



Chromatographic methods for the determination of pesticides residues in baby food

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GOAL

To present various experiences on sample preparation under the general interest of our laboratory on improving baby food analysis to solve market and demands.

OUTLINE

- ☐ Importance
- ☐ Antecedents: Fruit and vegetables ingredients
- ☐ Milk-based assays
- ☐ Cereal-based assays
- ☐ Conclusions

BABY FOOD



PRODUCTS

STANDARD (powder and liquid):

Baby formulas (Follow up/on) 0-6/6-12 months
Infant Milk (Toddler) 1-3 years

SPECIAL (powder and liquid)

Premature formulas. AR, HA, AC, LF

VOLUME

8000 ton/year (powder formulas)

20 million liters/year (liquid formulas)

12% (Growing rate -last 5 years trend-)

MARKET

USD 200 millions

SHARE

(vol) Sancor (50%) (Nutricia (Danone) (23%)
Nestlé (22%); Mastellone (4%) Others (1%)

LEGISLATION ON BABY FOOD AND INFANT FORMULAS

- ✓ SPECIFIC IN MOST COUNTRIES FOR NUTRITION QUALITY AND TRADE REQUISITES
- ✓ FOR PESTICIDE RESIDUES GENERALLY RELATED TO RAW INGREDIENTS (EXCEPTIONS -EU-)

ARGENTINA

Codigo Alimentario Argentino (CAA)

- ✓ MRLs pesticides in milk: Chapter XVII “Dietetic or regime food” and Chapter VIII Milk products
http://www.alimentosargentinos.gov.ar/programa_calidad/marco_regulatorio/caa.asp
- ✓ MRLs pesticides food: Res SAGPYA 507-08 Annex I, Argentina. <http://www.sagypa.mecon.gov.ar>,
- ✓ MRLs Codex Alimentarius FAO/WHO Food Standards Codex Alimentarius
<http://www.codexalimentarius.net/pestres/data/index.html>

EUROPEAN UNION

- ✓ Specifications on baby food: Commission Directive 2003/14/EC (OJEU L 41/37-40)
- ✓ EU harmonized MRLs on food and feed of plant and animal origin: EC N° 396/2005
http://ec.europa.eu/sanco_pesticides/public/index.cfm



BF: ANALYTICAL DIFFICULT FOOD MATRIX

- ✓ Mix in a same product of different kind and origin of foods
- ✓ Modifications during processing
- ✓ High amount of possible interferent compounds
- ✓ Enhanced risk in exposed infant population leads to estRICT regulations. Low LODs

BF: ANALYTICAL DIFFICULT FOOD MATRIX

FRUIT AND VEGETABLE-BASED



non-fatty baby food

MILK INFANT FORMULA



with various content of fat

CEREAL-BASED



with various content of fat

MEET/EGG/CHEESE-BASED



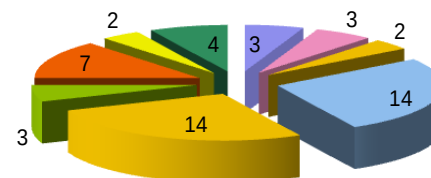
fatty baby food

VEGETAL RAW INGREDIENTS



- QuEChERS method [1]
- 54 compounds analysed
- 115 samples processed
- Results [2]:

strawberry samples (3/19)
wheat sample (1/15)



Benzimidazoles
 Dicarboximide
 Organophosphorus
 Pyrethroids
 Further chemical classes
 Carbamates
 Organochlorines
 Phthalimides
 Triazoles



[1] Lehotay, S.J. et. al., J AOAC Intern 88 (2005) 615-629.

[2] Garcia, S.R. et. al., 2nd LAPRW Santa Fe, Argentina (June 8-11 2009) PA8 p. 204.

