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Preparation of mesoporous ZrO_2-coated magnetic microsphere and its application in the multi-residue analysis of pesticides and PCBs in fish by GC–MS/MS

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ABSTRACT

A novel mesoporous ZrO_2 immobilized magnetic Fe_3O_4 microsphere (m-ZrO_2@Fe_3O_4) was successfully synthesized and characterized by transmission electron microscope (TEM), X-ray diffractometer (XRD), nitrogen adsorption measurement (NAM), energy-dispersive X-ray analysis (EDX), vibrating sample magnetometer (VSM). Then the resultant m-ZrO_2@Fe_3O_4 and an n-octadecylphosphonic acid modified magnetic microsphere (Fe_3O_4-OPA) were employed as clean-up co-adsorbents of QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method for the analysis of 42 pesticides and 7 polychlorinated biphenyls (PCBs) in fish samples. Lipid co-extractives such as fatty acids in QuEChERS extracts could be efficiently removed through the Lewis acid–Lewis base interaction between m-ZrO_2@Fe_3O_4 and carboxylic groups, while some other apolar interferents could be adsorbed through hydrophobic interaction by Fe_3O_4-OPA. Meanwhile, the magnetic property of adsorbents endows the clean-up procedure with manipulative convenience. Several parameters affecting the clean-up performance were investigated. Under the optimal conditions, the modified QuEChERS method combined with gas chromatography–tandem mass spectrometry (GC–MS/MS) for the multi-class, multi-residue analysis of pesticides and PCBs in fish samples was validated according to linearity, recovery and precision. Good linearities were obtained for all analytes with R^2 larger than 0.9903. Limits of detection (LODs) were found to be in the range of 0.02–4.40 ng/g. The method recoveries of all analytes spiked at three concentration levels in blank fish samples were from 69.8% to 117.1%, with the intra-day and inter-day relative standard deviations (RSDs) less than 13.4% and 16.5%, respectively.

1. Introduction

As an important source of proteins, minerals, vitamins and unsaturated essential fatty acids, fish have been considered to be an irreplaceable consumption component of a balanced human diet and their consumption has increased over worldwide [1,2]. However, fish can also significantly contribute to dietary exposure to various contaminants [1], such as pesticides and polychlorinated biphenyls (PCBs). Pesticides are widely used in agricultural and farming production all over the world to control a wide range of pests and diseases [3]. However, the unreasonable and excessive use of those substances present a concern in humanment health [4]. Polychlorinated biphenyls (PCBs) and some organochlorine pesticides, which are semivolatile, highly toxic, chemically stable, and persistent, have been identified as persistent organic pollutants (POPs) by the Stockholm Convention [5,6]. Those hazardous chemicals can be accumulated and amplified through the food chain, particularly in animal fat tissue [7]. Therefore, in order to decrease dietary exposure to pesticides and PCBs from fish, it is favorable to develop simple, efficient and sensitive method for the monitoring of their concentration level in fish.

Generally, the contaminants in fish are in low concentration and simultaneously accompanied by a large number of interferences, especially some lipid coextractives, which adversely affect the extraction efficiency and instrument performance [8,9]. Therefore, sample pretreatment techniques are highly required to remove those lipid coextractives prior to chromatography and/or mass spectrometry analysis. Conventional methods for analysis of pesticides and PCBs in fatty matrices such as fish always involve with Soxhlet extraction [10], pressurized liquid extraction (PLE)

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Table 1
The retention time and MS parameters of the target pesticides and PCBs for quantification and confirmation.

