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Rapid and Easy Multiresidue Method for Determination of Pesticide Residues in Foods Using Gas or Liquid Chromatography–Tandem Mass Spectrometry

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1. Introduction

To obtain a high yield of food grains, many types of pesticides have been developed, which in turn has facilitated the prosperity of the human race and brought relief to farmers. After WWII, organophosphorus and organochlorine pesticides were extensively used worldwide. These early organophosphorus pesticides occasionally caused poisoning, while some organochlorine pesticides persisted in the environment. These facts served as a warning against an improvident use of pesticides and revealed that residual pesticides in crops should be monitored. Thus, national and local governments should monitor imported and regional foods as a policy. In Japan, all pesticides are regulated under a uniform limit (0.01 µg/g), except for a combination of foods and pesticides set under the maximum residue limits (MRLs) (Notification No. 497-499, November 29, 2005). This regulation does not require analysis of all the pesticides; however, it does necessitate pesticide residue analysis of commodities. Thus far, the chemical industry has developed more than 800 pesticides that belong to many classes such as insecticides, fungicides, nematocides, and herbicides. Each class has a different target point and physical properties and this diversity limits the coverage of a single analytical method. It is also impossible to monitor all the pesticides pertaining to one foodstuff using hundreds of methods. Thus, analytical institutes require fast and efficient multiresidue methods in order to maximize the coverage of their monitoring activities. For this reason, researchers have reported many multiresidue analytical methods (Cook, J., et al., 1999, Fillion, J., et al., 2000, Hirahara, Y., et al., 2006, Luke, M. A., et al., 1975, Ueno, E., et al., 2004). These methods were optimized to monitor multiple residues efficiently and are used routinely in quarantine stations and laboratories.

Anastassiades et al. reported a rapid approach for the analysis of pesticide residues in fruits and vegetables, named QuEChERS (quick, easy, cheap, effective, rugged and safe) method in 2003 (Anastassiades, M., et al., 2003). The main focus of this report was to shorten the analytical process during extraction and cleanup without employing expensive instruments. The characteristic points of the method are as follows: (1) shaking extraction with acetonitrile in a disposable tube, (2) one step salting out and removal of water from the

acetonitrile using anhydrous magnesium sulfate (MgSO$_4$) and sodium chloride (NaCl), (3) purification with so called "dispersive-solid phase extraction" (dispersive-SPE), in which the extract is processed by shaking with primary secondary amine (PSA) silica gel and then centrifuged to separate the PSA before analysis. Compared to ordinary multiresidue methods, this method is a remarkably rapid and easy procedure. Other researchers have reported follow-up studies of this method (Lehotay, S. J., et al., 2005, Lehotay, S. J., et al., 2005, Schenck, F. J., et al., 2008, Wang, J.&Leung, D., 2009). We also examined the QuEChERS method and found that the characteristic points of the method (step (2)) are positive aspects; however, steps (1) and (3) are negative aspects due to the weak extraction potency (shaking) and the insufficient cleanup (dispersive-SPE). To overcome these negative aspects, we developed a new powerful extraction technique with a homogenizer and with an efficient cleanup with double-layered SPE (graphite carbon black (GCB) with PSA) on the basis of the QuEChERS method (Okihashi, M., et al., 2005, Okihashi, M., et al., 2007, Takatori, S., et al., 2008). We demonstrated that this method is applicable to the multiresidue analysis in agricultural products by the combination of analysis with gas chromatography equipped with (tandem) mass spectrometry (GC-MS or GC-MS/MS) and with high-performance liquid chromatography with tandem mass spectrometry (LC-MS/MS).

For agricultural products, multiresidue methods applicable to the analysis of pesticides in processed foods are also required. In Japan (in 2007~08), serious organophosphorus pesticide poisoning occurred after people consumed dumplings imported from China. An organophosphorus pesticide, methamidophos, was detected from the leftover of the Chinese dumplings in concentrations of 3,200 ppm (Ito, T., 2009, Sumi, Y., et al., 2008). Furthermore, dichlorvos, parathion, and parathion-methyl were also detected in other packages of the Chinese dumplings. This incident necessitated the monitoring of pesticide residues in processed foods in Japan. Multiresidue methods for processed foods such as tomato purees and baby foods have been reported (Botitsi, H., et al., 2007, Cajka, T., et al., 2008, Gilbert-Lopez, B., et al., 2007, Sannino, A.&Bandini, M., 2005, 2005, Sannino, A., et al., 2003). However, the number of multiresidue methods that can be adapted for processed foods that contain high lipid ratios (more than 10% w/w) are relatively limited (Fenske, R. A., et al., 2002, Lehotay, S. J., et al., 2005, Sannino, A., et al., 1995, 1996). Lipids are a problematic component of processed foods during pesticide detection. We categorized processed foods into three categories: (i) a high lipid group (lipid content > 10% w/w), (ii) a low lipid group (lipid content ≤ 10% w/w), and (iii) a non-lipid group. Chinese dumplings fall into the high lipid group. For this group, both the sufficient extraction of pesticides within the lipids and the removal of lipids before analysis are key aspects. The multiresidue method for agricultural products described above may be applicable to the low and non-lipid groups directly or with minor modifications such as adding water to samples prior to the extraction. As described above, the MRLs were set according to the combination of pesticides and the agricultural products. Except for some processed foods such as raisins and orange juice, the MRLs were not established for combinations of pesticides and processed foods; most of the pesticides detected in processed foods are regulated under the uniform limit (0.01 ppm/g). Thus, the uniform limit should be detectable using the multiresidue method for monitoring pesticides in processed foods. Here, we have developed a rapid and easy multiresidue method for the determination of pesticide residues in processed foods that fall in the high lipid group. The method could detect around 300 pesticides at the level of 0.01 ppm/g (Kitagawa, Y., et al., 2009, 2009, Okamoto, Y., et al., 2009).

In this chapter, we describe rapid and easy multiresidue methods for the determination of pesticide residues in foods, including agricultural products (vegetables, fruits, and cereals) and processed foods, on the basis of our recent studies (Kitagawa, Y., et al., 2009, 2009, Okamoto, Y., et al., 2009, Okihashi, M., et al., 2007, Takatori, S., et al., 2008).

2. Outline of the methods

2.1 Method for agricultural products

We extracted agricultural products weighed in disposable tubes with acetonitrile using a homogenizer. To the tube, we added NaCl and $MgSO_4$, shook it vigorously, and then centrifuged it to remove the water layer and the precipitant. The acetonitrile phase was applied onto a SPE column for purification (removing chlorophyll and fatty acids). The eluate was concentrated *in vacuo* and then reconstituted in an appropriate solvent for GC-MS, GC-MS/MS, or LC-MS/MS analysis.

2.2 Method for processed foods (high lipid containing group, Chinese dumplings, French fries, etc.)

We extracted the pesticides in homogenized processed foods with ethyl acetate in the presence of $MgSO_4$. After centrifuging, an aliquot of extract was concentrated *in vacuo*. The remainder was dissolved in hexane and then an acetonitrile/hexane partition step was conducted to remove the lipids from the extract. After centrifuging, we applied the acetonitrile phase onto a SPE column for further purification (to remove chlorophyll and fatty acids). We concentrated the eluate *in vacuo* and then reconstituted it in an appropriate solvent for GC-MS, GC-MS/MS, or LC-MS/MS analysis.

