127	60	115	100	102	90	24	10
Methyl parathion	89	22	116	111	118	137	70	131	153	127	108	38	10
Metribuzin	57	40	95	81	93	81	40	96	86	78	75	22	10
Metolachlor	47	37	80	82	83	82	41	83	80	78	69	19	10
Chlorpyrifos	91	56	125	59	135	121	42	128	162	134	105	41	10
Ethofumesate	63	50	98	67	99	114	50	102	109	90	84	24	10
Bioallethrin	124	60	115	130	114	124	60	70	113	124	103	28	10
Fipronil	66	49	91	94	88	91	48	106	97	97	83	21	10
Pendimethalin	69	42	93	91	90	91	50	96	95	117	83	23	10

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Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Bromacil	61	53	105	104	90	98	57	111	105	103	89	23	10
Penconazole	71	45	100	133	103	116	54	121	109	102	95	29	10
Triademenol	73	24	118	59	66	70	68	127	143	143	89	41	10
Procymidone	64	34	56	81	72	68	43	60	91	65	63	17	10
cis-Chlordane	190	109	239	246	219	231	127	242	242	204	205	49	10
trans-Chlordane	68	42	94	91	92	95	52	96	78	88	80	19	10
Pyrifenox	40	24	73	62	90	82	21	94	73	84	64	27	10
Prothiofos	67	40	87	84	83	90	49	89	89	87	77	18	10
Hexaconazole	59	43	70	71	71	77	47	78	78	78	67	13	10
p,p'DDE	82	22	91	0	88	105	47	102	90	90	72	36	10
Buprofezin	36	49	66	50	73	112	61	121	117	77	76	31	10
Napropamide	75	43	98	101	94	99	50	101	93	97	85	22	10
Methidathion	75	42	102	99	94	99	49	106	98	95	86	23	10
Dieldrin	81	52	105	110	100	100	51	117	117	104	94	25	10
Buprimate	70	42	95	87	89	92	47	101	94	94	81	21	10
Myclobutanil	31	18	33	39	38	38	24	42	49	49	36	10	10
Endrin	73	6	275	191	55	90	10	61	141	243	115	94	10
Cyproconazole	0	5	0	20	0	156	50	100	193	100	62	71	10
p,p'-DDT	0	0	839	554	0	0	494	962	1343	1148	534	522	10
Sulprofos	59	37	84	63	70	44	42	83	77	74	63	17	10
Benalaxyl	74	43	89	102	99	83	50	85	115	78	82	22	10
Propargite	0	36	0	0	218	0	0	0	0	0	25	68	10
Bifenthrin	71	45	96	96	91	99	52	102	100	91	84	21	10
Tebuconazole	51	34	68	82	90	93	41	86	92	88	72	23	10
Endosulfan sulphate	92	42	103	102	82	107	54	107	106	108	90	24	10
Methoxychlor	107	63	121	121	114	130	64	110	103	101	103	23	10
Norfluazon	63	49	99	103	92	102	44	118	105	87	86	25	10
Hexazinone	48	18	45	38	55	59	27	38	43	38	41	12	10
Fenoxycarb	50	32	82	72	74	87	43	70	79	79	67	19	10
Methoxychlor	107	63	121	121	114	130	64	110	103	101	103	23	10
Furathiocarb	104	54	142	117	103	129	67	124	125	126	109	28	10
Tetradifon	56	28	54	0	61	67	41	60	51	73	49	21	10
Pyrazophos	63	34	79	101	85	134	45	115	155	80	89	38	10
Permethrin I	79	44	99	97	86	85	52	91	79	68	78	18	10
Permethrin II	69	40	86	139	123	133	75	130	113	107	101	33	10
Fenarimol	68	41	86	89	86	85	48	84	71	67	73	17	10
Bitertanol	49	32	6	57	1	1	11	1	2	1	16	22	10

Celery 0.02 mg/Kg Level

Analyte	1	2	3	4	5	6	7	8	Avg Recovery %	Std Dev	n
Dichlorvos	96	109	108	74	103	112	82	94	97	14	8
Methamidophos	11	9	33	11	12	14	13	17	15	8	8
Diuron	2	1	1	3	3	1	2	1	2	1	8
3,5-Dichlorobenzonitrile	123	133	148	101	137	157	114	124	130	18	8
Pebulate	143	224	222	82	178	277	142	231	187	63	8
Mevinphos	72	74	75	58	86	75	65	67	72	8	8
Methiocarb	0	0	0	0	0	0	0	0	0	0	8
Trifluralin	85	68	85	69	75	89	75	75	78	8	8

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	Avg Recovery %	Std Dev	n
Benfluralin	101	92	103	81	98	104	89	90	95	8	8
Propachlor	103	95	105	77	98	100	84	85	93	10	8
Ethoprophos	667	689	693	443	609	862	574	764	662	126	8
Chlorpropham	0	0	0	0	0	0	0	0	0	0	8
Pencyuron	139	0	0	322	81	0	0	31	72	113	8
Phorate	24	6	11	27	47	5	17	3	17	15	8
Hexachlorobenzene	89	90	99	75	102	102	80	90	91	10	8
Bendiocarb	0	0	0	0	0	3	0	0	0	1	8
Terbufos	73	54	50	51	46	29	56	48	51	12	8
Propyzamide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8
Atrazine	161	74	78	35	51	58	70	92	77	38	8
Quintozene	0	0	0	0	0	0	0	0	0	0	8
Disulfoton	14	10	0	5	0	0	11	11	6	6	8
Dimethoate	71	60	72	63	82	60	53	37	62	13	8
Primicarb	33	26	30	19	22	1	23	39	24	11	8
Terbacil	121	98	99	72	113	94	86	44	91	24	8
Prometryn	145	3	3	1	2	2	1	4	20	50	8
Metalaxyl M	138	156	133	104	182	118	10	108	119	51	8
Methyl parathion	97	85	91	76	105	75	81	69	85	12	8
Metribuzin	133	128	125	107	157	132	111	122	127	15	8
Metolachlor	102	91	95	112	99	99	107	74	98	11	8
Chlorpyrifos	86	101	110	63	119	0	62	0	68	46	8
Ethofumesate	130	108	111	116	141	109	89	87	111	18	8
Bioallethrin	114	129	47	100	129	110	95	117	105	27	8
Fipronil	120	106	4	94	119	110	94	5	81	48	8
Pendimethalin	125	107	112	94	118	110	95	100	108	11	8
Bromacil	198	150	157	124	114	171	158	142	152	26	8
Penconazole	240	225	178	189	210	209	197	210	207	20	8
Triademenol	18	11	7	7	17	5	4	7	9	5	8
Procymidone	131	124	75	121	154	77	122	102	113	27	8
cis-Chlordane	134	110	107	85	126	128	129	106	116	17	8
trans-Chlordane	136	111	117	96	125	123	111	104	115	13	8
Pyrifenox	161	117	127	109	156	137	123	122	132	18	8
Prothiofos	143	124	116	104	139	128	120	109	123	14	8
Hexaconazole	176	99	61	48	99	77	80	108	94	39	8
p,p'DDE	155	121	132	44	128	136	113	115	118	33	8
Buprofezin	140	113	138	101	147	130	119	102	124	17	8
Napropamide	174	146	141	138	158	160	144	144	151	12	8
Methidathion	125	99	98	87	110	105	88	88	100	13	8
Dieldrin	211	240	205	193	240	219	186	194	211	21	8
Buprimate	111	96	104	80	112	106	89	93	99	11	8
Myclobutanil	174	142	154	135	175	163	142	132	152	17	8
Endrin	1574	37	67	2401	2052	0	42	55	778	1043	8
Cyproconazole	456	230	382	402	778	340	312	34	367	211	8
p,p'-DDT	216	189	209	196	240	229	199	200	210	17	8
Sulprofos	137	113	127	97	126	126	106	115	118	13	8
Benalaxyl	169	155	159	143	260	169	118	147	165	42	8
Propargite	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8
Bifenthrin	141	118	133	106	139	133	111	111	124	14	8
Tebuconazole	299	291	300	264	304	315	238	276	286	25	8
Endosulfan sulphate	103	80	108	96	101	83	7	70	81	33	8

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	Avg Recovery %	Std Dev	n
Methoxychlor	145	96	119	90	110	116	94	114	111	18	8
Norfluazon	126	118	123	94	152	126	47	93	110	32	8
Hexazinone	43	33	60	35	84	50	50	45	50	16	8
Fenoxycarb	268	234	252	190	265	253	211	228	238	27	8
Methoxychlor	145	96	119	90	110	116	94	114	111	18	8
Furathiocarb	87	88	71	79	107	80	90	66	83	13	8
Tetradifon	8	55	46	49	40	18	13	59	36	20	8
Pyrazophos	214	206	171	246	678	435	266	175	299	175	8
Permethrin I	132	124	136	108	135	145	123	120	128	12	8
Permethrin II	157	120	147	131	173	153	139	131	144	17	8
Fenarimol	162	142	145	118	162	147	139	141	145	14	8
Bitertanol	325	286	293	252	3	348	266	263	255	107	8