Pesticides and PCBs	Retention time (min)	Quantication ion (m/z)	CE1	Confirmation ion (m/z)	CE2
alpha-HCH	15.359	218.9 > 182.90	8	218.90 > 144.90	20
Dimethoate	15.596	125.00 > 79.00	8	125.00 > 47.00	14
beta-HCH	15.927	218.90 > 182.90	8	218.90 > 144.90	20
gamma-HCH	16.055	218.90 > 182.90	8	218.90 > 144.90	20
Quintozene	16.152	294.80 > 236.80	16	294.80 > 264.80	12
Pyrimethanil	16.266	198.10 > 183.10	14	198.10 > 158.10	18
Diazinon	16.271	304.10 > 179.10	10	304.10 > 162.10	8
delta-HCH	16.548	218.90 > 182.90	10	218.90 > 144.90	20
PCB28	17.184	256.00 > 186.00	26	256.00 > 221.00	10
Vinclozolin	17.287	285.00 > 212.00	12	285.00 > 178.00	14
Parathion-methyl	17.316	263.00 > 109.00	14	263.00 > 136.00	8
Fenitrothion	17.855	277.00 > 260.00	6	277.00 > 109.10	14
PCB52	17.868	292.00 > 220.00	25	292.00 > 257.00	20
Malathion	18.013	173.10 > 99.00	14	173.10 > 127.00	6
Chlorpyrifos	18.263	313.90 > 257.90	14	313.90 > 285.90	8
Parathion	18.286	291.10 > 109.00	14	291.10 > 137.00	6
Dicofol	18.328	208.10 > 181.00	10	208.10 > 127.00	14
Triadimefon	18.363	250.00 > 139.00	14	250.00 > 215.00	8
Isocarbophos	18.411	289.10 > 136.00	14	289.10 > 113.00	6
Isofenphos-methyl	18.761	199.00 > 121.00	14	241.10 > 121.10	22
Fipronil	19.049	366.90 > 212.90	30	366.90 > 254.90	22
Phenthoate	19.139	273.90 > 125.00	20	273.90 > 246.00	6
Procymidone	19.275	283.00 > 96.00	10	283.00 > 255.00	12
PCB101	19.582	326.00 > 256.00	30	326.00 > 291.00	20
alpha-Endosulfan	19.736	338.90 > 160.00	18	338.90 > 266.90	8
Profenofos	20.025	336.90 > 266.90	14	336.90 > 308.90	6
p,p′-DDE	20.123	246.00 > 176.00	30	246.00 > 211.00	22
PCB 118	20.787	326.00 > 256.00	25	326.00 > 291.00	15
p,p′-DDD	20.927	235.00 > 165.00	24	235.00 > 199.00	14
o,p′-DDT	21.004	235.00 > 165.00	24	235.00 > 199.00	14
PCB 153	21.198	360.00 > 290.00	25	360.00 > 325.00	15
Triazophos	21.206	257.00 > 162.00	8	257.00 > 134.00	22
p,p′-DDT	21.631	235.00 > 165.00	25	235.00 > 199.00	15
PCB 138	21.731	360.00 > 290.00	25	360.00 > 325.00	15
Iprodione	22.319	314.00 > 245.00	12	314.00 > 56.00	22
Bifenthrin	22.488	181.10 > 166.10	12	181.10 > 153.10	8
Phosmet	22.549	160.00 > 133.00	14	160.00 > 77.00	24
Fenpropathrin	22.64	265.10 > 210.10	12	265.10 > 172.10	14
PCB180	22.961	394.00 > 324.00	25	394.00 > 359.00	15
Phosalone	23.234	182.00 > 111.00	14	182.00 > 138.00	8
Cyhalothrin-1	23.281	197.00 > 161.00	8	197.00 > 141.00	12
Cyhalothrin-2	23.477	197.00 > 161.00	8	197.00 > 141.00	12
Pyridaben	24.434	147.10 > 117.10	22	147.10 > 132.10	14
Cyfluthrin-1	24.830	226.10 > 206.10	14	226.10 > 199.10	6
Cyfluthrin-2	24.911	226.10 > 206.10	14	226.10 > 199.10	6
Cyfluthrin-3,4	25.033	226.10 > 206.10	14	226.10 > 199.10	6
Cypermethrin-1	25.158	181.10 > 152.10	22	181.10 > 127.10	22
Cypermethrin-2	25.249	181.10 > 152.10	22	181.10 > 127.10	22
Cypermethrin-3	25.364	181.10 > 152.10	22	181.10 > 127.10	22
Flucythrinate-1	25.362	199.10 > 157.10	10	199.10 > 107.10	22
Cypermethrin-4	25.564	181.10 > 152.10	22	181.10 > 127.10	22
Flucythrinate-2	25.563	199.10 > 157.10	10	199.10 > 107.10	22
Fenvalerate-1	26.223	419.10 > 225.10	6	419.10 > 167.10	12
Fluvalinate-1	26.405	250.10 > 55.00	20	250.10 > 200.00	20
Fluvalinate-2	26.468	250.10 > 55.00	20	250.10 > 200.00	20
Fenvalerate-2	26.472	419.10 > 225.10	6	419.10 > 167.10	12
Difenoconazole-1	26.806	323.00 > 265.00	14	323.00 > 202.00	28
Deltamethrin-1	26.919	252.90 > 93.00	20	252.90 > 171.90	8
Difenoconazole-2	26.900	323.00 > 265.00	14	323.00 > 202.00	28
Deltamethrin-2	27.216	252.90 > 93.00	20	252.90 > 171.90	8