VEGETAL RAW INGREDIENTS

<i>Strawberry:</i>	Captan	16 ppb
	Carbedazim ^a	<LOQ ^c
	Endosulfan ^b	4-14 ppb
	Folpet	12 ppb

<i>Wheat:</i>	Fenitrothion	170 ppb
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^a sum of carbedazim and benomyl expressed as carbendazim

^b sum of alfa, beta isomers and ensosulfan sulfate

^c LOQ = 10 µg/kg

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MILK

DETERMINATION OF OCs IN MILK.

EXTRACTION OF LIPIDIC FRACTION

from fluid milk or reconstituted powder milk

CLEAN-UP

SPE alumina

GC-ECD determination

LOQ range: 0.7 – 1.5 ng/mL

20 OC Pesticides and 6 PCBs

MILK

EXTRACTION

1 g of dried whole or skimmed milk sample (or 10 mL of fluid milk) + 15 mL of water

add 15 mL of acetonitrile with 1% acetic acid + 6 g MgSO_4 anh. + 1.5 g NaAc

shake vigorously for 2 min

centrifuge for 5 minutes

CLEAN-UP

1 mL of the upper layer
+ 250 mg of MgSO_4 anh. + 50 mg of PSA + 50 mg of C18

shake 20 seconds

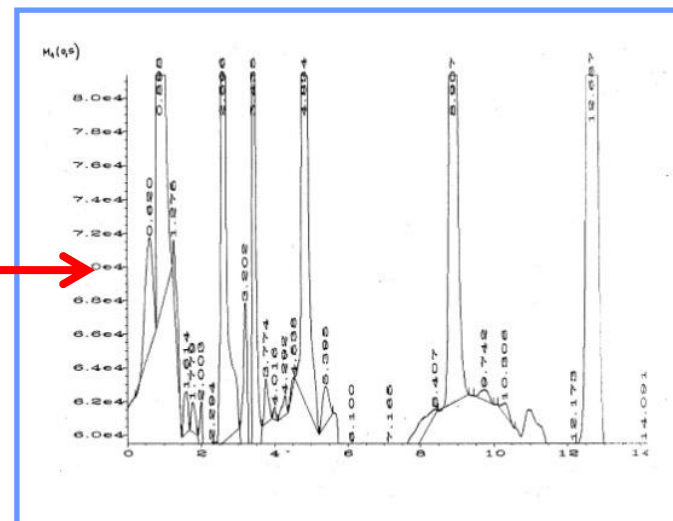
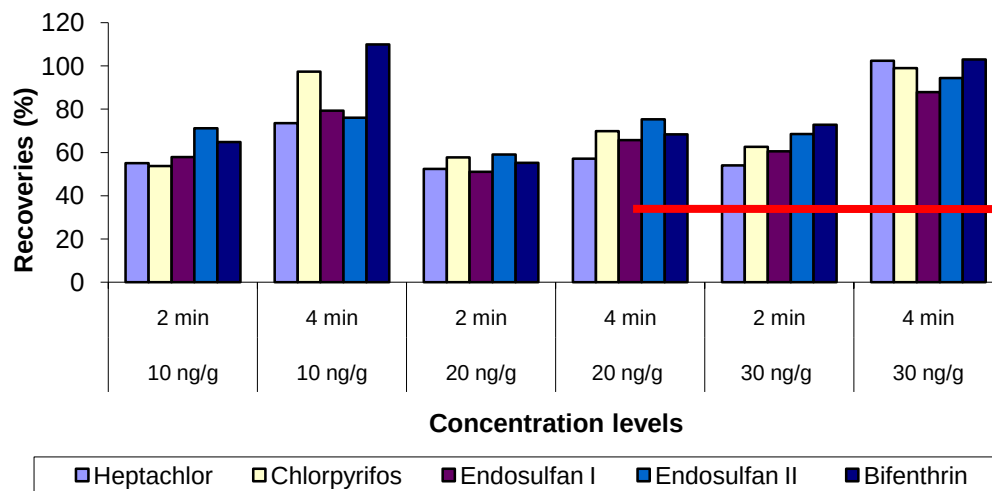
centrifuge for 1 min