3. Experimental

3.1 Chemicals

Pesticides used in this study were analytical grade obtained from Wako (Osaka, Japan), Kanto Chemical (Tokyo, Japan), Hayashi Pure Chemical (Osaka, Japan), Riedel-de-Haën (Seelze, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). Solvents and NaCl were pesticides analysis grade purchsed from Wako. Anhydrous $MgSO_4$ was the highest grade obtained from Wako. Water was prepared by Millipore system(Millipore, Bedford, MA). Other chemicals used in this study were the highest grade commercially avairable.

3.2 Apparatus

A 50 mL polypropyrene (PP) disporsal tube was purchased from Becton Dickinson (Franklin Lakes, NJ). A QS-7 conventional food processor (Toshiba, Tokyo, Japan) was used to comminute vegetable, fruit, cereal and processed foods samples. Polytron PT1200 high-speed homogenizer (KINEMATICA, Luzern, Switzerland) was used to blend sample and acetonitrile or ethyl acetate in the extraction step. A Hitachi Himac SCR 20B (Hitachi Koki, Tokyo, Japan) was utilized for centrifugation. Solvent evaporator, Iwaki REN-1000 rotary evaporators (Asahi Techno Glass, Chiba Japan), were used in this study. Double-layered cartridge column (6 mL) with 500 mg of GCB and 500mg of PSA and an octadecyl silica gel (C18) column (500 mg; 3mL) were obtained from SUPELCO (Bellefonte, PA).

3.3 Analytical systems
3.3.1 GC-MS

GCMS-QP2010 (Shimadzu, Kyoto, Japan) was used in EI (electroionization) mode. The analytical column was the Rtx-5MS (0.25 mm x 30 m, 0.25μm; Restek, Bellefonte, PA). The analysis was performed on a selected ion monitoring (SIM) mode.

3.3.2 GC-MS/MS

Quattro Micro GC (Waters/Micromass, Manchester, UK) was used in EI mode. The analytical column was the DB-5 (0.25 mm x 30 m, 0.25μm, Agilent, Santa Clara, CA). The analysis was performed on a selected reaction monitoring (SRM) mode.

3.3.3 LC-MS/MS

The LC-MS/MS system was composed of an LC system (1100 series; Agilent) and an MS/MS (API3000; Applied Biosystems, Foster City, CA) equipped with electroionization spray interface. The analytical column was Ascentis C18, 2.1 x 100 mm, 3 μm (SUPELCO). Eluents were 0.1% formic acid aquaous solution (A) and 0.1% formic acid contaning methanol (B), in whic the ratio was gradually changed as the analysis went on. The analysis was performed on an SRM mode.

The details of analytical conditions in 3.3.1~3 were omitted.

3.4 Procedure for sample preparation
3.4.1 Vegetables and fruits

We homogenized a sample (approximately 700~1,000 g) in a conventional food processor. To a 50 mL PP disposable tube containing a 10 g aliquot of the homogenized sample, we added 20 mL of acetonitrile and then homogenized it with a high-speed homogenizer for 1 min. Next, 4 g of $MgSO_4$ and 1 g of NaCl were added to the tube and it was shaken vigorously for a minute. After centrifugation, we applied 8.0 mL of the acetonitrile layer (equivalent to 4.0 g of the sample) onto a GCB/PSA, which was formerly conditioned with 30 mL of the elution solvent (acetonitrile-toluene, 3 + 1). We eluted the column with 30 mL of the elution solvent. All the eluate was concentrated *in vacuo*. For the GC-MS/MS analysis, the eluate was reconstituted in 4.0 mL of 10% acetone, containing hexane (the test solution, equivalent to 1.0 g/mL). This test solution is also applicable to the analysis via GC-MS. For the LC-MS/MS analysis, the eluate was reconstituted in 2.0 mL of methanol and then diluted four times with water before analysis (the test solution, equivalent to 0.5 g/mL) [Scheme I].

3.4.2 Cereals

We homogenized a sample (approximately 700~1,000 g) in a mill. To a 50 mL PP disposable tube containing a 5.0 g aliquot of the homogenized sample, 5.0 mL of water was added and stood for 30 min. Then, we added and homogenized 20 mL of acetonitrile with a high speed homogenizer for 1 min. We added 4 g $MgSO_4$ and 1 g NaCl to the tube and shook it vigorously for 1 min. After centrifugation, 10 mL of the acetonitrile layer (equivalent to 2.5 g of the sample) was applied onto a C18 column connecting above GCB/PSA, which was formerly conditioned with 10 mL acetonitrile and 30 mL of the elution solvent (acetonitrile-toluene, 3 + 1), respectively. We eluted the column with 10 mL acetonitrile. After removing the C18 column, the GCB/PSA column was eluted with the 30 mL of the elution solvent. The eluate was concentrated *in vacuo*. For the GC-MS/MS analysis, we reconstituted the

eluate in 2.5 mL of 10% acetone containing hexane (the test solution, equivalent to 1.0 g/mL). This test solution is also applicable to the analysis via GC-MS. For the LC-MS/MS analysis, we reconstituted the eluate in 1.25 mL of methanol and then diluted it four times with water to 5.0 mL before analysis (the test solution, equivalent to 0.5 g/mL) [Scheme II].

Sample (10 g) in a 50 mL PP disposal tube

> Add 20 mL of acetonitrile
> Homogenize (1 min)
> Add 4 g of $MgSO_4$ and 1 g of NaCl
> Shake (1 min) and centrifuge

Acetonitrile layer 8.0 mL (equivalent to 4.0 g sample)

> Load on a GCB/PSA column
> Elute with 30 mL acetonitrile–toluene (3+1)
> Collect loading and eluting fractions in a round bottom flask
> Evaporate and reconstituted in appropriate solvent

GC-MS/MS or LC-MS/MS analysis

Scheme I. Procedure of sample preparation for the determination of pesticides residues in agricultural products (for vegetables and fruits)

Sample (5.0 g) in a 50 mL PP disposal tube

> Add 5 mL of water and stand for 30 min
> Add 20 mL of acetonitrile
> Homogenize (1 min)
> Add 4 g of $MgSO_4$ and 1 g of NaCl
> Shake (1 min) and centrifuge

Acetonitrile layer 10.0 mL (equivalent to 2.5 g sample)

> Load on a C18 column connecting above a GCB/PSA column
> Elute with 10 mL of acetonitrile
> Remove the C18 column
> Elute with 30 mL acetonitrile–toluene (3+1)
> Collect loading and eluting fractions in a round bottom flask
> Evaporate and reconstituted in appropriate solvent

GC-MS/MS or LC-MS/MS analysis

Scheme II. Procedure of sample preparation for the determination of pesticides residues in agricultural products (for cereals)

3.4.3 Calibration curves and limits of quantification

For the GC-MS and GC-MS/MS analysis, we used the matrix-matched calibration curves to minimize the effects of the matrix in the test solution (Poole, C. F., 2007). The standard solutions for the matrix-matched calibration curves were prepared by mixing the serially diluted standard solutions with equivalent volumes of the doubly concentrated test solutions obtained from the same foods. We formerly determined that these foods did not contain the pesticide residues to be analyzed.

For LC-MS/MS analysis, we serially diluted the standard mixture solution with a 25% methanol aqueous solution. The limits of quantification (LOQ) of pesticides studied in this chapter were determined by LC-MS/MS and were found to be 0.01 ppm, except for flufenoxuron, lufenuron, pentoxazone, and propiconazole. The LOQs of these pesticides were 0.02 ppm.

