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Introduction

The QuEChERS method has been utilized to detect pesticides in final products and to screen incoming fruits, vegetables, feedstocks and nutraceutical ingredients to qualify (overseas) suppliers or ingredients as organic. The main purpose of this study is to make a QuEChERS formula that can clean up unwanted contaminants and excess water to purify the analytes for better recovery. Several different QuEChERS formulations have been tested with seven different pesticides in different matrices. Some typical compounds were chosen, such as carbamate insecticides (carbaryl, oxamyl), chloronicotinyl (imidacloprid), phenylurea (monuron, diuron), postemergence selective herbicides (propazine, atrazine). The best QuEChERS formulation was determined by asking four main questions: does it work with different matrices, have higher and consistent recovery of analytes, have high color-pigment removal, and does it absorb everything but analytes for the clean-up.

Instruments and Materials

Instruments: Centrifuge and vortexer. All LC-MS/MS methods used a Shimadzu LC system coupled to an API 3000 mass spectrometer with a turbo ionspray ESI source operated in positive ion mode

Materials: Orochem specialty QuEChERS tubes for stevia and hemp (Orochem Technologies Inc) were used for all extractions. Seven pesticides (carbaryl, oxamyl, imidacloprid, monuron, diuron, propazine) and NaCl were purchased from Sigma-Aldrich. Mass spec grade methanol, acetonitrile, water and formic acid (FA) were purchased from Pharmco-Aaper.

Experiments

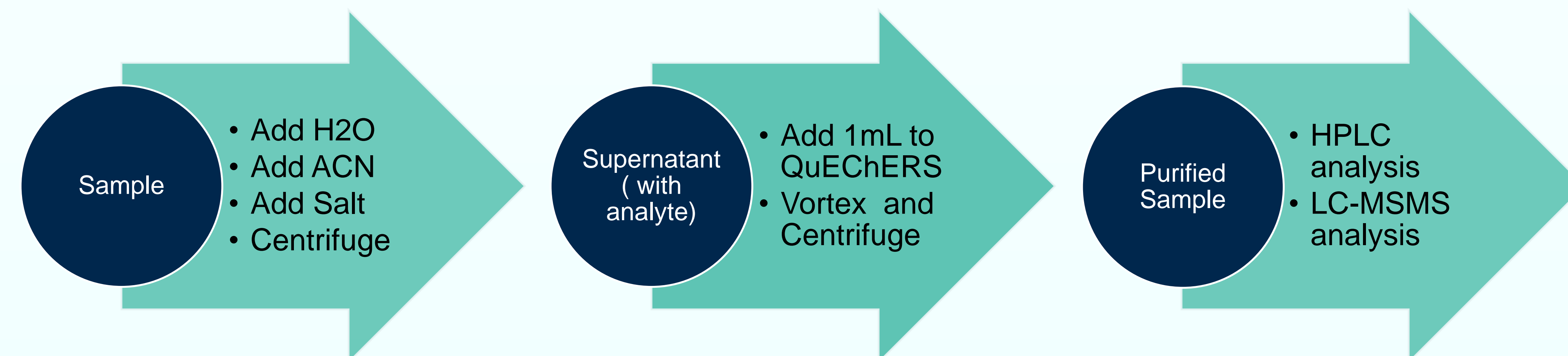


Figure 1. Standard AOAC procedures were used for pigment removal test.

For Pesticides recovery test in stevia and hemp leaves

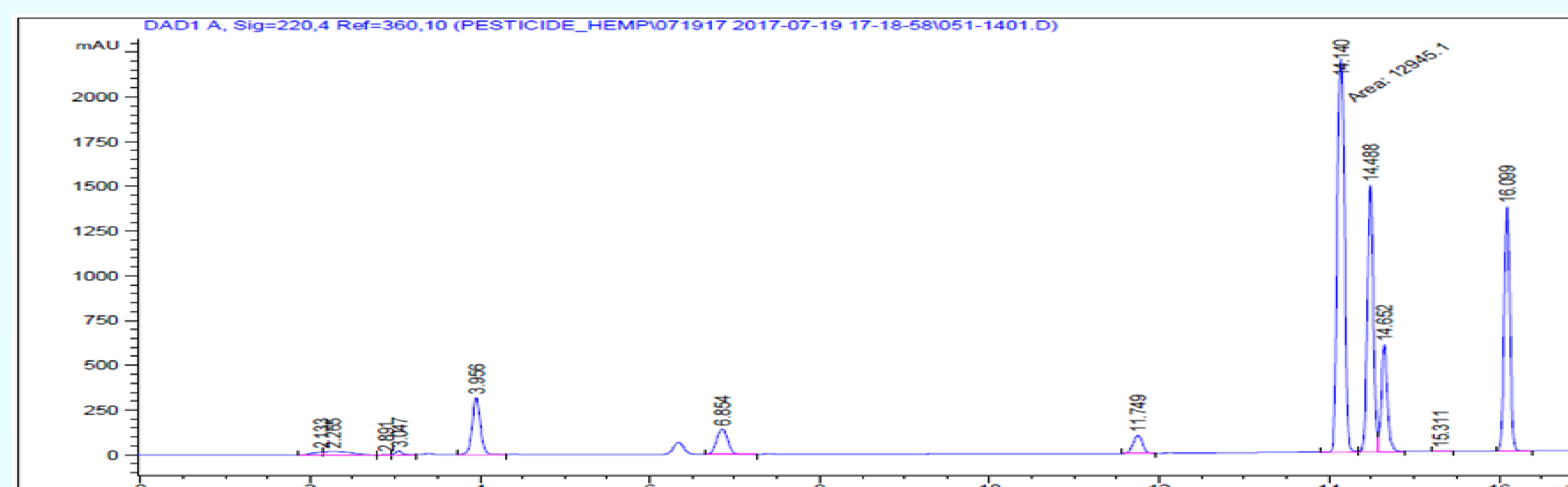
- 5 g of sample fortified with pesticides was mixed with 20 mL of various solvents each in centrifuge tube. Vortex 30 sec, centrifuge 2500 rpm for 5 min
- 1 mL of supernatant to different QuChERS composition tube, vortex 30 sec, centrifuge 2500 rpm for 5 min.

