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Application of dispersive solid phase extraction for trace analysis of toxic chemicals in foods

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ABSTRACT

The objectives of this study were to develop and validate a method for the identification of toxic organic chemicals, including groups of controlled substances, alkaloids and pesticides that are highly toxic and considered threats to public health. This project aims to ensure our laboratory's readiness to respond to emergencies involving our food supply in cooperation with the Food Emergency Response Network (FERN) program. The food matrices were homogenized in a blender or food processor prior to extraction with an acetonitrile-water mixture using a QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure. The extracts were then analyzed by either gas chromatography–mass spectrometry (GC–MS) or liquid chromatography-electrospray tandem mass spectrometry (LC-ESI/MS/MS). Method validation was performed on a variety of food matrices including lettuce, grapes, milk, chicken, pork and beef. MDLs for the toxic compounds ranged from 0.01 to 0.66 mg/kg (ppm). The findings in this study will provide a valuable resource for the determination of toxic chemicals in food matrices for emergency response situations.

1. Introduction

Contamination of the food supply with toxic chemicals is a significant public health concern. Food terrorism, or the intentional contamination of food sources, as well as unintentional contamination, have the potential to result in widespread illness or death and economic hardship. In 2007, pet food adulterated with melamine caused the deaths of many dogs and cats in the United States [1]. In the following year infant formula was similarly adulterated with melamine [2] which resulted in over 50,000 hospitalizations, six deaths, the imposition of multiple trade restrictions and a loss of approximately $30 million in revenue [3]. To prevent or minimize these types of detrimental effects, public health laboratories must be able to respond to emergencies in a timely and effective manner.

The Food Emergency Response Network (FERN) is a federal program established for the purpose of integrating the nation's food-testing laboratories at the federal, state and local levels into a network that is capable of responding to emergencies involving biological, chemical, or radiological contamination of food [4]. It is coordinated by the US Food and Drug Administration (FDA) and the Food Safety and Inspection Services (FSIS) — US Department of Agriculture (USDA). FERN strives to validate efficient and reliable food testing methods, ensuring an early means of detecting toxic compounds in foods if widespread contamination were to occur. The previously mentioned melamine incident is an example of an emergency to which FERN responded. There was a collaborative effort among federal and state laboratories to develop numerous methods for the analysis of melamine and its analogue residues, including cyanuric acid, ammelide, and ammeline in animal tissue and foods [5–12].

Additional activities performed by FERN laboratories include food surveillance and method development. The USDA and FDA have established methods for the screening of toxic organic chemicals in foods [13–15]. Using these methods, toxic organics in foods can be extracted by glycine buffers at pH 3 and pH 10 followed by acetonitrile prior to analysis by GC–MS [13,14] or LC-MS [15]. However, extracts produced by these methods without a cleanup step were found to contain substances such as chlorophylls, sugars, and lipids which may contaminate the GC or LC system and interfere with mass spectrometric detection [16].

The goal of this study was to develop and validate a method for quick and reliable detection of toxic organic chemicals in a variety of common foods to ensure an efficient response to food emergencies and to maintain effective surveillance capabilities. This method is a complement to CLG-TOX1.01 [13] or CHEM.0006 [14] and T022 [15] methods with an additional step for sample clean up using QuEChERS [17–20]. The food extracts can be analyzed by either GC–MS or LC-MS/

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MS. This method was validated with several food commodities: lettuce, grapes, milk, chicken, pork and beef.

2. Experimental

2.1. Instrumentation

2.1.1. GC/MS

Analyses of organochlorine pesticides (OCPs) were performed using a GC/MS system (Agilent, Wilmington, DE, USA) that consisted of a model 7890A gas chromatograph, model 7693 autosampler and model 5975C mass selective detector. Analytes were resolved on a Restek (Bellefonte, PA, USA) Rxi 5Sil MS column (30 m × 0.25 mm I.D., with 0.25 µm film thickness protected by a 5 m Integra-Guard column. Separation was achieved with the following the oven temperature program: column temperature was initiated at 90 °C with a hold for 1 min; a ramp to 220 °C at the rate of 10 °C/min and hold for 5 min; and a final ramp to 320 °C at 20 °C/min with a hold for 3 min. Data acquisition and processing were controlled using Agilent GC/MSD ChemStation Software, version E.02.02.1431. The 2011 National Institute of Standards and Technology (NIST) mass spectral library was queried for potential matches with acquired mass spectra of unknown compounds. The MSD was operated in both full scan and selected ion monitoring (SIM) modes for detection of OCPs (Table 1).

2.1.2. LC-ESI-MS/MS

LC-MS/MS analyses were performed using a system comprised of an Agilent Technologies (Santa Clara, CA) Series 1200 LC system interfaced with an API-2000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Canada). The LC instrument consisted of a vacuum degasser, thermostatted column compartment, and autosampler. The MS/MS system was equipped with a turbo ESI ion source and was operated in the positive-ion mode using nitrogen as the nebulizing sheath and collision gases. LC-MS/MS data were collected and processed by Analyst software, version 1.6.2 (Applied BioSystems/MDS SCIEX).

Separation of the analytes was performed on a Thermo Dionex Acclaim Polar Advantage II C18, 3 µm, 2.1 × 150 mm (ID × length) column using a gradient mobile phase composed of (A) methanol containing 2 mM ammonium acetate + 0.1% acetic acid and (B) water containing 2 mM ammonium acetate + 0.1% acetic acid at a flow rate of 0.2 mL/min. The gradient profile was programmed as follows: 55% A (0–3 min); 55–90% A (3–7 min); 90% A (7–16 min); 90–55% A (16–16.1 min); and 55% A (16.1–26 min). Sample injection volume was 5 µL. The MS/MS parameters of controlled drugs, alkaloids and organophosphorus pesticides are summarized in Tables 2, 3 and 4.