3.4.4 Processed foods in high lipid group

We homogenized a whole sample in a distributed package (approximately 200~1,000 g) in a conventional food processor. To a 50 mL PP disposable tube containing a 5.0 g aliquot of the sample, 20 mL of ethyl acetate and 3 g of $MgSO_4$ were added to the tube and then homogenized with a high speed homogenizer for 1 min. After centrifugation, 8.0 mL of ethyl acetate supernatant (equivalent to 2.0 g of the sample) was evaporated in a round bottom flask at 40°C *in vacuo* and then dried under a nitrogen stream to remove ethyl acetate. To remove the lipid from the extract, the acetonitrile-hexane partition was conducted. Briefly, we reconstituted the extract in 10 mL hexane in a new 50 mL disposable PP tube. To the tube, we added 20 mL hexane-saturated acetonitrile and then shook it vigorously for 1 min. After centrifugation, we applied the acetonitrile layer onto the GCB/PSA, which was formerly conditioned with 30 mL of the elution solvent (acetonitrile–toluene, 3 + 1). To the remaining hexane layer in the PP tube, we added 20 mL hexane-saturated acetonitrile and then again shook it vigorously for 1 min. After centrifugation, the acetonitrile layer was applied onto the column. The column was eluted with 30 mL of elution solvent. The eluate was concentrated *in vacuo*. For GC-MS or GC-MS/MS analysis, the eluate was reconstituted in 2 mL of 10% acetone containing hexane (the test solution, equivalent to 1.0 g/mL). For LC-MS/MS analysis, we reconstituted the eluate in 2 mL of methanol (the test solution stock, equivalent to 1.0 g/mL) and then diluted it ten times with a 25% methanol aqueous solution before analysis [Scheme III].

4. Evaluation

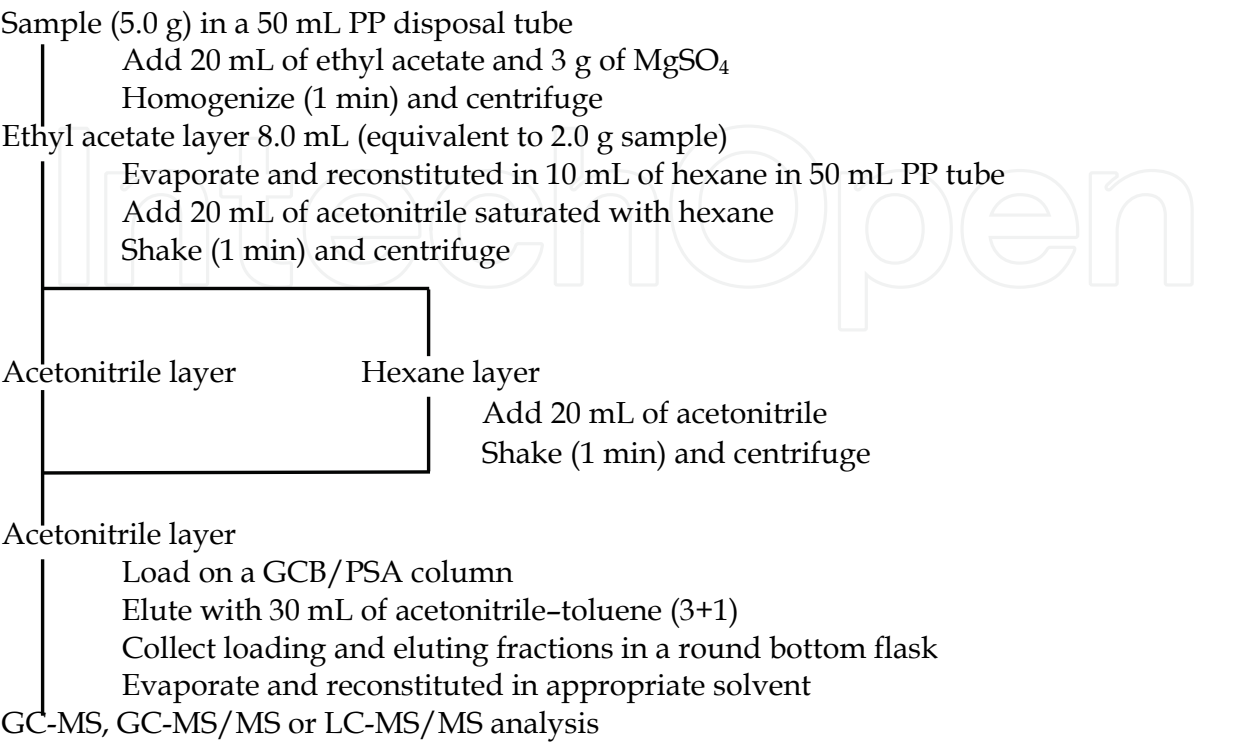### 4.1 Method for vegetables, fruits and cereals

4.1.1 Rapidity of the method

The merits of the method (saving time and solvent) are due to its simple procedure. The preparation time for the test solutions of the 12 samples was approximately 3~4.5 h for one chemist. More time for the chromatographic data analysis is necessary when increasing the number of analyzed pesticides in the method. Thus, the time saved from the sample preparation and the spare time from the chromatographic data analysis are important for the multiresidue analysis. This simple procedure would also be required to revise the method studying the applicability of new target pesticides in foods. Furthermore, this simple method does not require a long time to master the procedure and would also be effective in reducing the errors of the procedure. The ruggedness of the method derives from these points. The solvent and the amount of glassware used for the procedure are lesser than those used for the original method. Now, this method, which is used for routine monitoring of pesticides in our laboratory, would be more economic and safe than the ordinary methods.

4.1.2 Recovery tests

Recovery tests were conducted to examine the applicability of the method using GC-MS/MS (250 pesticides) and LC-MS/MS (99 pesticides). We defined an acceptable result as

the one with a recovery of about 70~120% with a relative standard deviation (RSD) ≤ 20% at both concentrations.

Sample (5.0 g) in a 50 mL PP disposal tube
    Add 20 mL of ethyl acetate and 3 g of MgSO$_4$
    Homogenize (1 min) and centrifuge
Ethyl acetate layer 8.0 mL (equivalent to 2.0 g sample)
    Evaporate and reconstituted in 10 mL of hexane in 50 mL PP tube
    Add 20 mL of acetonitrile saturated with hexane
    Shake (1 min) and centrifuge

Acetonitrile layer   Hexane layer
                    Add 20 mL of acetonitrile
                    Shake (1 min) and centrifuge

Acetonitrile layer
    Load on a GCB/PSA column
    Elute with 30 mL of acetonitrile–toluene (3+1)
    Collect loading and eluting fractions in a round bottom flask
    Evaporate and reconstituted in appropriate solvent
GC-MS, GC-MS/MS or LC-MS/MS analysis

Scheme III. Procedure of sample preparation for the determination of pesticides residues in processed foods categorized as the high-lipid group

4.1.2.1 Analysis of 250 pesticides via GC-MS/MS (agricultural products)

We spiked the 250 pesticides for 3 agricultural products (bananas (Ba), carrots (Ca), and grapefruits (Gf)) at concentrations of 0.02 and 0.10 ppm. We conducted 3 trials for each test. These pesticides were classified into 3 groups as per the number of foods with acceptable results at both concentrations: A, 3; B, 2; and C, 1. Details are described below.