HPLC-MS/MS Conditions:

Column: Orochem Orosil C18 UHPLC column 4.6x250 mm, 3 µm.

Mobile phase: gradient 35% -85% acetonitrile in 16 min

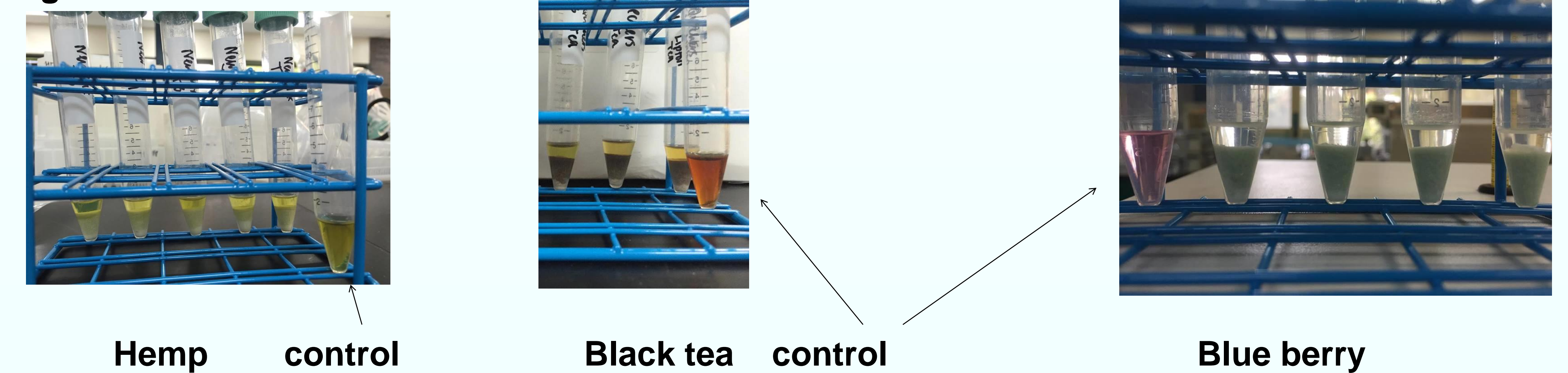
Mass spectrometer: API 3000, ESI+



Retention Time of the analytes. (from left to right): Oxamyl, Imidacloprid, Monuron, Carbaryl, Atrazine, Diuron, and Propazine.

Results

1) Pigment removal:



2) Pesticides recoveries at different formulation and different extraction solvents:

Stevia									
Composition	Extraction solvent	Oxamyl	Imidacloprid	Monuron	Carbaryl	Atrazine	Diuron	Propazine	STDEV%
A	acetonitrile	90.6	114.0	108.7	105.2	92.6	104.6	113.1	9.3
A, NaCl (1 g)	50% ethanol				112.0	115.7	116.9	111.1	2.8
A	50% ethanol				97.6	95.2	95.1	99.6	2.2
B	acetonitrile	71.1	93.7	90.5	95.1	93.4	93.9	85.6	8.5
B	acetonitrile/etoh 1 : 1		184.1	152.7	97.6	102.9	101.5	106.7	35.7
C	acetonitrile		111.3	168.0	101.8	105.4	104.4	110.2	25.3
C	acetonitrile/etoh 1 : 1			67.2	98.3	100.0	100.9	91.4	14.1

Hemp									
Composition	Extraction solvent	Oxamyl	Imidacloprid	Monuron	Carbaryl	Atrazine	Diuron	Propazine	STDEV%
A	acetonitrile	244.7	85.6	76.2	93.4	69.3	80.0	669.9	
A, NaCl (1 g)	Ethanol		132.2	89.9	93.3	107.7	94.6	78.9	18.5
A	ethanol		129.9	54.1	100.4	84.3	75.9	78.0	25.8
B	acetonitrile	90.2	104.0	98.2	92.3	112.2	103.5	96.6	7.6
B	acetonitrile/etoh 1 : 1		102.9	72.1	86.1	97.9	100.0	110.2	13.6
C	acetonitrile	92.6	104.1	105.8	85.0	105.1	108.1	109.0	9.0
C	acetonitrile/etoh 1 : 1		82.9	90.6	73.2	102.5	97.6	46.5	20.4

Conclusions

We developed specialty QuEChERS products based on composition A for stevia samples, and composition B for hemp samples. For test two types of samples, simple acetonitrile extraction of leaves are enough. No salt or water is needed. Compared to standard AOAC method, they provided higher recoveries.

* Worked as summer intern at Orochem Technologies Inc