Potato 0.02 mg/Kg Level

Analyte	1	2	3	4	5	6	7	8	9	Avg Recovery %	Std Dev	n
Dichlorvos	0	0	12	0	0	11	0	0	6	3	5	9
Methamidophos	33	0	34	0	0	26	0	0	3	11	15	9
Diuron	142	133	118	129	129	134	114	148	140	132	11	9
3,5-Dichlorobenzonitrile	5	7	34	24	19	65	0	19	30	23	20	9
Pebulate	19	26	99	44	44	161	44	38	79	61	45	9
Mevinphos	19	20	58	42	45	40	44	41	52	40	13	9
Methiocarb	132	106	130	128	87	104	104	91	120	111	17	9
Trifluralin	60	53	63	80	61	74	68	62	68	66	8	9
Benfluralin	63	47	65	79	61	72	69	63	66	65	9	9
Propachlor	81	73	104	88	87	100	89	84	101	90	10	9
Ethoprophos	85	93	129	106	113	138	93	113	141	112	20	9
Chlorpropham	102	96	115	109	99	116	98	104	119	106	9	9
Pencyuron	0	0	0	0	0	0	0	0	0	0	0	9
Phorate	65	51	38	53	44	10	48	56	59	47	16	9
Hexachlorobenzene	41	60	59	51	51	86	48	60	73	59	14	9
Bendiocarb	40	37	49	41	40	11	34	14	43	34	13	9
Terbufos	78	72	60	82	67	23	78	81	80	69	19	9
Propyzamide	107	105	111	43	0	105	0	0	31	56	51	9
Atrazine	102	88	101	103	68	96	95	101	90	94	11	9
Quintozene	85	74	93	83	80	94	81	77	97	85	8	9
Disulfoton	26	11	0	35	0	0	44	42	28	21	18	9
Dimethoate	4	6	101	2	28	98	93	3	ND	0	0	8
Primicarb	97	90	92	100	101	93	106	103	110	99	7	9
Terbacil	119	109	112	102	103	95	98	104	104	105	7	9
Prometryn	111	100	105	100	97	97	109	116	105	104	7	9
Metalaxyl M	114	113	121	113	116	107	116	107	114	114	4	9
Methyl parathion	146	128	164	145	156	118	128	128	143	139	15	9
Metribuzin	61	50	74	44	17	62	14	16	25	40	23	9
Metolachlor	114	102	116	110	109	109	104	111	114	110	5	9
Chlorpyrifos	104	105	132	100	97	116	83	104	118	107	14	9
Ethofumesate	88	79	97	107	99	85	133	96	105	99	16	9
Bioallethrin	107	93	11	98	104	100	100	104	107	91	30	9
Fipronil	85	76	79	75	81	67	84	73	92	79	7	9
Pendimethalin	122	110	115	109	113	110	117	117	114	114	4	9

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	Avg Recovery %	Std Dev	n
Bromacil	103	96	105	98	98	89	98	96	111	99	6	9
Penconazole	146	136	138	131	129	126	122	118	129	131	9	9
Triademenol	536	210	386	465	715	355	355	725	524	475	171	9
Procymidone	124	105	111	101	98	95	105	100	107	105	9	9
cis-Chlordane	115	105	126	111	111	111	122	115	117	115	7	9
trans-Chlordane	106	95	112	100	94	102	108	100	106	103	6	9
Pyrifenox	86	79	90	80	73	87	70	78	86	81	7	9
Prothiofos	116	104	112	108	107	112	114	104	111	110	4	9
Hexaconazole	99	0	107	96	102	103	107	99	105	91	34	9
p,p'DDE	165	195	138	98	122	119	109	122	122	132	30	9
Buprofezin	123	108	107	89	103	104	129	112	114	110	12	9
Napropamide	117	90	112	110	104	105	108	109	116	108	8	9
Methidathion	115	93	107	91	80	94	69	72	81	89	15	9
Dieldrin	104	98	116	96	94	107	103	101	117	104	8	9
Buprimate	96	82	81	86	32	82	38	48	54	67	24	9
Myclobutanil	112	95	113	98	102	97	99	100	106	103	7	9
Endrin	91	118	89	88	116	106	70	32	75	87	26	9
Cyproconazole	9	23	85	91	106	64	184	79	100	82	51	9
p,p'-DDT	147	112	133	143	162	147	158	163	159	147	16	9
Sulprofos	89	67	33	94	84	7	89	96	92	72	32	9
Benalaxyl	127	110	121	102	108	109	106	114	118	113	8	9
Propargite	192	67	101	140	124	177	123	43	71	115	50	9
Bifenthrin	122	105	113	106	106	109	110	114	116	111	6	9
Tebuconazole	106	96	98	83	89	90	91	90	95	93	7	9
Endosulfan sulphate	85	64	77	74	86	65	83	81	80	77	8	9
Methoxychlor	97	82	0	69	61	69	52	55	65	61	27	9
Norfluazon	86	73	82	80	70	78	75	79	75	78	5	9
Hexazinone	14	9	77	39	34	12	41	35	35	33	21	9
Fenoxycarb	72	55	67	66	58	55	58	60	56	61	6	9
Methoxychlor	97	82	86	69	61	69	52	55	65	71	15	9
Furathiocarb	235	203	215	202	231	98	196	121	185	187	47	9
Tetradifon	115	105	108	96	101	102	145	99	83	106	17	9
Pyrazophos	93	82	67	85	82	73	149	84	76	88	24	9
Permethrin I	69	69	4	55	57	62	57	66	52	55	20	9
Permethrin II	130	118	135	87	89	53	90	62	82	94	28	9
Fenarimol	88	120	83	77	67	76	63	74	74	80	17	9
Bitertanol	0	0	29	33	35	31	42	1	51	25	19	9

Asparagus 0.02 mg/Kg Level]

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Dichlorvos	139	116	141	153	137	159	157	165	151	167	148	15	10
Methamidophos	0	0	26	10	0	9	5	0	3	0	5	8	10
Diuron	100	75	600	100	75	50	50	50	100	100	130	167	10
3,5-Dichlorobenzonitrile	56	57	52	65	60	60	57	63	63	61	59	4	10
Pebulate	66	57	90	98	86	92	86	90	108	99	87	15	10
Mevinphos	63	51	57	58	57	51	56	66	63	64	59	5	10
Methiocarb	69	63	36	79	80	78	83	87	88	79	74	15	10
Trifluralin	74	64	65	73	73	73	71	88	89	79	75	8	10

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Benfluralin	77	69	73	78	81	81	78	90	93	87	81	8	10
Propachlor	73	73	78	83	81	82	77	77	90	85	80	6	10
Ethoprophos	82	68	219	85	97	109	100	135	142	97	113	44	10
Chlorpropham	74	61	75	75	94	82	78	101	96	77	81	12	10
Pencyuron	102	92	8	101	98	86	109	41	9	62	71	39	10
Phorate	69	65	69	70	70	71	78	62	83	67	70	6	10
Hexachlorobenzene	76	64	66	67	75	73	74	85	83	79	74	7	10
Bendiocarb	96	84	159	78	76	91	93	89	107	78	95	24	10
Terbufos	73	67	76	74	80	75	74	85	91	81	78	7	10
Propyzamide	89	79	86	89	93	90	96	98	100	91	91	6	10
Atrazine	86	79	71	91	93	87	93	102	99	88	89	9	10
Quintozene	73	61	71	71	72	73	71	77	77	77	72	5	10
Disulfoton	52	58	55	59	62	59	58	62	71	68	60	6	10
Dimethoate	0	109	0	116	4	0	122	4	0	5	36	55	10
Primicarb	71	66	82	75	79	75	82	87	90	85	79	8	10
Terbacil	82	70	0	86	91	76	88	100	103	88	78	29	10
Prometryn	88	78	86	85	88	89	96	98	104	91	90	7	10
Metalaxyl M	73	80	76	65	30	106	102	105	100	85	82	23	10
Methyl parathion	61	51	145	97	57	60	55	48	120	63	76	33	10
Metribuzin	81	77	51	87	90	91	94	117	103	99	89	17	10
Metolachlor	83	77	89	86	91	87	93	97	102	89	90	7	10
Chlorpyrifos	77	73	85	91	90	95	73	74	91	71	82	9	10
Ethofumesate	81	80	107	90	99	96	114	133	125	98	102	18	10
Bioallethrin	85	73	64	85	91	84	93	99	104	86	86	11	10
Fipronil	85	77	5	85	89	89	85	90	103	82	79	27	10
Pendimethalin	84	73	106	86	88	88	91	94	99	90	90	9	10
Bromacil	81	69	57	85	84	86	91	86	98	87	82	12	10
Penconazole	84	72	96	88	100	95	102	108	117	96	96	13	10
Triademenol	76	85	134	85	87	88	186	92	93	99	102	33	10
Procymidone	86	76	65	106	94	110	115	95	98	97	94	15	10
cis-Chlordane	86	77	53	87	88	90	96	99	103	87	87	14	10
trans-Chlordane	81	79	83	89	96	85	92	93	103	85	89	7	10
Pyrifenox	81	74	87	89	94	87	92	93	102	86	88	8	10
Prothiofos	87	78	86	88	97	90	94	102	106	89	92	8	10
Hexaconazole	89	79	85	92	101	96	110	108	110	107	98	11	10
p,p'DDE	82	65	84	80	84	85	85	61	111	10	75	27	10
Buprofezin	95	85	77	88	85	105	94	82	100	84	90	9	10
Napropamide	88	77	114	87	97	95	103	98	118	88	97	12	10
Methidathion	83	73	101	80	89	84	92	100	102	88	89	10	10
Dieldrin	87	75	116	115	125	114	117	150	133	127	116	22	10
Buprimate	80	70	76	84	90	85	92	97	104	86	86	10	10
Myclobutanil	81	75	0	84	91	88	90	90	96	86	78	28	10
Endrin	176	101	6142	229	137	127	278	83	180	148	760	1892	10
Cyproconazole	30	82	57	220	155	225	82	155	203	257	146	80	10
p,p'-DDT	85	80	109	89	89	88	92	93	112	87	92	10	10
Sulprofos	78	70	78	83	85	81	83	83	98	83	82	7	10
Benalaxyl	75	80	87	75	84	86	132	100	82	75	88	17	10
Propargite	0	30	0	0	0	123	137	0	415	0	71	132	10
Bifenthrin	85	76	71	86	90	88	97	80	102	92	87	9	10
Tebuconazole	90	74	83	109	102	119	118	93	132	96	102	18	10
Endosulfan sulphate	91	68	102	34	62	21	68	49	98	160	75	40	10