Group A (207 pesticides with the acceptable results in 3 agricultural products at the both concentrations):

2-Phenylphenol, Acetochlor, Aldrin, Allidochlor, Ametryn, Anilofos, Atrazine, Azinphos-methyl, Azoxystrobin, Benalaxyl, Bendiocarb, Benfluralin, Benfuresate, Benoxacor, BHC (total), Bifenthrin, Bitertanol, Bromacil, Bromophos, Bromopropylate, Bupirimate, Buprofezin, Butachlor, Butafenacil, Butamifos, Cadusafos, Cafenstrole, Carbaryl, Carbofuran, Carfentrazone-ethyl, Chlorfenvinphos, Chlorobenzilate, Chlorpropham, Chlorpyrifos, Chlorpyrifos-methyl, Chlorthal-dimethyl, Clomazone, Cloquintocet-1-methylhexyl, Cyanazine, Cyanophos, Cyflufenamid, Cyfluthrin, Cyhalofop-butyl, Cyhalothrin, Cypermethrin, Cyproconazole, Cyprodinil, DDT (total), Diazinon, Dichlofenthion, Diclobutrazol, Diclofop-methyl, Dicloran, Diethofencarb, Difenoconazole, Diflufenican, Dimepiperate, Dimethametryn, Dimethenamid, Dimethipin, Dimethylvinphos, Diofenolan, Dioxabenzofos, Diphenamid, Disulfoton, Dithiopyr, Edifenphos, Esprocarb, Ethalfluralin, Ethiofencarb, Ethion, Ethofumesate, Ethoprophos, Etobenzanid, Etoxazole, Etrimfos, Fenamiphos, Fenarimol, Fenbuconazole, Fenchlorphos, Fenitrothion, Fenobucarb, Fenothiocarb, Fenoxanil, Fenoxycarb, Fenpropimorph,

Fensulfothion, Fenthion, Fenvalerate, Fipronil, Flamprop-methyl, Fluacrypyrim, Flucythrinate, Fludioxonil, Fluquinconazole, Flusilazole, Flutolanil, Flutriafol, Fosthiazate, Fthalide, Furathiocarb, Furilazole, Halfenprox, Heptachlor, Hexazinone, Indoxacarb-MP, Iprobenfos, Iprodione, Iprovalicarb, Isazofos, Isofenphos, Isoprothiolane, Isoxathion, Kresoxim-methyl, Lactofen, Lenacil, Malathion, Mefenacet, Mepronil, Metalaxyl, Methacrifos, Methidathion, Methiocarb, Methoxychlor, Metolachlor, Metolcarb, Metominostrobin, Metribuzin, Mevinphos, Molinate, Myclobutanil, Napropamide, Nitrothal-isopropyl, Oxadiazon, Oxadixyl, Oxyfluorfen, Paclobutrazol, Parathion, Parathion-methyl, Penconazole, Pencycuron, Pendimethalin, Permethrin, Phenothrin, Phenthoate, Phorate, Phosalone, Phosphamidon, Picolinafen, Piperophos, Pirimicarb, Pirimiphos-ethyl, Pirimiphos-methyl, Pretilachlor, Procymidone, Profenofos, Promecarb, Prometryn, Propachlor, Propanil, Propaphos, Propham, Propiconazole, Propoxur, Propyzamide, Prothiofos, Pyraclofos, Pyraflufen-ethyl, Pyrazophos, Pyributicarb, Pyridaphenthion, Pyrimethanil, Pyrimidifen, Pyriminobac-methyl, Pyriproxyfen, Quinalphos, Quinoxyfen, Quintozene, Silafluofen, Simazine, Simeconazole, Simetryn, Sulprofos, Tebuconazole, Tebufenpyrad, Tecnazene, Tefluthrin, Terbacil, Terbufos, Terbutryn, Tetrachlorvinphos, Tetradifon, Thenylchlor, Thifluzamide, Thiobencarb, Thiometon, Tolclofos-methyl, Tralomethrin, Tri-allate, Triadimefon, Triazophos, Tribuphos, Triflumizole, Trifluralin, Uniconazole P, Vinclozolin, XMC

Group B (36 pesticides with the acceptable results in 2 agricultural products at the both concentrations of 0.02 and 0.1 ppm except for the agricultural product exhibited in parentheses):

Acephate (Gf), Bifenox (Gf), Bioallethrin (Gf), Bromobutide (Gf), Chlorfenapyr (Gf), Clodinafop-propargyl (Ca), Clomeprop (Gf), Cyanofenphos (Gf), Deltamethrin (Ba), Dieldrin (Ca), Dimethoate (Gf), Diphenylamine (Ba), Endrin (Gf), EPN (Ba), Fenpropathrin (Gf), Flumioxazin (Gf), Fluvalinate (Gf), Furametpyr (Gf), Heptachlor-epoxide (Ca), Hexaconazole (Gf), Isoprocarb (Ca), Methamidophos (Gf), Monocrotophos (Gf), Norflurazon (Gf), Omethoate (Gf), Phosmet (Ba), Prochloraz (Gf), Propargite (Ba), Pyridaben (Gf), Pyrifenox (Gf), Quinoclamine (Ba), Tetraconazole (Gf), Thiazopyr (Ca), Triadimenol (Gf), Trifloxystrobin (Gf), Xylylcarb (Ba)

Group C (7 pesticides with the acceptable results in 1 agricultural products at the both concentrations of 0.02 and 0.1 ppm exhibited in square brackets):

Acrinathrin [Ca], Dichlorvos [Ca], Dicofol-metabolite (4,4'-Dichlorobenzophenone) [Gf], Diphenyl [Gf], Endosulfan (α+β) [Ba], Flumiclorac-pentyl [Ca], Hexythiazox [Gf]

4.1.2.2 Analysis of 99 pesticides via LC-MS/MS (agricultural products)

We spiked the 99 pesticides for 7 agricultural products (cabbage (Cb), potatoes (Po), spinach (Sp), apples (Ap), oranges (Or), brown rice (Br), and soybeans (Sy)) at concentrations of 0.02 and 0.1 ppm. We conducted 5 trials for each test. These pesticides were classified into 6 groups as per the number of foods with acceptable results: A, 7; B, 6; C, 5; D, 4; E, 3; and F, 2. Details are described below.

Group A (47 pesticides with the acceptable results in all the 7 agricultural products):

Acetamiprid, Acetochlor, Alachlor, Atrazine, Bensulide, Bitertanol, Bromobutide, Bupirimate, Clomeprop, Cumyluron, Diethofencarb, Difenoconazole, Diflufenican, Dimethametryn, Dimethoate, Dimethomorph, Esprocarb, Fenbuconazole, Fenoxycarb, Flusilazole, Hexaconazole, Imazalil, Indanofan, Iprovalicarb, Isoxathion, Mepanipyrim, Methabenzthiazuron, Methomyl, Monocrotophos, Napropamide, Paclobutrazol,

Penconazole, Pirimicarb, Pretilachlor, Prochloraz, Propoxur, Propyzamide, Pyroquilon, Tebuconazole, Tebufenozide, Teflubenzuron, Thenylchlor, Thiacloprid, Thiobencarb, Triadimefon, Triadimenol, Triflumizole

Group B (29 pesticides with acceptable results in 6 agricultural products except for the agricultural product exhibited in parentheses):