Table 1
GC–MS SIM parameters for OCPs.

#	Compound name	Ion 1	Ion 2	Ion 3	Ion 4	RT (min)
1	α-HCH	180.8	182.8	216.8	218.8	12.07
2	γ-HCH	180.8	182.8	216.8	218.8	12.58
3	β-HCH	180.8	182.8	216.8	218.8	12.78
4	δ-HCH	180.8	182.8	216.8	218.8	13.33
5	Heptachlor	271.8	273.8	269.9	236.8	14.31
6	Aldrin	262.9	260.9	264.8	292.9	15.13
7	HEB	352.9	350.8	354.9	356.9	16.14
8	γ-Chlordane	372.8	370.7	374.9	376.8	16.86
9	α-Chlordane[a]	373	375			17.30
10	Endosulfan I[a]	195	170			17.30
11	p,p′-DDE	246	248	317.9	315.9	18.08
12	Dieldrin	262.9	260.9	264.9	276.9	18.30
13	Endrin	262.8	260.8	264.8	280.9	19.17
14	Endosulfan II	195	207	236.7	240.9	19.56
15	p,p′-DDD	235	237	165	199	19.77
16	Endosulfan sulfate	271.8	273.8	236.8	228.9	20.72
17	p,p′-DDT	235	237	165	199	20.86
18	Endrin ketone	316.9	314.9	318.9	320.8	21.77
19	Methoxychlor	227.1	228.1	212.1	274	22.03
20	Triphenylphosphate (TPP)	326	325	233	77	18.94

[a] α-Chlordane and Endosulfan I coeluted at 17.3 min.

2.2. Reagents

Glycine (purity > 99%) and sodium hydroxide (purity > 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ammonium acetate (purity > 99%), glacial acetic acid (purity > 99%), magnesium sulfate anhydrous (purity 97.9%) and sodium chloride (purity 99.9%), were purchased from Mallinckrodt Baker (Paris, KY, USA). LC-MS grade acetonitrile, methanol and water were purchased from Thermo Fisher (Waltham, MA, USA). De-ionized (DI) water, purified to 18.0 MΩ-cm resistivity, was prepared in our laboratory with a Nanopure Diamond water system (Barnstead International, Inc., Dubuque, IA, USA). QuEChERS universal dispersive solid phase extraction materials (part number 8224) were purchased from United Science (Center City, MN, USA).

Toxic organic compounds studied include the following: (i) an OCP mixture consisting of 19 compounds (Table 1, Fig. 1) and a carbamates pesticide mixture containing 8 components (Table 4) were purchased from Ultra Scientific (Kingstown, RI, USA); (ii) 18 controlled substances and methamphetamine-d8 (Table 2) were purchased from Cerilliant (Round Rock, TX, USA), (iii) 16 toxic alkaloids (Table 3) were purchased from Sigma-Aldrich (St. Louis, MO, USA), and (iv) a Canadian organophosphorus pesticide mixture consisting of 9 compounds (Table 4) was purchased from Accustandard (New Haven, CT, USA), and thionazin, disulfoton and ethion were purchased from Absolute Standards (Hamden, CT, USA). Triphenylphosphate (TPP) standard was purchased from Restek (Belleforte, PA, USA). The LC-MS/MS profiles for some controlled drugs, alkaloids and pesticides are presented in Fig. 2.

2.2.1. Preparation of 1 M glycine buffer at pH 10

Glycine (13 g) was added to 100 mL DI water. The pH was adjusted to 10.00 (± 0.05) by addition of 20 M aqueous sodium hydroxide and the solution was brought up to volume in a 200-mL volumetric flask with DI water.

2.3. Sample extraction and cleanup

Lettuce, grapes, milk, chicken, pork and beef were purchased from local retail stores. The chicken, pork and beef were purchased as uncooked ground meat. The matrices were homogenized in a blender (Black and Decker, model CBG100) (Towson, MD, USA) or food processor (Cuisinart FP-14DCN Elite Collection 2.0) (Stamford, CT, USA). The lettuce was homogenized with dry ice as described in the original QuEChERS procedure [17]. The matrices were stored in a freezer at −20 °C until needed.

A 1-g sample of homogenized matrix was weighed into a 15-mL centrifuge tube. For the low water content samples such as meat, 1 mL of DI water was added and vortexed. A 1-mL of pH 10 glycine buffer was added to the tube. The solution was then spiked with an appropriate amount of a toxin solution and an internal standard (IS) solution. For extraction, 1 mL of acetonitrile was added to the tube, which was then vortexed for 1 min at maximum speed. Sodium chloride (100 mg) and anhydrous magnesium sulfate (400 mg) were added to the mixture and followed by vortexing for 1 min. The sample was then centrifuged at 4000 rpm (approximately 2600*g*) for 15 min using a Heraeus Megafuge 11 centrifuge (Thermo Fisher Scientific, Waltham, MA, USA).

After centrifugation, a 400 µL aliquot of the supernatant was transferred to a 1.5 mL micro centrifuge tube (Axygen, Union City, CA, USA) containing 75 mg of d-SPE sorbent. The mixture was vortexed at maximum speed for 1 min followed by centrifugation at 12,000 rpm (approximately 14,000*g*) for 10 min using an Eppendorf centrifuge,