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Methoxychlor	87	79	98	85	89	91	92	102	99	102	92	8	10
Norfluazon	94	102	91	111	129	100	119	129	129	5	101	37	10
Hexazinone	37	19	19	38	29	14	34	25	31	28	27	8	10
Fenoxycarb	91	89	86	87	105	106	105	122	113	96	100	12	10
Methoxychlor	88	77	83	81	99	97	115	110	116	72	94	16	10
Furathiocarb	102	87	78	106	91	90	108	0	81	32	78	35	10
Tetradifon	87	81	78	56	59	60	53	85	46	69	68	15	10
Pyrazophos	86	108	124	92	148	124	139	127	118	106	117	20	10
Permethrin I	107	84	85	85	102	78	95	102	99	95	93	10	10
Permethrin II	78	78	110	87	82	79	93	82	91	86	87	10	10
Fenarimol	84	67	75	81	81	99	89	90	96	81	84	10	10
Bitertanol	82	79	75	95	98	89	97	106	115	95	93	12	10
Cyfluthrin	98	60	41	123	128	91	128	115	162	78	102	36	10
Cyfluthrin II	58	93	42	49	71	92	75	85	57	76	70	18	10
Cyfluthrin III	125	94	0	150	23	117	76	129	79	134	93	49	10
Cypermethrin	0	94	0	0	0	0	0	118	0	0	21	45	10
Cypermethrin	45	50	63	57	80	55	43	49	0	77	52	22	10
Cypermethrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10
Fluvalinate	111	104	127	57	112	99	89	102	120	101	102	19	10
Fluvalinate II	118	103	114	57	112	99	89	104	120	105	102	18	10
Deltamethrin I	63	67	76	69	80	67	61	88	62	71	70	9	10
Deltamethrin II	82	81	99	99	106	62	92	56	120	104	90	20	10

Cucumber 0.02 mg/Kg Level

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Dichlorvos	99	76	97	102	65	64	103	122	121	140	99	25	10
Methamidophos	0	0	9	0	0	36	0	23	33	3	10	15	10
Diuron	73	91	36	45	23	32	27	55	18	55	45	23	10
3,5-Dichlorobenzonitrile	93	74	81	78	51	46	74	73	86	93	75	16	10
Pebulate	72	59	62	64	48	44	56	67	60	83	62	11	10
Mevinphos	72	57	58	72	65	57	62	69	89	94	69	13	10
Methiocarb	106	86	99	103	96	69	106	104	132	141	104	20	10
Trifluralin	94	80	84	87	86	65	91	101	103	115	91	14	10
Benfluralin	98	84	86	90	89	62	95	99	113	121	94	16	10
Propachlor	105	90	89	99	99	67	102	108	134	130	102	20	10
Ethoprophos	94	76	81	85	86	51	90	101	120	125	91	21	10
Chlorpropham	99	85	89	97	89	58	98	95	118	118	95	17	10
Pencyuron	122	133	168	201	172	179	186	164	211	208	174	30	10
Phorate	82	77	83	90	77	48	83	86	113	101	84	17	10
Hexachlorobenzene	99	82	89	84	79	58	89	86	113	119	90	17	10
Bendiocarb	91	78	65	69	86	65	94	88	54	111	80	17	10
Terbufos	94	85	89	91	84	62	96	100	127	128	96	20	10
Propyzamide	114	97	103	106	98	72	112	113	140	140	110	20	10
Atrazine	102	91	94	100	101	65	106	109	139	135	104	21	10
Quintozene	105	86	89	91	83	61	90	98	111	131	94	19	10
Disulfoton	63	69	59	69	46	35	57	72	84	72	63	14	10

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Dimethoate	0	81	83	83	93	83	96	98	136	139	89	38	10
Primicarb	81	75	80	79	70	43	81	86	104	111	81	18	10
Terbacil	104	89	100	102	102	90	102	115	127	140	107	16	10
Prometryn	104	88	110	99	93	70	105	117	123	128	104	17	10
Metalaxyl M	51	83	100	81	105	41	72	92	121	109	85	25	10
Methyl parathion	68	79	86	91	97	80	97	121	128	141	99	24	10
Metribuzin	100	83	99	87	78	77	99	101	122	130	98	17	10
Metolachlor	102	89	101	97	98	71	106	105	129	127	102	17	10
Chlorpyrifos	90	82	118	95	92	82	120	101	129	144	105	21	10
Ethofumesate	120	111	129	116	108	68	97	132	138	143	116	22	10
Bioallethrin	102	89	103	102	96	83	112	108	117	119	103	12	10
Fipronil	112	99	109	116	104	66	106	117	120	150	110	21	10
Pendimethalin	115	100	112	109	104	74	118	120	140	148	114	20	10
Bromacil	102	91	98	101	104	96	106	109	130	124	106	12	10
Penconazole	184	156	174	157	157	111	172	215	251	255	183	45	10
Triademenol	160	92	150	137	185	61	103	319	162	491	186	128	10
Procymidone	99	92	304	100	93	76	92	123	104	128	121	66	10
cis-Chlordane	108	91	96	98	96	68	100	99	122	125	100	16	10
trans-Chlordane	100	84	90	91	89	65	99	101	124	120	96	17	10
Pyrifenox	93	93	86	99	93	77	106	110	128	134	102	18	10
Prothiofos	100	90	97	103	102	68	107	104	129	122	102	17	10
Hexaconazole	107	92	112	99	94	69	110	106	118	124	103	16	10
p,p'DDE	57	13	82	47	87	69	107	63	93	89	71	27	10
Buprofezin	95	84	79	81	80	70	81	97	116	116	90	16	10
Napropamide	97	67	98	101	97	58	99	96	110	108	93	17	10
Methidathion	111	104	105	117	112	72	113	113	147	134	113	20	10
Dieldrin	121	99	143	161	164	88	130	138	150	146	134	25	10
Buprimate	95	87	90	89	82	59	102	100	123	123	95	19	10
Myclobutanil	104	75	69	81	86	50	97	91	130	109	89	23	10
Endrin	38	67	34	43	8	16	63	23	195	0	49	56	10
Cyproconazole	198	121	67	99	188	94	16	93	184	162	122	60	10
p,p'-DDT	92	87	95	107	78	14	80	85	128	119	89	31	10
Sulprofos	96	89	87	98	86	61	98	101	132	107	95	18	10
Benalaxyl	136	71	95	75	120	66	99	105	116	84	97	23	10
Propargite	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	0	10
Bifenthrin	113	88	90	95	88	66	97	95	114	118	96	15	10
Tebuconazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	0	10
Endosulfan sulphate	177	392	0	0	371	0	208	349	141	319	196	159	10
Methoxychlor	20	0	0	92	27	49	112	70	88	122	58	45	10
Norfluazon	717	835	896	1026	970	883	1152	0	2874	0	935	791	10
Hexazinone	32	14	23	32	23	19	13	21	34	47	26	10	10
Fenoxycarb	94	99	81	96	96	60	98	115	134	134	101	23	10
Methoxychlor	90	87	65	80	109	51	91	97	118	105	89	20	10
Furathiocarb	123	111	105	120	98	66	114	111	153	112	111	22	10
Tetradifon	52	99	69	83	0	0	113	130	143	177	87	58	10
Pyrazophos	928	0	147	0	0	315	222	78	115	0	180	284	10
Permethrin I	116	92	100	100	83	71	84	101	77	111	94	14	10
Permethrin II	113	98	124	123	107	40	111	94	123	155	109	30	10
Fenarimol	100	101	89	89	90	65	90	93	123	118	96	16	10
Bitertanol	113	3	105	1	116	61	2	127	137	135	80	58	10
Cyfluthrin	0	93	92	31	75	141	146	111	36	181	91	57	10

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Cyfluthrin II	117	0	0	0	83	0	0	189	155	36	58	73	10
Cyfluthrin III	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	0	10
Fluvalinate	142	128	0	142	121	96	126	122	111	154	114	43	10
Fluvalinate II	142	128	140	122	116	80	126	122	136	151	126	20	10
Bendiocarb	93	71	88	84	74	68	85	74	91	114	84.23	13.64	10
Carbofuran	105	83	77	86	84	61	102	117	126	171	101.10	31.38	10

Carrot 0.1 mg/Kg Level

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Methomyl	15	26	28	39	39	32	41	32	33	30	31	8	10
Dichlorvos	110	107	118	105	117	92	129	10	81	78	95	34	10
Methamidophos	2	0	4	0	5	3	2	0	0	0	2	2	10
Diuron	2	2	5	4	2	2	2	2	9	4	4	2	10
3,5-Dichlorobenzonitrile	116	141	144	146	154	127	178	47	129	122	130	34	10
Pebulate	140	154	169	178	175	148	204	48	148	139	150	41	10
Mevinphos	71	95	93	106	113	92	109	94	101	75	95	14	10
Methiocarb	133	156	152	164	154	132	179	39	147	135	139	38	10
Trifluralin	133	145	142	147	165	145	178	50	154	132	139	34	10
Benfluralin	132	141	143	142	158	144	172	49	150	130	136	33	10
Propachlor	125	133	140	139	152	137	166	37	148	131	131	35	10
Ethoprophos	210	213	221	233	247	223	276	34	222	194	207	65	10
Chlorpropham	146	152	156	159	173	156	201	45	169	140	150	40	10
Pencyuron	17	9	8	9	363	7	14	7	439	8	88	166	10
Phorate	123	137	136	146	157	138	166	45	144	132	132	33	10
Hexachlorobenzene	128	141	147	148	156	138	183	50	149	129	137	34	10
Bendiocarb	114	90	114	116	140	127	145	10	140	115	111	39	10
Terbufos	138	148	151	154	163	144	178	47	161	134	142	36	10
Propyzamide	118	123	120	126	140	124	152	50	139	122	121	27	10
Atrazine	11	141	138	135	158	139	164	30	150	133	120	53	10
Quintozene	128	137	144	144	154	145	169	42	146	126	133	34	10
Disulfoton	118	119	120	127	142	123	148	44	133	119	119	28	10
Dimethoate	0	19	37	3	42	36	42	19	36	34	27	16	10
Primicarb	127	135	134	143	152	135	163	25	148	129	129	38	10
Terbacil	134	134	137	142	170	140	173	28	155	127	134	40	10
Prometryn	131	130	137	140	162	137	166	51	154	127	134	32	10
Metalaxyl M	126	127	133	133	153	131	161	17	143	123	125	40	10
Methyl parathion	121	122	141	139	172	150	158	71	166	144	138	29	10
Metribuzin	126	138	144	146	157	139	161	8	145	124	129	44	10
Metolachlor	111	131	134	132	161	136	167	54	147	127	130	31	10
Chlorpyrifos	128	129	133	135	102	121	128	38	147	125	119	30	10
Ethofumesate	135	137	147	146	181	172	204	58	161	135	148	39	10
Dichlofluanid	55	73	65	79	59	42	11	11	31	23	45	25	10
Bioallethrin	119	120	149	131	145	146	188	138	161	132	143	21	10
Fipronil	165	162	166	175	191	167	206	16	177	156	158	52	10
Pendimethalin	107	107	111	107	128	108	134	60	121	99	144	35	10
Bromacil	142	144	147	150	169	148	184	51	162	139	108	20	10
Pyrethrum	114	137	90	75	162	131	131	48	130	135	115	34	10
Penconazole	134	132	131	143	127	155	131	38	138	126	126	32	10