Acephate (Or), Allethrin (Or), Azoxystrobin (Or), Buprofezin (Sy), Carbaryl (Sy), Chlorpropham (Sy), Cyanazine (Po), Cyflufenamid (Cb), Cyhalofop-butyl (Po), Daimuron (Sy), Diflubenzuron (Sy), Dimepiperate (Br), Diphenamid (Sp), Ethofumesate (Ap), Etobenzanid (Po), Fenobucarb (Po), Flufenoxuron (Sp), Hexaflumuron (Sp), Imibenconazole (Sp), Isoprocarb (Sy), Isoprothiolane (Or), Mefenacet (Sy), Metalaxyl (Cb), Methamidophos (Po), Omethoate (Po), Oxamyl (Br), Pencycuron (Or), Quizalofop-ethyl (Po), Tebufenpyrad (Sy)

Group C (10 pesticides with acceptable results in 5 agricultural products except for the agricultural products exhibited in parentheses):

Carbofuran (Sp, Ap), Fenoxaprop-ethyl (Po, Sy), Fenpropimorph (Cb, Ap), Furathiocarb (Sp, Sy), Lufenuron (Sp, Br), Pentoxazone (Br, Sy), Pyriproxyfen (Cb, Sy), Quinoclamine (Cb, Sy), Tri-allate (Cb, Sy), Trichlamide (Cb, Sy)

Group D (11 pesticides with acceptable results in 4 agricultural products except for the agricultural products exhibited in parentheses):

Bendiocarb (Ap, Br, Sy), Benfuresate (Po, Sp, Br), Cafenstrole (Or, Br, Sy), Carfentrazone-ethyl (Po, Br, Sy), Ethiofencarb (Po, Ap, Sy), Fenarimol (Cb, Or, Br), Inabenfide (Sp, Ap, Sy), Metolcarb (Cb, Po, Sy), Phenmedipham (Po, Br, Sy), Phoxim (Cb, Po, Sy), Propamocarb (Po, Br, Sy)

Group E (1 pesticide with acceptable results in 3 agricultural products exhibited in square brackets):

Molinate [Cb, Sp, Or]

Group F (1 pesticide with acceptable results in 2 agricultural products exhibited in square brackets):

Propiconazole [Cb, Sy]

4.2 Method for processed foods in high lipid group
4.2.1 Rapidity of the method

In this procedure, we used ethyl acetate for the first extraction step given its lipid solubility. The time for one chemist to prepare test solutions for 12 samples was approximately 5~6 h. For rapidity, we adopted the acetonitrile-hexane partition to remove lipids from the extract in this procedure. A chemist can conduct the procedure simultaneously for up to 12 samples. Furthermore, the collected acetonitrile layer can be applied onto the GCB/PSA column directly. Gel permeation column chromatography is an established technique to remove lipid from the extract in pesticide analysis (Gilbert-Lopez, B., et al., 2009, Sannino, A., et al., 1999). However, this technique cannot be used to analyze many samples simultaneously; for more than 12 samples, the collected fraction should be concentrated and reconstituted in an appropriate solvent for further purification. To confirm the effectiveness of the acetonitrile-hexane partition, we recorded the weight of the residues in the analysis of pesticides in Chinese dumplings. The remaining residue prior to the acetonitrile-hexane partition was 8.9%, corresponding to the original sample weight in the aliquot (2.0 g). After the acetonitrile-hexane partition, the remaining residue was less than 0.1%. Thus, the acetonitrile-hexane partition would be one of the most efficient and suitable techniques for removing lipids.

4.2.2 Recovery tests

We performed recovery tests of pesticides sensitively detectable with GC-MS or GC-MS/MS via fortification of the pesticide mixtures of the 5 processed foods (Chinese dumplings, curry, French fries, fried chicken, and fried fish) at the final concentrations of 0.02 and 0.10 ppm, respectively. We conducted 3 trials for each test and defined an acceptable result as the one with a recovery of 70~120% with a RSD ≤ 20% for both concentrations.

4.2.2.1 Analysis of 225 pesticides via GC-MS (processed foods in high lipid group)

We conducted recovery tests of 225 pesticides detectable at a concentration of 0.01 ppm by GC-MS. These pesticides were classified into 6 groups as per the number of processed foods with acceptable results: A, 5; B, 4; C, 3; D, 2; E, 1; and F, 0. Details are described below. Notations of the processed foods are as follows: D, Chinese dumplings; C, curry; P, French fries; Ck, fried chicken; and F, fried fish.

Group A (99 pesticides with the acceptable results in all the 5 processed foods):

Acetochlor, Alachlor, Ametryn, Anilofos, Atrazine, Azinphos-methyl, Azoxystrobin, Benfluralin, Benfuresate, Benoxacor, Bromacil, Bupirimate, Butafenacil, Chlorfenvinphos-*E*, Clodinafop-propargyl, Cyflufenamid, Cyhalofop-butyl, Cyprodinil, Dichlofenthion, Diflufenican, Dimethamethryn, Dioxabenzofos, Diphenylamine, Dithiopyr, Edifenphos, Esprocarb, Ethalfluralin, Ethion, Ethoprophos, Etofenprox, Etoxazole, Etrimfos, Fenoxanil, Fenthion, Flamprop-methyl, Fluacrypyrim, Fludioxonil, Flumiclorac-pentyl, Fluquinconazole, Flusilazole, Flutolanil, Fluvalinate, Furathiocarb, Hexaconazole, Iprobenfos, Isazofos, Isofenphos, Isoprocarb, Kresoxim-methyl, Mefenacet, Mepronil, Metolachlor, Metolcarb, Metribuzin, Mevinphos, Nitrothal-isopropyl, Oxadiazon, Parathion, Parathion-methyl, Penconazole, Phenthoate, Phorate, Picolinafen, Piperophos, Pirimiphos-methyl, Pretilachlor, Prometryn, Propachlor, Propanil, Propaphos, Propiconazole, Prothiofos, Pyraclofos, Pyrazophos, Pyridaben, Pyridaphenthion, Pyrimethanil, Pyrimidifen, Pyriminobac-methyl-*E*, Pyriminobac-methyl-*Z*, Qunalphos, Simazine, Simetryn, Sulprofos, Tebuconazole, Tebufenpyrad, Terbufos, Terbutryn, Tetraconazole, Thenylchlor, Thiobencarb, Thiazopyr, Tolclofos-methyl, Triadimefon, Triadimenol, Triazophos, Trifluralin, Uniconazole P, Vinclozolin, Xylylcarb

Group B (65 pesticides with the acceptable results in the 4 processed foods except for the processed food exhibited in parentheses):

Acrinathrin (D), Bendiocarb (C), β-BHC (C), γ-BHC (D), Butachlor (C), Butamifos (Ck), Cafenstrole (Ck), Carbofuran (F), Carfentrazone-ethyl, (Ck) Chlorfenvinphos-Z (C), Chlorobenzilate (C), Chlorpropham (Ck), Clomeprop (C), Cyanophos (Ck), p,p'-DDD (C), Diazinon (D), Diclobutrazol (Ck), Diclofop-methyl (C), Diethofencarb (C), Dimethenamid (Ck), Dimethoate (D), Dimethylvinphos (C), Diofenolan (P), EPN (F), Ethofumesate (P), Etobenzanid (P), Fenamiphos (Ck), Fenbuconazole (D), Fenitrothion (Ck), Fenobucarb (C), Flucythrinate (F), Flumioxazin (D), Furametpyr (P), Furilazole (C), Halfenprox (C), Hexazinone (P), Isoprothiolane (C), Malathion (C), Methacrifos (P), Methiocarb (C), Metominostrobin-*E* (C), Metominostrobin-Z (Ck), Monocrotophos (C), Myclobutanil (P), Napropamide (F), Norflurazon (P), Oxyfluorfen (Ck), Pendimethalin (Ck), 2-Phenylphenol (Ck), Phosalone (C), Primiphos-ethyl (C), Promecarb (C), Propham (C), Propoxur, (C) Pyributicarb (F), Pyriproxyfen (C), Silafluofen (Ck), Simeconazole (Ck), Tefluthrin (C), Terbacil (Ck), Tetradifon (C), Thiabendazole (Ck), Thifluzamide (D), XMC (Ck)