[11,12], microwave assisted extraction (MAE) [13,14], followed by elimination of co-extracts using gel permeation chromatography (GPC) or solid-phase extraction (SPE) with different sorbents. Nevertheless, those methods usually need tedious extraction steps and use a great amount of organic solvent, which makes the whole analysis process time-consuming, labor-intensive and environmentally-unfriendly. Therefore, development of new sample pretreatment methods for determination of pesticides and PCBs in fish would be necessary.

The QuEChERS (quick, easy, cheap, effective, rugged and safe) method, which was originally developed by Anastassiades et al. for pesticide residue analysis in fruit and vegetables [15], has recently been applied to the analysis of various environmental contaminants in fish and shrimp [1,5,7,16–18], and other food [19,20]. In conventional QuEChERS methods, adsorbents are separated from the acetonitrile extract by centrifugation, which takes extra time and is not conducive to the high-throughput detection of a large number of samples [21]. Magnetic solid phase extraction (MSPE) is a novel sample preparation technique, in which the magnetic materials are first dispersed in a sample solution to adsorb target analytes or matrix components, and then the powdery magnetic materials can be easily and rapidly isolated from the solution with the help of an external magnetic field [22]. Recently, our group proposed a modified QuEChERS method by using magnetic graphitized carbon black and primary secondary amine as adsorbents for the analysis of pesticide residues in vegetables [21]. To the best of our knowledge, there were no available literatures using magnetic adsorbents in QuEChERS method for the simultaneous analysis of pesticides and PCBs in fish.

Zirconium dioxide (ZrO_2) has an amphoteric characteristic and its surface has amount of Lewis acid sites, which make it a good adsorbent of Lewis bases such as fatty acids. It has been reported that Lewis acid–Lewis base interaction and electrostatic interaction contributed to the adsorption of fatty acids on the surface of ZrO_2 [23]. Recently, a commercial sorbent composed of C_{18} and silica coated with ZrO_2 was used to remove matrix components for the analysis of hazardous substances in fish [5], bovine muscle [24], avocado and almonds [9,25], and edible oils [26]. Their results indicated that the matrix components such as fatty acids and glycerides could be efficiently removed from sample extracts by this ZrO_2 composite.

Although the appropriate sample preparation methods can remove most of the sample matrix components, the selection of chromatographic separation and detection methods for the qualitative and quantitative analysis of target analytes is of equal importance, especially for those complex food matrices accompanied with a low residue level of target analytes. Gas chromatography (GC) combined with various detectors was frequently used to inspect pesticides and PCBs in fish samples. In order to meet the growing number of test items and increasingly strict limits, the application of gas chromatography–tandem mass spectrometry (GC–MS/MS) for the simultaneous detection of multi-component has become popular due to its higher sensitivity and higher specificity [1,5,27,28]. In the present study, a novel mesoporous ZrO_2 immobilized magnetic Fe_3O_4 microspheres (m-ZrO_2@Fe_3O_4) and an n-octadecylphosphonic acid modified magnetic microspheres (Fe_3O_4-OPA) were prepared and employed as co-adsorbents of QuEChERS method for the analysis of 42 pesticides and 7 PCBs in fish. The mesoporous structure gave m-ZrO_2@Fe_3O_4 with a high surface area and high adsorption capacity, which was very significant to remove abundant coextractives in QuEChERS extract. At the same time, the magnetic property of adsorbents endows the clean-up procedure with manipulative convenience compared to traditional dispersed solid phase extraction (dSPE) in QuEChERS method. Based on this modified QuEChERS method using the magnetic m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA as co-adsorbents, a rapid, simple, efficient and sensitive GC–MS/MS method for the monitoring of 42 pesticides and 7 PCBs in fish samples was developed.

2. Experimental

2.1. Reagents and materials

Individual standard solution (1000 μg/mL) of 42 high purity pesticides and a mixture standard solution (10 μg/mL) of 7 PCBs