Title: **Multi-Residue Screening in Vegetables**

Analyte	1	2	3	4	5	6	7	8	9	10	Avg Recovery %	Std Dev	n
Triademenol	96	767	99	740	119	138	688	43	167	163	302	299	10
Procymidone	133	134	144	141	155	142	169	51	158	130	136	32	10
cis-Chlordane	137	139	143	145	162	140	168	56	148	129	137	31	10
trans-Chlordane	131	132	139	146	161	144	171	56	149	135	136	31	10
Pyrifenox	139	144	150	138	190	157	189	57	169	147	148	37	10
Prothiofos	145	138	143	148	163	148	177	51	161	140	141	34	10
Hexaconazole	127	135	141	136	152	136	171	42	147	133	132	34	10
p,p'DDE	145	144	143	153	155	143	157	56	150	136	138	30	10
Buprofezin	130	129	130	149	154	146	161	54	151	128	133	30	10
Napropamide	149	150	145	153	166	146	193	47	150	140	144	37	10
Methidathion	99	96	102	104	120	112	132	31	128	107	103	28	10
Dieldrin	136	131	134	148	155	135	163	49	146	146	134	31	10
Buprimate	134	137	133	139	162	143	173	49	151	130	135	33	10
Myclobutanil	118	126	129	129	145	127	154	24	144	126	122	36	10
Endrin	137	121	130	133	121	115	160	54	137	128	124	27	10
Cyproconazole	139	61	134	29	137	124	141	8	154	134	106	53	10
Carboxin	108	113	108	112	139	120	135	18	121	107	108	34	10
p,p'-DDT	156	191	188	212	216	176	260	84	158	152	179	47	10
Sulprofos	150	146	145	154	176	155	180	46	161	141	146	37	10
Benalaxyl	138	140	139	148	166	143	180	57	158	133	140	33	10
Propargite	61	202	32	143	253	237	50	68	95	135	128	80	10
Bifenthrin	134	133	134	137	153	133	149	46	140	130	129	30	10
Tebuconazole	139	136	145	139	159	132	178	19	159	133	134	43	10
Norfluazon	110	116	112	121	140	124	145	11	136	125	114	38	10
Endosulfan sulphate	97	90	89	80	105	96	118	23	116	90	90	27	10
Methoxychlor	194	236	217	245	256	213	284	88	222	192	215	53	10
Hexazinone	23	44	17	30	31	31	37	65	22	21	32	14	10
Fenoxycarb	131	124	134	137	169	145	165	40	152	134	133	36	10
Methoxychlor	111	92	102	98	126	120	124	31	129	108	104	29	10
Furathiocarb	105	106	113	114	145	126	129	40	134	124	114	29	10
Tetradifon	113	123	123	137	113	119	140	53	128	119	117	24	10
Fluvalinate	610	587	520	586	547	409	472	150	402	327	461	143	10
Pyrazophos	96	100	111	109	224	156	213	71	130	104	131	51	10
Permethrin I	140	140	140	139	161	144	161	52	153	131	136	31	10
Permethrin II	134	128	132	152	157	139	173	35	149	131	137	33	10
Fenarimol	137	140	142	145	162	145	176	51	145	131	133	37	10
Bitertanol	119	126	129	134	149	134	158	14	144	127	123	40	10
Cyfluthrin	121	134	152	132	200	200	183	59	191	200	157	47	10
Cyfluthrin II	172	228	139	212	310	158	313	93	295	129	205	80	10
Cyfluthrin III	91	114	129	108	150	147	157	49	171	128	125	36	10
Cypermethrin	112	107	129	126	191	69	195	38	158	154	128	50	10
Cypermethrin	83	74	78	86	156	113	122	60	132	98	100	30	10
Cypermethrin	22	57	18	0	17	0	0	0	0	27	14	18	10
Fluvalinate	96	140	179	172	94	210	145	30	225	211	150	62	10
Fluvalinate II	89	125	175	153	129	200	79	36	225	197	141	61	10
Deltamethrin I	90	97	109	99	142	121	137	51	148	125	112	29	10
Deltamethrin II	78	99	105	101	124	130	127	25	151	137	108	36	10
Bendiocarb	136	161	147	159	164	140	191	7	145	129	138	49	10
Carbofuran	196	231	203	227	213	188	259	65	212	170	197	52	10

Title: **Multi-Residue Screening in Vegetables**

Appendix C: Rentention Time Variability

The retention time on the GC column was measured from ten subsequent samples for each analyte and on two different matrices. The results are presented below.

Carrot Matrix

Analyte	AVERAGE (minutes)	Std Dev	%RSD
Methomyl	9.684	0.004	0.041
Dichlorvos	11.029	0.056	0.510
Bendiocarb	11.332	0.004	0.036
Carbofuran	11.572	0.004	0.036
Methamidophos	11.709	0.003	0.028
Diuron	11.722	0.006	0.047
5-Dichlorobenzonitrile	12.663	0.004	0.032
Pebulate	12.871	0.004	0.028
Mevinphos	13.194	0.004	0.029
Methiocarb	14.611	0.005	0.036
Trifluralin	14.691	0.005	0.034
Benfluralin	14.785	0.005	0.034
Propachlor	15.452	0.005	0.030
Ethoprophos	15.503	0.004	0.026
Chlorpropham	15.619	0.006	0.036
Pencyuron	15.800	0.000	0.000
Phorate	16.256	0.005	0.033
Hexachloro Benzene	16.478	0.006	0.034
Bendiocarb	16.772	0.005	0.032
Terbufos	16.989	0.005	0.032
Propyzamide	17.083	0.006	0.034
Atrazine	17.295	0.017	0.098
Quintozene	17.472	0.006	0.035
Disulfoton	17.718	0.006	0.033
Dimethoate	17.885	0.005	0.029
Pirimicarb	18.622	0.006	0.030
Terbacil	18.734	0.006	0.031
Prometrin	19.147	0.008	0.039
Metalaxyl M	19.371	0.007	0.034
Methyl parathion	19.443	0.006	0.030
Metribuzin	19.535	0.006	0.033
Metolachlor	19.696	0.006	0.029
Chlorpyrifos	19.880	0.005	0.024
Ethofumesate	19.906	0.006	0.029
Dichlofluanid	20.087	0.007	0.034
Bioallethrin	20.249	0.017	0.082
Fipronil	20.359	0.031	0.153
Bromacil	20.668	0.007	0.034
Pendimethalin	20.704	0.006	0.029
Pyrethrum	20.944	0.045	0.213
Penconazole	21.007	0.020	0.096
Triadimenol	21.316	0.082	0.383
Procymidone	21.335	0.007	0.032
cis-Chlordane	21.441	0.006	0.029
Trans-Chlordane	21.684	0.006	0.028

Title: **Multi-Residue Screening in Vegetables**

Analyte	AVERAGE (minutes)	Std Dev	%RSD
Pyrefinox	21.786	0.006	0.029
Prothiophos	21.945	0.007	0.031
Hexaconazole	22.138	0.009	0.040
p,p-DDE	22.240	0.006	0.028
Buprofezin	22.319	0.006	0.026
Napropamide	22.350	0.004	0.019
Methidathion	22.371	0.006	0.025
Dieldrin	22.513	0.006	0.028
Buprimate	22.603	0.006	0.025
Endosulfan II	23.031	0.000	0.000
Myclobutanil	23.063	0.012	0.053
Endrin	23.288	0.008	0.033
Cyproconazole	23.381	0.026	0.113
Carboxin	23.567	0.007	0.028
p,p-DDT	23.672	0.007	0.030
Sulprofos	23.975	0.006	0.027
Benalaxyl	24.303	0.005	0.022
Propargite	24.338	0.007	0.030
Bifenthrin	24.590	0.006	0.025
Tebuconazole	24.822	0.007	0.026
Norflurazon	24.976	0.006	0.025
Endosulfan sulfate	25.026	0.007	0.026
Cyhalothryn	25.047	0.078	0.310
Methoxychlor	25.114	0.006	0.024
Hexazinone	25.791	0.006	0.025
Fenoxycarb	25.930	0.007	0.029
Methoxychlor	26.012	0.006	0.023
Furathiocarb	26.068	0.006	0.024
Tetradifon	26.752	0.006	0.024
Fluvalinate	27.179	0.109	0.401
Pyrazophos	27.195	0.006	0.021
Permethrin1	27.564	0.006	0.022
Fenarimol	27.629	0.005	0.018
Permethrin2	27.747	0.006	0.020
Bitertanol	27.778	0.015	0.053
Cyfluthrin I	28.248	0.007	0.026
Cyfluthrin II	28.498	0.012	0.043
Cyfluthrin III	28.493	0.045	0.157
Cypermethrin I	28.864	0.012	0.041
Cypermethrin II	29.022	0.009	0.030
Cypermethrin III	29.181	0.110	0.376
Fluvalinate	29.940	0.009	0.031
Fluvalinate II	30.017	0.082	0.273
Deltamethrin I	30.743	0.009	0.030
Deltamethrin II	31.154	0.010	0.033