Group C (36 pesticides with the acceptable results in the 3 processed foods except for the processed foods exhibited in parentheses):

Acephate (P, F), δ-BHC (D, Ck), Bifenthrin (C, Ck), Bromobutide (D, C), Chlorpyrifos (C, P), Chlorpyrifos-methyl (C, P), Cyanazine (C, P), Cyanofenphos (C, Ck), Cyhalothrin (D, C), Cyproconazole (D, P), o,p'-DDT (C, Ck), p,p'-DDT (C, Ck), Dimepiperate (C, P), Diphenamid (P, Ck), Fenarimol (Ck, F), Fenchlorphos (C, P), Fenothiocarb(P, Ck), Fenpropathrin (D, F), Fensulfothion (C, P), Fipronil (C, P), Flutriafol (C, P), Iprovalicarb (D, C), Methidathion (Ck, F), Molinate (C, P), Omethoate (C, Ck), Phenothrin (C ,Ck), Primicarb (C, Ck), Procymidone (C, F), Propyzamide (D, Ck), Quinoxyfen (C, Ck), Tecnazene (C, P), Tetrachlorvinphos (C, P), Tri-allate (C, P), Tribufos (P, Ck)

Group D (18 pesticides with the acceptable results in the 2 processed foods exhibited in parentheses):

Benalaxyl [D, F], Cadusafos [P, F], Carbaryl [D, P], Clomazone [C, F], Cloquintocet-1-methylhexyl [C, F], p,p'-DDE [D, F], Dichlorvos [Ck, F], Diphenyl [Ck, F], Fthalide [Ck, F], Metalaxyl [D, F], Oxadixyl [D, P], Paclobutrazol [D, C], Pencycuron [Ck, F], Phosmet [P, F], Phosphamidon, [D, P] Profenofos [Ck, F], Pyraflufen-ethyl [Ck, F]

Group E (6 pesticides with the acceptable results in the 1 processed foods exhibited in square brackets):

Allidochlor [D], α-BHC [F], Bromophos [F], Chlorthal-dimethy,l [F], Fenoxycarb [D], Methamidophos [P]

Group F (1 pesticide without the acceptable results in all the 5 processed foods):

Fenpropimorph

4.2.2.2 Analysis of 258 pesticides via GC-MS/MS (processed foods in high lipid group)

On the chromatograms obtained via GC-MS analysis, some pesticides were interfered from the matrix derived from the foods. A GC-MS/MS is one of the most useful tools to overcome the interference on these chromatograms. As a relevant example, Figure 1 shows the chromatograms of methidathion fortified in the fried fish at a concentration of 0.02 ppm obtained via GC-MS and GC-MS/MS (Kitagawa, Y., et al., 2009, 2009). On the GC-MS chromatogram, methidathion could not be detected with either of the selected ion monitoring channels because of the interference. On the other hand, methidathion could be clearly detected with quantitative accuracy on the GC-MS/MS chromatogram. The improvement in the signal to noise ratio on the chromatogram (i.e. sensitivity) was due to the use of GC-MS/MS, given its high selectivity in monitoring pesticides. The GC-MS/MS also expanded the pesticides detectable at a concentration of 0.01 ppm. We conducted recovery tests of 258 pesticides detectable at this concentration via GC-MS/MS. The pesticides with asterisks were examined only with GC-MS/MS in this section. These pesticides were classified into 6 groups (A~F) as described above. The percentage of pesticides classified in group "A" increased from 44.0% with GC-MS to 71.3% using GC-MS/MS. The sensitivity and selectivity of GC-MS/MS would be helpful for the determination of pesticides in foods with interference, such as processed foods classified in the high lipid group. The relevant details are as follows.

Group A (184 pesticides with the acceptable results in all the 5 processed foods):

Acetochlor, Alachlor, Ametryn, Anilofos, Azinphos-methyl, Azoxystrobin, Benalaxyl, Benfluralin, Benfuresate, Benoxacor, β-BHC, δ-BHC, γ-BHC, Bifenox, Bifenthrin, Bitertanol, Bromacil, Bromobutide, Bromophos, Bromopropylate, Bupirimate, Buprofezin, Butafenacil,

Butamifos, Cadusafos, Cafenstrole, Carbaryl, Carbofuran, Carfentrazone-ethyl, Chlorfenapyr, α-Chlorfenvinphos, β-Chlorfenvinphos, Chlorobenzilate, Chlorpropham, Chlorpyrifos, Chlorpyrifos-methyl, Chlorthal-dimethyl, Clomazone, Clomeprop, Cloquintocet-1-methylhexyl, Cyanazine, Cyanophos, Cyflufenamid, Cyfluthrin, Cyhalofop-butyl, Cyhalothrin, Cypermethrin, Cyproconazole, Cyprodinil, p,p'-DDD, p,p'-DDT, Diazinon, Dichlofenthion, Diclobutrazol, Dicloran, Dieldrin, Diethofencarb, Diflufenican, Dimethametryn, Dimethenamid, Dimethylvinphos, Diofenolan, Dioxabenzofos, Diphenamid, Diphenylamine, Dithiopyr, Edifenphos, α-Endosulfan, β-Endosulfan, EPN, Esprocarb, Ethalfluralin, Ethion, Ethofumesate, Ethoprophos, Etobenzanid, Etofenprox, Etoxazole, Etrimfos, Fenarimol, Fenbuconazole, Fenchlorphos, Fenitrothion, Fenothiocarb, Fenoxanil, Fenpropathrin, Fenvalerate, Fipronil, Flamprop-methyl, Fluacrypyrim, Flucythrinate, Fludioxonil, Flumioxazin, Fluquinconazole, Flusilazole, Flutolanil, Fluvalinate, Fosthiazate, Fthalide, Furametpyr, Furathiocarb, Halfenprox, Iprobenfos, Iprovalicarb, Isofenphos, Mefenacet, Mepronil, Metalaxyl, Methidathion, Methiocarb, Methoxychlor, Metolachlor, Metominostrobin-E, Metominostrobin-Z, Metribuzin, Monocrotophos, Myclobutanil, Napropamide, Nitrothal-isopropyl, Omethoate, Oxadiazon, Oxadixyl, Oxyfluorfen, Paclobutrazol, Parathion, Parathion-methyl, Penconazole, Pencycuron, Pendimethalin, Permethrin, Phenothrin, Phenthoate, 2-Phenylphenol, Phosalone, Phosphamidon, Piperophos, Pirimicarb, Pirimiphos-ethyl, Pirimiphos-methyl, Pretilachlor, Procymidone, Profenofos, Promecarb, Prometryn, Propachlor, Propanil, Propoxur, Propyzamide, Prothiofos, Pyraclofos, Pyraflufen-ethyl, Pyrazophos, Pyributicarb, Pyridaphenthion, Pyrifenox-E, Pyrimethanil, Pyriminobac-methyl-E, Pyriminobac-methyl-Z, Quinalphos, Quinoxyfen, Silafluofen, Simazine, Simeconazole, Simetryn, Tebuconazole, Tebufenpyrad, Tefluthrin, Terbutryn, Tetrachlorvinphos, Tetraconazole, Thenylchlor, Thifluzamide, Thiobencarb, Tolclofos-methyl, Triadimefon, Triadimenol, Tri-allate, Triazophos, Tribufos, Trifloxystrobin, Triflumizole, Trifluralin, Uniconazole P, XMC, Xylylcarb