QuEChERS method



ASSAY ON SHAKING TIME CONDITIONS

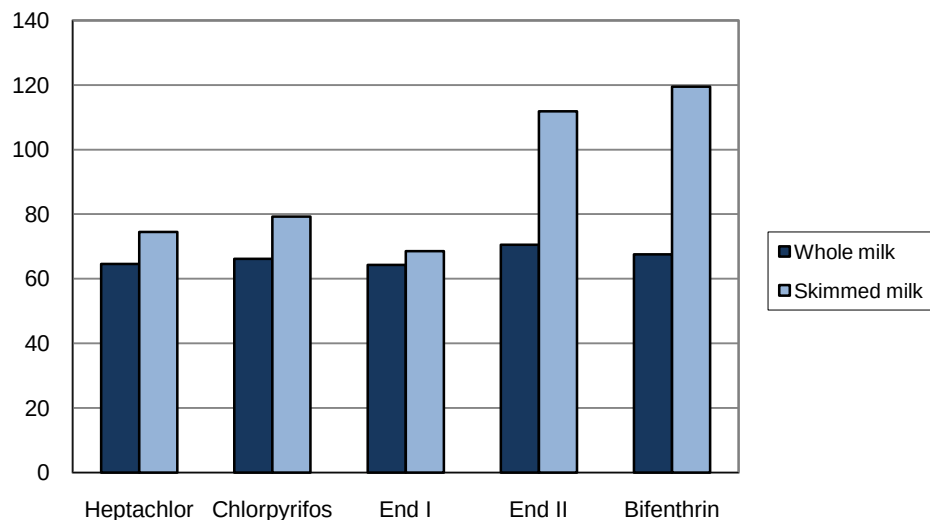
WHOLE DRIED MILK



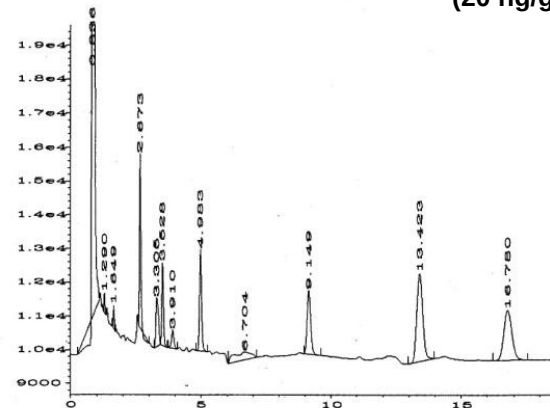
2 MIN SHAKE

WHOLE AND SKIMMED MILK

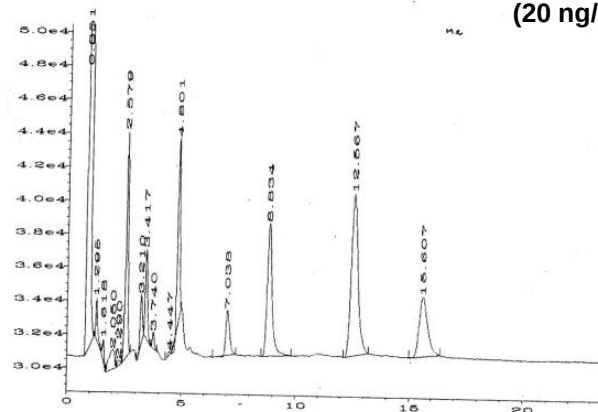
RECOVERIES – 2 MIN SHAKE



Dried whole milk spiked at reference level (20 ng/g).



Dried skimmed milk spiked at reference level (20 ng/g).