Title: **Multi-Residue Screening in Vegetables**

Potato Matrix

Analyte	AVERAGE (minutes)	Std Dev	%RSD
Methomyl	9.684	0.003	0.029
Dichlorvos	11.183	0.003	0.028
Bendiocarb	11.334	0.003	0.028
Carbofuran	11.573	0.003	0.024
Methamidophos	11.701	0.005	0.044
Diuron	11.728	0.009	0.073
5-Dichlorobenzonitrile	12.665	0.003	0.023
Pebulate	12.870	0.003	0.025
Mevinphos	13.193	0.004	0.029
Methiocarb	14.601	0.004	0.026
Trifluralin	14.691	0.003	0.023
Benfluralin	14.785	0.003	0.022
Propachlor	15.449	0.003	0.021
Ethoprophos	15.497	0.004	0.028
Chlorpropham	15.619	0.004	0.025
Pencyuron	15.825	0.055	0.346
Phorate	16.257	0.004	0.023
Hexachloro Benzene	16.481	0.003	0.021
Bendiocarb	16.770	0.004	0.026
Terbufos	16.990	0.004	0.024
Propyzamide	17.073	0.004	0.022
Atrazine	17.301	0.004	0.025
Quintozene	17.473	0.004	0.023
Disulfoton	17.705	0.004	0.024
Dimethoate	17.874	0.003	0.019
Pirimicarb	18.607	0.004	0.023
Terbacil	18.694	0.004	0.023
Prometrin	19.191	0.005	0.028
Metalaxyl M	19.363	0.004	0.023
Methyl parathion	19.434	0.004	0.021
Metribuzin	19.526	0.004	0.019
Metolachlor	19.685	0.004	0.022
Chlorpyrifos	19.857	0.006	0.031
Ethofumesate	19.874	0.004	0.020
Dichlofluanid	20.119	0.008	0.038
Bioallethrin	20.202	0.004	0.018
Fipronil	20.350	0.004	0.021
Bromacil	20.633	0.005	0.025
Pendimethalin	20.693	0.004	0.020
Pyrethrum	20.961	0.046	0.221
Penconazole	20.997	0.005	0.023
Triadimenol	21.183	0.104	0.492
Procymidone	21.323	0.004	0.020
cis-Chlordane	21.431	0.004	0.021
Trans-Chlordane	21.676	0.004	0.019
Pyrefinox	21.777	0.004	0.021
Prothiophos	21.940	0.004	0.017
Hexaconazole	22.129	0.005	0.021
p,p-DDE	22.238	0.004	0.020
Buprofezin	22.313	0.004	0.018

Title: **Multi-Residue Screening in Vegetables**

Analyte	AVERAGE (minutes)	Std Dev	%RSD
Napropamide	22.339	0.005	0.021
Methidathion	22.362	0.004	0.018
Dieldrin	22.508	0.004	0.019
Buprimate	22.599	0.005	0.021
Endosulfan II	23.031	0.000	0.000
Myclobutanil	23.064	0.004	0.016
Endrin	23.305	0.053	0.226
Cyproconazole	23.367	0.025	0.108
Carboxin	23.559	0.005	0.020
p,p-DDT	23.664	0.004	0.016
Sulprofos	23.967	0.004	0.017
Benalaxyl	24.293	0.004	0.018
Propargite	24.420	0.020	0.081
Bifenthrin	24.587	0.004	0.018
Tebuconazole	24.810	0.004	0.018
Norflurazon	24.967	0.005	0.020
Endosulfan sulfate	25.018	0.005	0.022
Cyhalothryn	25.020	0.153	0.610
Methoxychlor	25.111	0.004	0.015
Hexazinone	25.782	0.004	0.017
Fenoxycarb	25.924	0.003	0.012
Methoxychlor	26.008	0.004	0.017
Furathiocarb	26.057	0.005	0.017
Tetradifon	26.746	0.005	0.019
Fluvalinate	27.306	0.128	0.470
Pyrazophos	27.191	0.005	0.018
Permethrin1	27.563	0.005	0.018
Fenarimol	27.622	0.004	0.014
Permethrin2	27.747	0.004	0.014
Bitertanol	27.780	0.005	0.017
Cyfluthrin I	28.244	0.007	0.026
Cyfluthrin II	28.497	0.015	0.054
Cyfluthrin III	28.487	0.038	0.134
Cypermethrin I	28.867	0.010	0.033
Cypermethrin II	29.021	0.011	0.039
Cypermethrin III	29.150	0.025	0.085
Fluvalinate	29.947	0.006	0.019
Fluvalinate II	29.992	0.071	0.237
Deltamethrin I	30.745	0.006	0.020
Deltamethrin II	31.161	0.006	0.019

Title: **Multi-Residue Screening in Vegetables**

Appendix D: Instrument Variation

The repeatability of injection on the GC/Ion-Trap Mass Spectrometer was examined over a period of ten injections for two different matrices. The results were obtained by comparing the actual results obtained in the spiked matrix extract (in ug/mL) and are presented below.

Carrot Matrix

Analyte	Average (ug/mL)	Std Dev	%RSD
Methomyl	0.52	0.03	6.7
Dichlorvos	0.08	0.12	151.2
Bendiocarb	2.23	0.13	6.0
Carbofuran	5.89	0.29	5.0
Methamidophos	0.15	0.01	9.3
Diuron	0.03	0.00	18.4
5-Dichlorobenzonitrile	0.52	0.02	4.6
Pebulate	0.57	0.05	8.5
Mevinphos	0.37	0.02	5.0
Methiocarb	1.25	0.05	3.9
Trifluralin	0.35	0.01	3.4
Benfluralin	0.31	0.01	3.6
Propachlor	0.40	0.01	3.6
Ethoprophos	0.70	0.04	5.3
Chlorpropham	0.22	0.02	6.7
Phorate	0.56	0.03	4.7
Hexachloro Benzene	0.80	0.02	2.8
Bendiocarb	0.08	0.00	3.1
Terbufos	0.43	0.01	3.2
Propyzamide	0.30	0.01	4.7
Atrazine	0.23	0.07	30.2
Quintozene	0.42	0.01	2.9
Disulfoton	0.25	0.03	11.0
Dimethoate	0.37	0.01	4.0
Pirimicarb	0.25	0.01	4.8
Terbacil	0.23	0.01	4.6
Prometrin	0.06	0.03	43.2
Metalaxyl M	0.19	0.01	7.4
Methyl parathion	0.56	0.05	9.6
Metribuzin	0.29	0.03	9.9
Metolachlor	0.33	0.03	9.6
Chlorpyrifos	0.17	0.01	8.5
Ethofumesate	0.29	0.01	3.6
Dichlofluanid	0.14	0.02	11.0
Bioallethrin	0.98	0.36	36.7
Fipronil	0.17	0.06	33.8
Bromacil	0.23	0.01	3.7
Pendimethalin	0.22	0.01	3.4
Pyrethrum	0.46	0.36	78.3
Penconazole	0.30	0.11	35.8
Triadimenol	0.97	0.43	44.8
Procymidone	0.27	0.02	7.9
cis-Chlordane	0.23	0.01	3.5
Trans-Chlordane	0.25	0.01	4.9

Title: **Multi-Residue Screening in Vegetables**

Analyte	Average (ug/mL)	Std Dev	%RSD
Pyrefinox	0.26	0.03	12.4
Prothiophos	0.28	0.01	4.9
Hexaconazole	0.30	0.11	35.9
p,p-DDE	0.23	0.02	7.1
Buprofezin	0.24	0.03	14.1
Napropamide	0.21	0.06	28.0
Methidathion	0.13	0.01	8.4
Dieldrin	0.23	0.07	28.9
Buprimate	0.26	0.01	3.9
Myclobutanil	0.40	0.06	14.2
Endrin	0.80	0.19	24.0
Cyproconazole	0.27	0.03	10.5
Carboxin	0.20	0.01	7.0
p,p-DDT	3.48	0.25	7.2
Sulprofos	0.26	0.01	3.8
Benalaxyl	0.27	0.02	8.1
Bifenthrin	0.24	0.01	3.2
Tebuconazole	0.32	0.02	7.3
Norflurazon	0.24	0.02	7.7
Endosulfan sulfate	0.15	0.03	22.8
Methoxychlor	3.15	0.14	4.6
Hexazinone	0.23	0.01	5.6
Fenoxycarb	0.40	0.09	22.5
Methoxychlor	0.12	0.01	10.7
Furathiocarb	0.14	0.01	6.6
Tetradifon	0.14	0.04	27.8
Fluvalinate	0.42	0.11	25.6
Pyrazophos	0.20	0.03	15.8
Permethrin1	0.25	0.02	7.4
Fenarimol	0.22	0.02	9.8
Permethrin2	0.27	0.01	5.5
Bitertanol	0.32	0.11	35.1
Cyfluthrin I	0.41	0.12	28.4
Cyfluthrin II	0.27	0.12	44.2
Cyfluthrin III	0.53	0.16	29.7
Cypermethrin I	0.40	0.12	31.0
Cypermethrin II	0.18	0.10	53.2
Cypermethrin III	0.02	0.04	221.0
Fluvalinate	0.17	0.04	21.5
Fluvalinate II	0.17	0.03	16.6
Deltamethrin I	0.11	0.01	10.9
Deltamethrin II	0.12	0.04	31.5

Title: **Multi-Residue Screening in Vegetables**

Potato Matrix

Analyte	Average (ug/mL)	Std Dev	%RSD
Methomyl	0.71	0.03	3.7
Dichlorvos	0.45	0.02	5.1
Bendiocarb	1.98	0.07	3.4
Carbofuran	5.86	0.28	4.9
Methamidophos	0.12	0.01	5.8
Diuron	0.01	0.01	44.4
5-Dichlorobenzonitrile	0.68	0.03	4.1
Pebulate	0.62	0.04	6.6
Mevinphos	0.30	0.02	5.8
Methiocarb	1.24	0.10	7.9
Trifluralin	0.32	0.01	4.7
Benfluralin	0.28	0.01	3.3
Propachlor	0.34	0.01	3.9
Ethoprophos	0.47	0.03	5.5
Chlorpropham	0.23	0.01	3.1
Pencyuron	0.04	0.05	133.0
Phorate	0.52	0.02	4.7
Hexachloro Benzene	0.75	0.03	4.3
Bendiocarb	0.01	0.01	39.7
Terbufos	0.41	0.01	3.6
Propyzamide	0.34	0.01	4.1
Atrazine	0.27	0.01	3.5
Quintozene	0.42	0.02	5.2
Disulfoton	0.34	0.02	4.6
Dimethoate	0.13	0.02	17.4
Pirimicarb	0.23	0.01	4.4
Terbacil	0.21	0.01	5.8
Prometrin	0.26	0.01	2.8
Metalaxyl M	0.18	0.01	4.5
Methyl parathion	0.19	0.01	7.9
Metribuzin	0.27	0.01	3.0
Metolachlor	0.27	0.01	2.7
Chlorpyrifos	0.10	0.03	29.8
Ethofumesate	0.43	0.03	6.6
Dichlofluanid	0.14	0.06	39.7
Bioallethrin	0.23	0.01	4.3
Fipronil	0.20	0.01	3.7
Bromacil	0.24	0.01	4.5
Pendimethalin	0.23	0.01	3.2
Pyrethrum	0.28	0.27	99.0
Penconazole	0.29	0.02	5.5
Triadimenol	0.67	0.41	61.1
Procymidone	0.27	0.01	4.6
cis-Chlordane	0.25	0.01	3.1
Trans-Chlordane	0.27	0.01	4.6
Pyrefinox	0.29	0.01	3.2
Prothiophos	0.26	0.01	3.2
Hexaconazole	0.34	0.01	4.3
p,p-DDE	0.35	0.04	10.5
Buprofezin	0.24	0.01	5.2