Group B (39 pesticides with the acceptable results in the 4 processed foods except for the processed food exhibited in parentheses):

Bendiocarb (C), α-BHC (C), Butachlor (D), Clodinafop-propargyl (C), p,p'-DDE (C), o,p'-DDT (C), Diclofop-methyl (D), Difenoconazole (C), Dimethoate (D), Fenobucarb (C), Fensulfothion (C), Flumiclorac-pentyl (C), Furilazole (Ck), Heptachlor (C), Heptachlor-epoxide (D), Hexaconazole (Ck), Indoxacarb-MP (C), Iprodione (P), Isazofos (C), Isoprocarb (C), Isoprothiolane (D), Isoxathion (D), Kresoxim-methyl (C), Lactofen (D), Lenacil (P), Malathion (D), Metolcarb (P), Mevinphos (P), Norflurazon (P), Picolinafen (C), Prochloraz (D), Propiconazole (F), Pyridaben (Ck), Pyrimidifen (C), Quintozene (C), Terbacil (C), Terbufos (P), Vinclozolin (C)

Group C (18 pesticides with the acceptable results in the 3 processed foods except for the processed foods exhibited in parentheses):

Atrazine (D, C), Bioallethrin (C, Ck), Cyanofenphos (D, F), Deltamethrin (C, Ck), Dimepiperate (C, P), Endrin (C, P), Fenoxycarb (D, Ck), Fenthion (P, Ck), Flutriafol (P, F), Hexazinone (P, F), Methacrifos (C, P), Molinate (C, P), Propargite (D, Ck), Pyrifenox-Z (C, P), Pyriproxyfen (D, F), Tecnazene (C, P), Tetradifon (D, Ck), Tralomethrin (D, Ck)

Group D (7 pesticides with the acceptable results in the 2 processed foods exhibited in square brackets):

Acrinathrin [D, P], Dicofol [D, F], Fenamiphos [D, Ck], Propaphos [D, F], Propham [P, Ck], Sulprofos [D, C], Thiazopyr [C, Ck]

Group E (6 pesticides with the acceptable results in the 1 processed foods exhibited in square brackets):

Acephate [Ck], Allidochlor [F], Methamidophos [F], Phorate [D], Phosmet [F], Thiabendazole [D]

Group F (4 pesticides without the acceptable results in all the 5 processed foods):
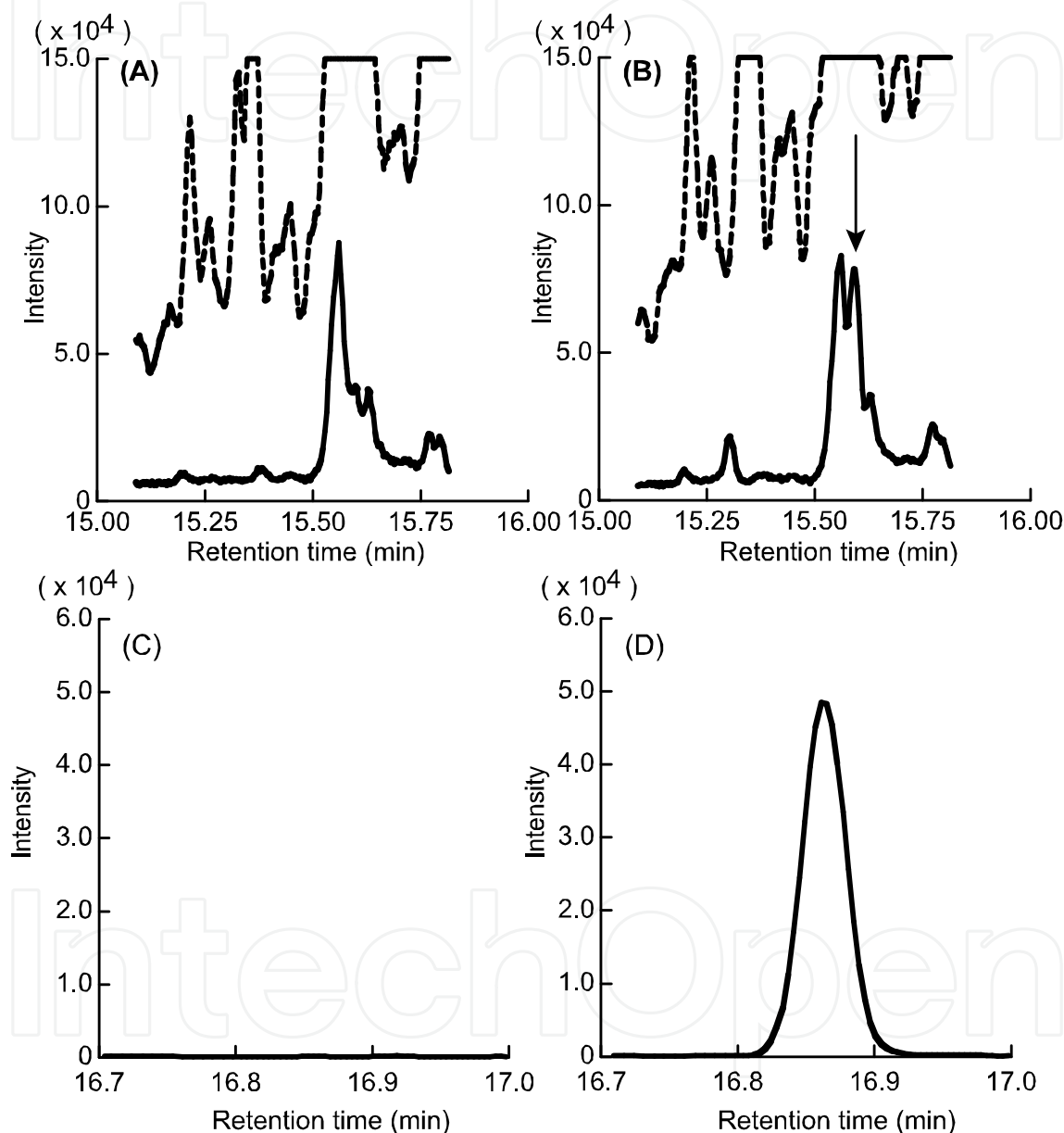Aldrin, Dichlorvos, Diphenyl, Fenpropimorph

Fig. 1. SIM [(A) and (B)] and SRM [(C) and (D)] chromatograms of methidathion (0.02 ppm) in the test solution obtained from the recovery test of fried fish. (A) and (C), non-fortified fried fish; (B) and (D), fortified fried fish. The broken and solid lines in (A) and (B) are monitoring at m/z's of 145 and 85, respectively. The solid lines in (C) and (D) are monitoring the transition from 145 to 85. An arrow in (B) indicates the retention time of methidathion. The retention time of methidathion in SIM and SRM were 15.60 and 16.87, respectively. (The time programs of the GC oven temperature were not the same in these experiments)

4.2.2.3 Analysis of 99 pesticides via LC-MS/MS (Chinese dumplings)

The 99 pesticides detectable via LC-MS/MS were fortified to the Chinese dumplings at the concentrations of 0.02 and 0.10 ppm, respectively. We conducted 5 trials for each test. The pesticides were categorized into 4 groups on the basis of the results.