MILK

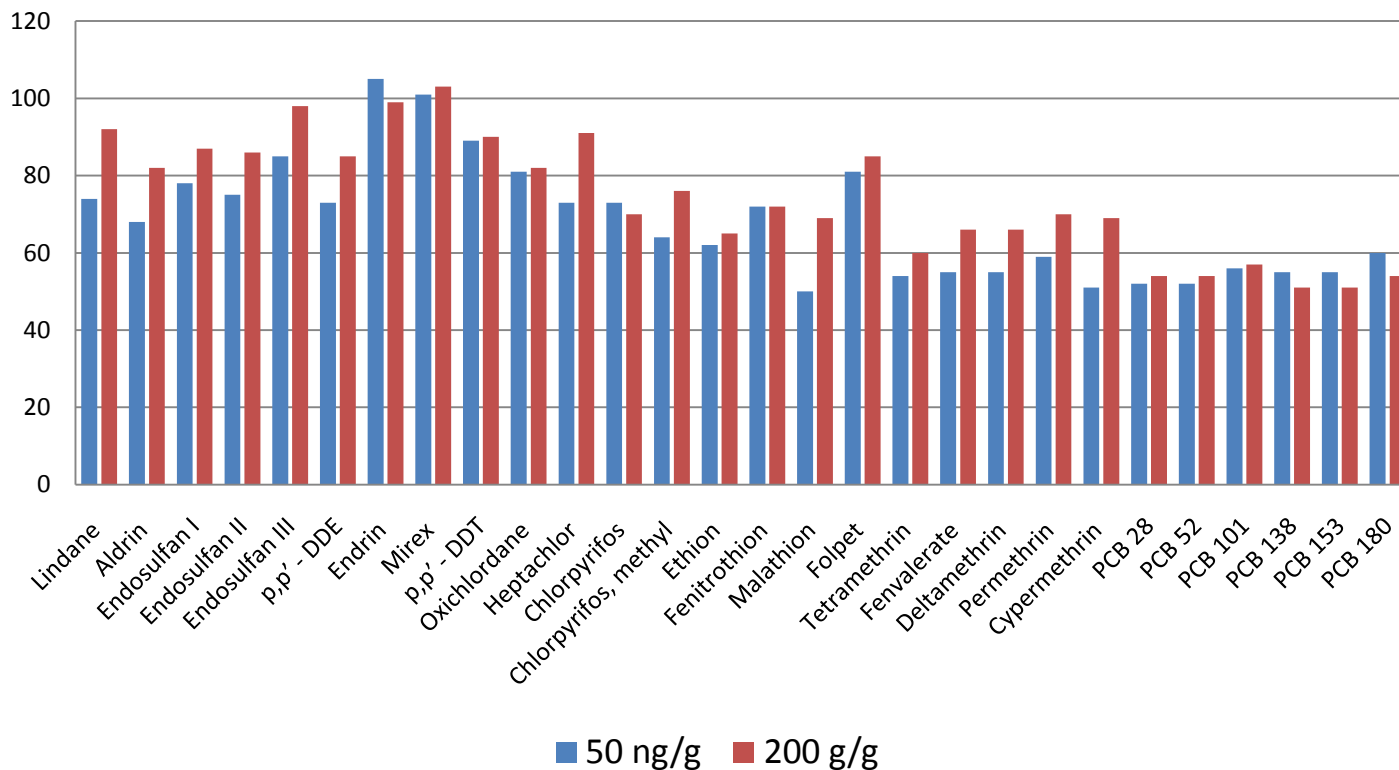
VALIDATION PARAMETERS – QuEChERS, GC-ECD

- 28 pesticides validated
- LODs: 1-15 $\mu\text{g}/\text{kg}$
- RECOVERIES

MILK

VALIDATION PARAMETERS – QuEChERS, GC-ECD

RECOVERIES – Whole dried milk - Spiked sample (n=6)