Title: **Multi-Residue Screening in Vegetables**

Analyte	Average (ug/mL)	Std Dev	%RSD
Napropamide	0.22	0.01	4.4
Methidathion	0.10	0.00	4.6
Dieldrin	0.29	0.03	10.3
Buprimate	0.25	0.01	3.1
Myclobutanil	0.27	0.01	3.6
Endrin	0.15	0.08	53.5
Cyproconazole	0.19	0.07	37.8
Carboxin	0.22	0.01	5.3
p,p-DDT	3.79	0.22	5.8
Sulprofos	0.24	0.01	2.3
Benalaxyl	0.36	0.04	10.3
Propargite	0.36	0.26	73.3
Bifenthrin	0.27	0.01	2.6
Tebuconazole	0.33	0.02	5.5
Norflurazon	0.23	0.02	6.7
Endosulfan sulfate	0.11	0.02	13.8
Methoxychlor	3.13	0.17	5.6
Hexazinone	0.23	0.01	5.0
Fenoxycarb	0.28	0.02	6.1
Methoxychlor	0.09	0.01	6.3
Furathiocarb	0.15	0.01	5.0
Tetradifon	0.18	0.02	13.7
Fluvalinate	0.16	0.11	67.3
Pyrazophos	0.38	0.11	29.4
Permethrin1	0.25	0.02	8.8
Fenarimol	0.25	0.02	8.3
Permethrin2	0.28	0.01	5.0
Bitertanol	0.34	0.02	6.0
Cyfluthrin I	0.47	0.13	27.5
Cyfluthrin II	0.24	0.12	51.4
Cyfluthrin III	0.47	0.18	37.9
Cypermethrin I	0.34	0.14	40.1
Cypermethrin II	0.17	0.05	31.5
Cypermethrin III	0.00	0.00	0.0
Fluvalinate	0.12	0.01	10.1
Fluvalinate II	0.13	0.02	14.3
Deltamethrin I	0.10	0.02	18.4
Deltamethrin II	0.13	0.03	20.9

Title: **Multi-Residue Screening in Vegetables**

Appendix E: Matrix-Matched Standard and Solvent Prepared Standard: Response Factors and Comparison

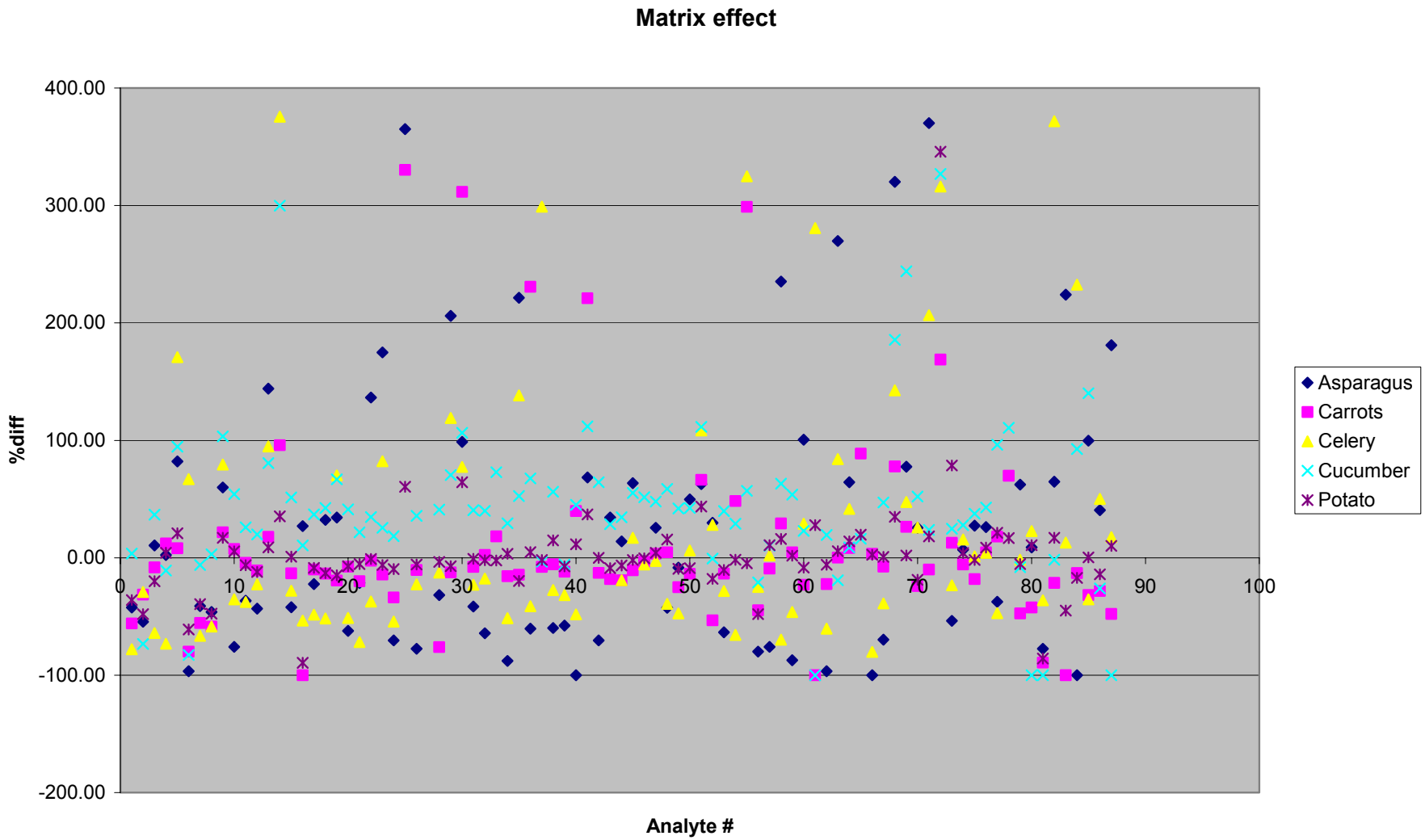
The response factors (RF) were calculated according to Equation 5. for both the Standard solution prepared in acetonitrile and for the Standard solution prepared in a blank extract (taken through the method) identified as the matrix-matched standard. Matrix-Matched Standards were prepared in the extract of the matrix under investigation. Response Factors for each and a %difference are presented below. A chart of the % differerences is also presented.

#	Analyte	RF Solvent Prepared Std	RF MM-Std Aspar	% Diff Aspar	RF MM-Std Carrot	% Diff Carrot	RF MM-Std Celery	% Diff Celery	RF MM-Std Cucum	% Diff Cucum	RF MM-Std Potato	% Diff Potato
1	Methomyl	0.028	0.016	-42	0.012	-56	0.006	-78	0.029	4	0.018	-36
2	Dichlorvos	0.041	0.019	-54	0.028	-31	0.029	-29	0.011	-73	0.022	-48
3	Bendiocarb	0.049	0.055	11	0.045	-8	0.018	-64	0.067	37	0.039	-20
4	Carbofuran	0.021	0.022	2	0.024	12	0.006	-73	0.019	-11	0.022	4
5	Methamidophos	0.026	0.047	82	0.028	8	0.069	171	0.050	95	0.031	21
6	Diuron	0.029	0.001	-97	0.006	-80	0.049	67	0.005	-83	0.011	-61
7	5-Dichlorobenzonitrile	0.146	0.086	-41	0.065	-56	0.049	-67	0.137	-6	0.088	-39
8	Pebulate	0.092	0.050	-46	0.038	-59	0.038	-59	0.095	3	0.048	-48
9	Mevinphos	0.079	0.127	60	0.097	22	0.143	79	0.162	103	0.093	17
10	Methiocarb	0.091	0.022	-76	0.098	7	0.059	-36	0.141	54	0.096	5
11	Trifluralin	0.182	0.115	-37	0.174	-4	0.113	-38	0.229	26	0.170	-6
12	Benfluralin	0.384	0.217	-43	0.342	-11	0.297	-23	0.460	20	0.337	-12
13	Propachlor	0.159	0.389	144	0.188	18	0.310	95	0.288	81	0.173	9
14	Ethoprophos	0.022	0.251	1054	0.043	96	0.103	376	0.087	300	0.029	35
15	Chlorpropham	0.086	0.050	-42	0.074	-13	0.062	-28	0.130	51	0.086	1
16	Pencyuron	0.080	0.101	27	0.000	-100	0.037	-54	0.088	10	0.008	-90
17	Phorate	0.113	0.088	-22	0.102	-10	0.058	-48	0.155	37	0.103	-9
18	Hexachloro Benzene	0.096	0.127	32	0.083	-13	0.046	-52	0.136	42	0.083	-13
19	Bendiocarb	0.069	0.092	34	0.055	-19	0.117	70	0.115	67	0.058	-15
20	Terbufos	0.176	0.066	-62	0.163	-8	0.086	-51	0.249	41	0.164	-7
21	Propyzamide	0.246	0.194	-21	0.197	-20	0.069	-72	0.299	22	0.233	-5
22	Atrazine	0.098	0.233	136	0.096	-2	0.062	-37	0.133	35	0.097	-1
23	Quintozene	0.038	0.104	175	0.032	-14	0.069	82	0.048	25	0.036	-6
24	Disulfoton	0.142	0.042	-70	0.094	-34	0.065	-54	0.168	18	0.128	-10
25	Dimethoate	0.030	0.137	365	0.127	330	0.193	552	0.280	848	0.047	60
26	Pirimicarb	0.296	0.067	-77	0.265	-10	0.229	-23	0.402	36	0.279	-6
27	Terbacil	0.081	3.901	4746	0.530	558	3.181	3852	1.755	2080	1.380	1614
28	Prometrin	0.172	0.117	-32	0.041	-76	0.150	-13	0.243	41	0.166	-3
29	Metalaxyl M	0.058	0.179	206	0.051	-12	0.128	119	0.100	71	0.054	-7
30	Methyl parathion	0.041	0.082	99	0.169	312	0.073	77	0.085	106	0.067	64
31	Metribuzin	0.147	0.086	-42	0.135	-8	0.113	-23	0.206	41	0.145	-1
32	Metolachlor	0.435	0.155	-64	0.445	2	0.357	-18	0.608	40	0.426	-2
33	Chlorpyrifos	0.036	0.452	1153	0.043	18	0.293	713	0.062	73	0.035	-2
34	Ethofumesate	0.392	0.047	-88	0.331	-16	0.190	-51	0.508	29	0.406	3
35	Dichlofluanid	0.107	0.343	221	0.091	-14	0.254	138	0.163	53	0.085	-20
36	Bioallethrin	0.220	0.087	-60	0.726	231	0.129	-41	0.368	68	0.230	5
37	Fipronil	0.031	0.231	636	0.029	-8	0.125	299	0.030	-3	0.031	-2
38	Bromacil	0.080	0.032	-60	0.076	-6	0.058	-27	0.126	56	0.092	15
39	Pendimethalin	0.261	0.110	-58	0.230	-12	0.178	-32	0.246	-6	0.242	-7
40	Penconazole	0.022	0.000	-100	0.031	40	0.011	-48	0.032	45	0.025	12
41	Triadimenol	0.018	0.030	68	0.058	221	0.355	1867	0.038	112	0.025	37