Group A (72 pesticides exhibiting the acceptable results at the both concentrations):
Acetochlor, Allethrin, Atrazine, Azoxystrobin, Benfuresate, Bensulide, Bitertanol, Bromobutide, Bupirimate, Buprofezin, Cafenstrole, Carfentrazone-ethyl, Carbaryl, Carbofuran, Chlorpropham, Cyanazine, Cyhalofop-butyl, Daimuron, Diethofencarb, Difenoconazole, Diflubenzuron, Diflufenican, Dimepiperate, Dimethametryn, Dimethoate, Dimethomorph, Diphenamid, Ethofumesate, Etobenzanid, Fenarimol, Fenbuconazole, Fenoxycarb, Fenoxaprop-ethyl, Flusilazole, Furathiocarb, Hexaconazole, Hexaflumuron, Imibenconazole, Inabenfide, Indanofan, Iprovalicarb, Isoprocarb, Isoprothiolane, Isoxathion, Mefenacet, Mepanipyrim, Metalaxyl, Methabenzthiazuron, Methomyl, Metolcarb, Monocrotophos, Napropamide, Omethoate, Paclobutrazol, Penconazole, Pencycuron, Pirimicarb, Pretilachlor, Prochloraz, Propoxur, Pyriproxyfen, Pyroquilon, Quizalofop-ethyl, Tebuconazole, Tebufenozide, Teflubenzuron, Thenylchlor, Thiacloprid, Thiobencarb, Tri-allate, Triadimefon, Triadimenol

Group B (15 pesticides exhibiting the acceptable results at only 0.10 ppm):
Acetamiprid, Acephate, Alachlor, Clomeprop, Cyflufenamid, Fenobucarb, Flufenoxuron, Imazalil, Lufenuron, Pentoxazone, Phoxim, Propyzamide, Quinoclamine, Tebufenpyrad, Triflumizole

Group C (4 pesticides exhibiting the semi-acceptable recovery results, 50~69% or 120~150%, at least at the concentrations 0.10 ppm with RSD ≤ 20%):
Cumyluron, Esprocarb, Methamidophos, Oxamyl

Group D (8 pesticides could not be categorized as A~C):
Bendiocarb, Ethiofencarb, Fenpropimorph, Molinate, Phenmedipham, Propamocarb, Propiconazole, Trichlamide

4.2.3 Case of a pesticide detected with our method

The method should be useful for analyzing pesticide residues in foods with complaints, such as odors derived from uncertain chemicals. As an example, we present a case in which we successfully detected the pesticide, phenothrin, from a suspected consumers' food (omelets in catering lunch boxes) at a concentration of 0.06 ppm in a half-day period. In this case, the pesticide, which was used to sanitize the catering kitchen, migrated into the refrigerator due to a faulty door and contaminated the omelets inside. To analyze the pesticide residues in foods in cases such as this, rapidity is one of the most pivotal aspects. Thus, governments and food industries should develop rapid methods to analyze pesticide residues in foods as a part of crisis management.

4.3 Method for processed foods in non- and low lipid groups (under study)

We are currently studying methods to determine the presence and quantities of pesticide residues in processed food in the low and non-lipid groups, such as dried fruits, marmalade, pickles (including soured vegetables and fruits), and seasonings. In this method, the process for removing lipids is not necessary. For the sake of efficiency, a method should be developed with minimum modification of the method described in 3.4.1 to determine pesticides in agricultural products. We conducted pilot studies for the development of such

a method and found that dried fruits and marmalades were not miscible with acetonitrile in the extraction step. This problem was successfully overcome by adding an equal weight of water to the sample and allowing it to stand for 30 min prior to the extraction with acetonitrile. We are currently validating the method in our laboratory. Details will be published later.

Homogenized sample 5.0 g in a 50 mL PP disposal tube
    Add 5 mL of water and stand for 30 min
    Add 20 mL of acetonitrile
    Homogenize (1 min)
    Add 4 g of $MgSO_4$ and 1 g of NaCl
    Shake (1 min) and centrifuge
Acetonitrile layer 16 mL (equivalent to 4.0 g sample)
    Load on a GCB/PSA column
    Elute with 30 mL acetonitrile–toluene (3+1)
    Collect loading and eluting fractions in a round bottom flask
    Evaporate and reconstituted in appropriate solvent

GC-MS (/MS) or LC-MS/MS analysis

Scheme IV. Procedure of sample preparation for the determination of pesticides residues in processed foods categorized as the non or low-lipid group.

	Foods			
Category	Agricultural Products		Processed Food	
Group	Vegetables and fruits	Cereals	High-lipid	Non or Low-lipid
Water #	No	Yes	No	Yes
Extraction ##	AcCN	AcCN	EtOAc	AcCN
Cleanup $	GCB/PSA	C18 GCB/PSA	AcCN/Hex GCB/PSA	GCB/PSA
Time (h) $$	3~4	3.5~4.5	5~6	3.5~4.5
Analysis	GC-MS, GC-MS/MS and LC-MS/MS			
Scheme	I	II	III	IV

#: Add water before extraction.
##: Extraction solvents; acetonitrile and ethyl acetate are abbreviated to AcCN and EtOAc, respectively.
$: Using columns and extraction procedure; GCB/PSA, GCB, and PSA double layer column; C18, octadecylsilyl column; AcCN/Hex, acetonitrile-hexane partition.
$$: Time for preparation of 12 samples by a chemist.

Table 1. Summary of the analytical methods of pesticides in foods.

5. Conclusion

"Rapid and easy" multiresidue methods for the determination of pesticide residues in foods have been developed. Table 1 summarizes these methods. The methods are based on a simple extraction with organic solvents, a purification with SPE cleanup, and determinations with GC-MS, GC-MS/MS, and LC-MS/MS. The proposed methods

exhibited good sensitivity and recovery and allowed for rapid analysis. For agricultural products, a single chemist could prepare test solutions from 12 corresponding homogenized samples within 4.5 h. For processed foods, a single chemist could prepare test solutions for 12 corresponding homogenized samples within 6 h. Our method does not require special techniques in sample preparation. The characteristic points of the methods, "rapid and easy," would induce substantial benefits: (a) reduction of time and costs for sample preparation, (b) reduction of time for mastering the operations, and (c) reduction of the errors within the procedures. These reductions would produce more time and money to simultaneously analyze more pesticides with better performance and to test the adaptation of new pesticides to this method. The methods described here have a high potential covering a wide range of pesticides. Thus, they would be applicable to various foods and ideally suited for use in regulatory laboratories.

6. Acknowledgement

7. References

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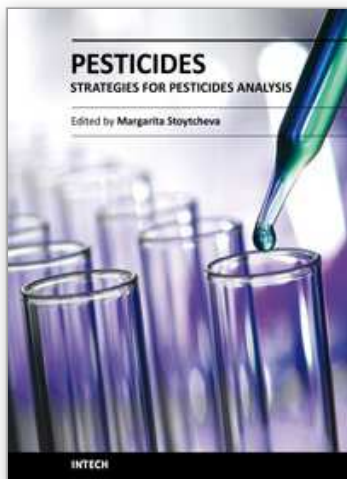
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