Title: **Multi-Residue Screening in Vegetables**

#	**Analyte**	**RF** Solvent Prepared Std	**RF** MM-Std **Aspar**	**% Diff Aspar**	**RF** MM-Std **Carrot**	**% Diff Carrot**	**RF** MM-Std **Celery**	**% Diff Celery**	**RF** MM-Std **Cucum**	**% Diff Cucum**	**RF** MM-Std **Potato**	**% Diff Potato**
42	Procymidone	0.149	0.044	-70	0.130	-13	6.100	3988	0.245	64	0.149	0
43	cis-Chlordane	0.130	0.175	34	0.106	-18	4.598	3435	0.167	29	0.119	-9
44	Trans-Chlordane	0.108	0.123	14	0.087	-19	0.087	-19	0.145	34	0.101	-7
45	Pyrefinox	0.064	0.104	64	0.057	-11	0.075	17	0.099	55	0.063	-2
46	Prothiophos	0.072	0.070	-3	0.069	-3	0.068	-6	0.109	52	0.071	-1
47	Hexaconazole	0.063	0.080	25	0.066	3	0.062	-3	0.094	48	0.066	4
48	p,p-DDE	0.108	0.062	-42	0.113	5	0.065	-39	0.171	59	0.124	16
49	Buprofezin	0.126	0.116	-8	0.095	-25	0.066	-47	0.180	42	0.114	-9
50	Napropamide	0.081	0.122	50	0.070	-14	0.086	6	0.116	42	0.074	-9
51	Methidathion	0.052	0.084	63	0.086	66	0.108	108	0.109	111	0.074	44
52	Dieldrin	0.079	0.103	30	0.037	-53	0.102	28	0.079	-1	0.065	-18
53	Buprimate	0.178	0.065	-63	0.154	-14	0.128	-28	0.249	40	0.160	-10
54	Myclobutanil	0.172	0.000	-100	0.255	48	0.059	-66	0.221	29	0.169	-2
55	Endrin	0.023	0.183	698	0.092	299	0.098	325	0.036	57	0.022	-5
56	Cyproconazole	0.098	0.020	-80	0.054	-45	0.074	-25	0.077	-21	0.051	-48
57	Carboxin	0.137	0.033	-76	0.124	-9	0.140	2	0.151	10	0.152	11
58	p,p-DDT	0.062	0.209	235	0.081	29	0.019	-70	0.102	63	0.072	16
59	Sulprofos	0.491	0.063	-87	0.514	5	0.264	-46	0.755	54	0.499	2
60	Benalaxyl	0.297	0.596	101	0.229	-23	0.383	29	0.365	23	0.272	-8
61	Propargite	0.032	0.289	807	0.000	-100	0.121	281	0.000	-100	0.041	28
62	Bifenthrin	0.493	0.017	-97	0.382	-22	0.195	-60	0.589	19	0.464	-6
63	Tebuconazole	0.133	0.493	270	0.133	0	0.245	84	0.108	-19	0.141	6
64	Norflurazon	0.094	0.154	64	0.102	8	0.133	42	0.102	9	0.107	14
65	Endosulfan sulfate	0.015	0.148	900	0.028	89	0.087	491	0.017	16	0.018	20
66	Methoxychlor	0.174	0.000	-100	0.180	3	0.035	-80	1.585	812	0.178	3
67	Hexazinone	0.507	0.154	-70	0.468	-8	0.310	-39	0.746	47	0.511	1
68	Fenoxycarb	0.142	0.597	320	0.252	78	0.344	142	0.406	186	0.191	35
69	Methoxychlor	0.147	0.262	77	0.186	26	0.217	47	0.507	244	0.150	2
70	Furathiocarb	0.171	0.215	26	0.130	-24	0.215	26	0.260	52	0.139	-19
71	Tetradifon	0.035	0.164	370	0.031	-10	0.107	207	0.043	24	0.041	18
72	Fluvalinate	0.005	0.050	968	0.013	169	0.019	316	0.020	327	0.021	346
73	Pyrazophos	0.086	0.040	-54	0.097	13	0.066	-23	0.107	25	0.153	78
74	Permethrin1	0.129	0.138	7	0.122	-6	0.149	15	0.165	28	0.134	4
75	Fenarimol	0.102	0.130	27	0.084	-18	0.103	1	0.140	38	0.100	-2
76	Permethrin2	0.083	0.104	26	0.087	5	0.086	4	0.118	43	0.090	9
77	Bitertanol	0.199	0.125	-37	0.235	18	0.105	-47	0.390	96	0.241	21
78	Cyfluthrin I	0.019	0.281	1365	0.033	70	0.129	574	0.040	111	0.022	17
79	Cyfluthrin II	0.023	0.037	62	0.012	-47	0.022	-2	0.021	-8	0.021	-5
80	Cyfluthrin III	0.027	0.030	9	0.016	-42	0.033	23	0.000	-100	0.030	11
81	Cypermethrin I	0.113	0.025	-77	0.012	-89	0.072	-36	0.000	-100	0.016	-86
82	Cypermethrin II	0.012	0.020	65	0.009	-21	0.056	372	0.012	-2	0.014	17
83	Cypermethrin III	0.009	0.029	224	0.000	-100	0.010	13	0.138	1426	0.005	-45
84	Fluvalinate	0.045	0.000	-100	0.039	-13	0.149	233	0.086	92	0.037	-17
85	Fluvalinate II	0.040	0.081	100	0.028	-32	0.026	-35	0.097	140	0.041	0
86	Deltamethrin I	0.058	0.081	41	0.041	-28	0.086	50	0.042	-26	0.049	-14
87	Deltamethrin II	0.026	0.074	181	0.014	-48	0.031	18	0.000	-100	0.029	10

Title: **Multi-Residue Screening in Vegetables**



Title: **Multi-Residue Screening in Vegetables**

Appendix F: Matrix-Matched Standard Variation

A series of five matrix-matched standards were prepared with the carrot matrix. The variability observed in the data presented below represents the variability of preparation of the matrix-matched standard, the variability of the matrix extraction and cleanup, and the variability of the instrument. The data is presented as actual results in ug/mL.

ND: Not Determined

Analyte	Std 1 (ug/mL)	Std 2 (ug/mL)	Std 3 (ug/mL)	Std 4 (ug/mL)	Std 5 (ug/mL)	n	Average	Std Dev	%RSD
Methomyl	0.82	0.71	0.73	1.20	0.69	5	0.83	0.21	26
Dichlorvos	0.58	0.65	0.57	0.76	0.50	5	0.61	0.10	16
Bendiocarb	2.67	2.55	2.59	3.36	2.47	5	2.73	0.36	13
Carbofuran	6.08	6.73	5.50	8.48	5.70	5	6.50	1.20	19
Methamidophos	0.11	0.16	0.18	0.15	0.18	5	0.15	0.03	17
Diuron	0.05	0.06	0.07	0.11	0.05	5	0.07	0.03	40
5-Dichlorobenzonitrile	0.78	0.76	0.76	1.02	0.67	5	0.80	0.13	16
Pebulate	0.77	0.81	0.99	1.07	0.84	5	0.89	0.13	14
Mevinphos	0.37	0.42	0.44	0.49	0.41	5	0.42	0.04	10
Methiocarb	1.42	1.34	1.48	1.97	1.32	5	1.51	0.26	18
Trifluralin	0.37	0.40	0.40	0.47	0.39	5	0.41	0.04	10
Benfluralin	0.33	0.34	0.34	0.42	0.34	5	0.35	0.04	11
Propachlor	0.46	0.48	0.48	0.57	0.46	5	0.49	0.05	10
Ethoprophos	0.81	0.91	0.80	0.57	0.79	5	0.77	0.12	16
Chlorpropham	0.26	0.29	0.28	0.28	0.28	5	0.28	0.01	4
Pencyuron	0.08	0.10	0.02	0.02	0.09	5	0.06	0.04	66
Phorate	0.70	0.71	0.69	0.79	0.67	5	0.71	0.05	7
Hexachloro Benzene	1.01	1.07	1.06	1.20	1.00	5	1.07	0.08	8
Bendiocarb	0.11	0.17	0.13	0.09	0.15	5	0.13	0.03	22
Terbufos	0.52	0.52	0.53	0.61	0.52	5	0.54	0.04	8
Propyzamide	0.38	0.39	0.41	0.48	0.37	5	0.41	0.04	10
Atrazine	0.12	0.05	0.35	0.40	0.11	5	0.21	0.16	77
Quintozene	0.53	0.57	0.54	0.66	0.54	5	0.57	0.05	9
Disulfoton	0.33	0.35	0.38	0.47	0.32	5	0.37	0.06	16
Dimethoate	0.35	0.37	0.42	0.42	0.46	5	0.40	0.04	11
Pirimicarb	0.29	0.31	0.32	0.38	0.30	5	0.32	0.04	11
Terbacil	0.27	0.29	0.29	0.32	0.29	5	0.29	0.02	6
Prometrin	0.13	0.05	0.17	0.36	0.09	5	0.16	0.12	76
Metalaxyl M	0.23	0.23	0.21	0.25	0.22	5	0.23	0.02	7
Methyl parathion	0.62	0.59	0.73	0.72	0.67	5	0.66	0.06	9
Metribuzin	0.35	0.35	0.41	0.39	0.35	5	0.37	0.03	8
Metolachlor	0.36	0.43	0.41	0.55	0.38	5	0.42	0.08	18
Chlorpyrifos	0.19	0.18	0.20	0.24	0.18	5	0.20	0.02	12
Ethofumesate	0.40	0.46	0.38	0.35	0.40	5	0.40	0.04	10
Dichlofluanid	0.22	0.25	0.22	0.20	0.22	5	0.22	0.02	9
Bioallethrin	1.18	0.63	0.64	2.11	2.06	5	1.32	0.73	55
Fipronil	0.26	0.26	0.26	0.29	0.24	5	0.26	0.02	6
Bromacil	0.29	0.31	0.30	0.38	0.32	5	0.32	0.03	11
Pendimethalin	0.28	0.27	0.29	0.31	0.28	5	0.29	0.02	6
Pyrethrum	ND	ND	ND	ND	ND				
Penconazole	0.34	0.35	0.35	0.42	0.32	5	0.36	0.04	11
Triadimenol	0.50	0.59	2.56	1.36	0.86	5	1.17	0.85	72
Procymidone	0.49	0.43	0.38	0.45	0.38	5	0.42	0.05	11
cis-Chlordane	0.30	0.30	0.32	0.35	0.28	5	0.31	0.03	8
Trans-Chlordane	0.36	0.33	0.32	0.36	0.32	5	0.34	0.02	6

Title: **Multi-Residue Screening in Vegetables**

Analyte	Std 1 (ug/mL)	Std 2 (ug/mL)	Std 3 (ug/mL)	Std 4 (ug/mL)	Std 5 (ug/mL)	n	Average	Std Dev	%RSD
Pyrefinox	0.40	0.42	0.34	0.31	0.32	5	0.36	0.05	14
Prothiophos	0.35	0.35	0.36	0.36	0.34	5	0.35	0.01	3
Hexaconazole	0.45	0.44	0.47	0.45	0.42	5	0.45	0.02	5
p,p-DDE	0.36	0.33	0.33	0.35	0.30	5	0.33	0.02	7
Buprofezin	0.37	0.32	0.31	0.34	0.31	5	0.33	0.02	7
Napropamide	0.33	0.30	0.31	0.31	0.27	5	0.30	0.02	7
Methidathion	0.13	0.17	0.16	0.10	0.16	5	0.14	0.03	18
Dieldrin	0.32	0.27	0.36	0.34	0.31	5	0.32	0.03	10
Buprimate	0.32	0.30	0.31	0.35	0.31	5	0.32	0.02	6
Endosulfan II	ND	ND	ND	ND	ND				
Myclobutanil	0.52	0.48	0.51	0.64	0.49	5	0.53	0.06	12
Endrin	1.17	0.13	1.28	1.50	1.04	5	1.02	0.53	52
Cyproconazole	0.38	0.33	0.36	0.31	0.37	5	0.35	0.03	9
Carboxin	0.27	0.26	0.28	0.32	0.24	5	0.27	0.03	10
p,p-DDT	4.30	0.24	4.97	5.79	3.20	5	3.70	2.15	58
Sulprofos	0.31	0.32	0.32	0.33	0.32	5	0.32	0.01	3
Benalaxyl	0.35	0.38	0.32	0.38	0.33	5	0.35	0.03	8
Propargite	ND	ND	ND	ND	ND				
Bifenthrin	0.43	0.37	0.33	0.38	0.31	5	0.36	0.05	13
Tebuconazole	0.39	0.44	0.39	0.46	0.42	5	0.42	0.03	7
Norflurazon	0.30	0.33	0.30	0.36	0.31	5	0.32	0.02	8
Endosulfan sulfate	0.10	0.15	0.14	0.06	0.13	5	0.11	0.04	32
Methoxychlor	4.10	3.78	3.66	5.18	3.58	5	4.06	0.66	16
Hexazinone	0.32	0.32	0.30	0.41	0.31	5	0.33	0.05	14
Fenoxycarb	0.54	0.60	0.56	0.52	0.57	5	0.56	0.03	5
Methoxychlor	0.00	0.20	0.17	0.09	0.16	5	0.13	0.08	62
Furathiocarb	0.22	0.23	0.23	0.22	0.24	5	0.23	0.01	4
Tetradifon	0.23	0.16	0.20	0.22	0.12	5	0.19	0.05	26
Fluvalinate	0.12	0.45	0.49	0.07	0.47	5	0.32	0.21	65
Pyrazophos	0.27	0.39	0.31	0.27	0.35	5	0.32	0.05	16
Permethrin1	0.47	0.37	0.33	0.37	0.33	5	0.37	0.06	15
Fenarimol	0.30	0.26	0.27	0.31	0.26	5	0.28	0.02	8
Permethrin2	0.53	0.42	0.42	0.42	0.35	5	0.43	0.07	15
Bitertanol	0.46	0.48	0.49	0.47	0.49	5	0.48	0.01	3
Cyfluthrin I	0.72	0.63	0.62	0.50	0.70	5	0.63	0.09	14
Cyfluthrin II	0.62	0.18	0.19	0.30	0.22	5	0.30	0.18	60
Cyfluthrin III	0.87	0.67	0.69	0.41	0.63	5	0.65	0.16	25
Cypermethrin I	0.58	0.62	0.49	0.11	0.00	5	0.36	0.28	79
Cypermethrin II	0.41	0.38	0.19	0.17	0.32	5	0.29	0.11	37
Cypermethrin III	ND	ND	ND	ND	ND				
Fluvalinate	0.50	0.48	0.32	0.34	0.30	5	0.39	0.10	25
Fluvalinate II	0.58	0.45	0.34	0.28	0.27	5	0.38	0.13	34
Deltamethrin I	0.23	0.21	0.15	0.18	0.16	5	0.19	0.04	19
Deltamethrin II	0.31	0.32	0.25	0.00	0.18	5	0.21	0.13	62

Title: **Multi-Residue Screening in Vegetables**

Appendix G: Analysis of Variance (ANOVA) on variability of recoveries

Several spiked samples were analysed on each of three separate days (minimum separation of 9 days) for each of the matrices. An Analysis of Variance (ANOVA) was calculated for each analyte for two of the matrices and the F values determined. The F values for each analyte for Carrot and Potato matrices and the F_{crit} value are presented below.

F_{crit} for a total of 5 degrees of freedom = 9.552

Analyte	F Value Potato	F Value Carrot
methomyl	n/a	51.67
Dichlorrvos	50.23	35.87
Methamidophos	n/a	2.52
Diuron	72.47	13.65
3,5-Dichlorobenzonitrile	1.96	1.30
Pebulate	18.75	4.84
Mevinphos	6.13	9.26
Methiocarb	31.58	0.88
Trifluralin	131.84	1.18
Benfluralin	1.07	1.32
Propachlor	3.80	3.27
Ethoprophos	11.27	8.65
Chlorpropham	3672.23	5.91
Pencyuron	1.01	n/a
Phorate	11.65	35.18
Hexachlorobenzene	19.58	0.54
Bendiocarb	74.62	25.18
Terbufos	25.72	1.21
Propyzamide	1.20	5.28
Atrazine	3.36	8.71
Quintozene	41.68	4.03
Disulfoton	2661.75	7.63
Dimethoate	1.05	6.70
Primicarb	3.06	1.28
Terbacil	621.04	136.34
Prometryn	16.44	7.81
Metalaxyl M	n/a	17.02
Methyl parathion	162.52	4.18
Metribuzin	2.24	0.25
Metolachlor	3.68	0.40
Chlorpyrifos	1.55	25.87
Ethofumesate	78.72	1.77
Dichlofluanid	34.16	3.76
Bioallethrin	3.23	1.69
Fipronil	6.41	1.23
Pendimethalin/Penoxaline	0.03	2.33
Bromacil	1.87	7176.59
Penconazole	27.12	2.58
Triademenol	5.81	0.24
Procymidone	9.95	0.71
cis-Chlordane	1.40	49.90
trans-Chlordane	633.15	0.30
Pyrifenox	0.19	6.96
Prothiofos	4.54	0.52
Hexaconazole	44.87	0.10
p,p'DDE	42.77	11.90

Title: **Multi-Residue Screening in Vegetables**

Analyte	F Value Potato	F Value Carrot
Buprofezin	2.17	1.12
Napropamide	40.71	2.22
Methidathion	1.36	1.06
Dieldrin	50.98	0.66
Buprimate	177.41	1.37
Myclobutanil	1076.32	1.99
Endrin	1.31	13.94
Cyproconazole	292.21	2.15
Carboxin	429.28	53.10
p,p'-DDT	17.84	145.00
Sulprofos	37.49	0.26
Benalaxyl	4.35	1.55
Propargite	2.12	1.97
Bifenthrin	343.18	0.36
Tebuconazole	19.56	60.55
Endosulfan sulphate	476.38	4150.08
Methoxychlor	1957.60	143.59
Norfluazon	41008.58	10.62
Hexazinone	71272.70	2.26
Fenoxycarb	66.38	8.22
Methoxychlor	0.21	4.19
Furathiocarb	7.90	32.59
Tetradifon	29.63	1.00
Fluvalinate	1.71	2.95
Pyrazophos	1.82	3.72
Permethrin I	5.59	n/a
Permethrin II	128.73	4.70
Fenarimol	8.51	74.56
Bitertanol	33.40	22.59
Cyfluthrin	16.53	1.35
Cyfluthrin II	4.10	n/a
Cyfluthrin III	2.60	n/a
Cypermethrin	48.01	0.47
Cypermethrin II	30.63	n/a
Fluvalinate I	12.34	n/a
Fluvalinate II	7.31	4.21
Deltamethrin I	992.91	3.76
Deltamethrin II	446.28	1.27