MILK

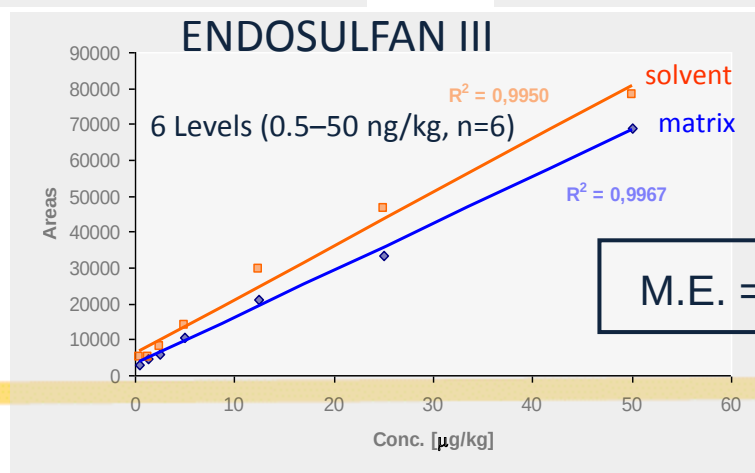
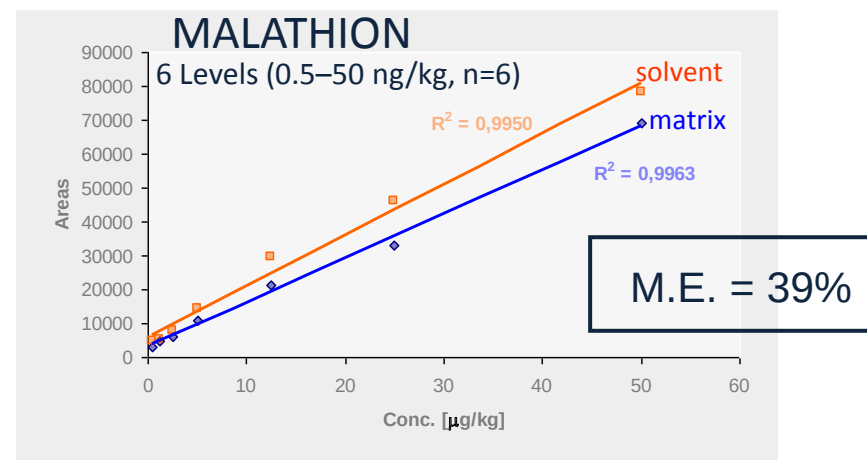
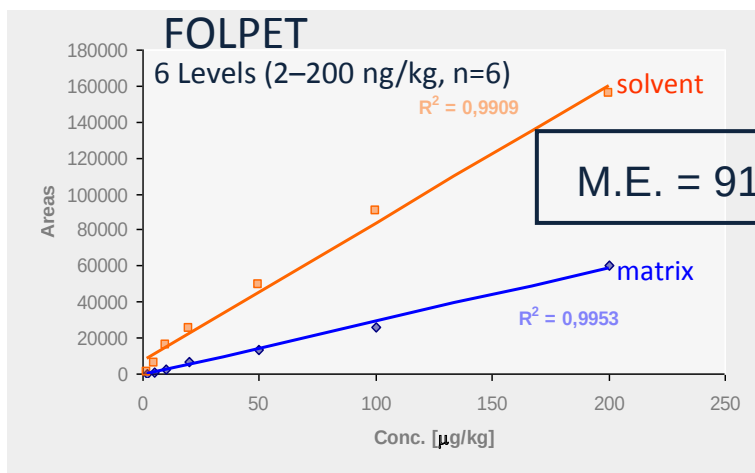
VALIDATION PARAMETERS – QuEChERS, GC-ECD

- 28 pesticides validated
- LODs: 1-15 ng/g
- RECOVERIES
- MATRIX EFFECT: Not Significant for 25 compounds

MILK

VALIDATION PARAMETERS – QuEChERS, GC-ECD

➤ MATRIX EFFECT



MILK

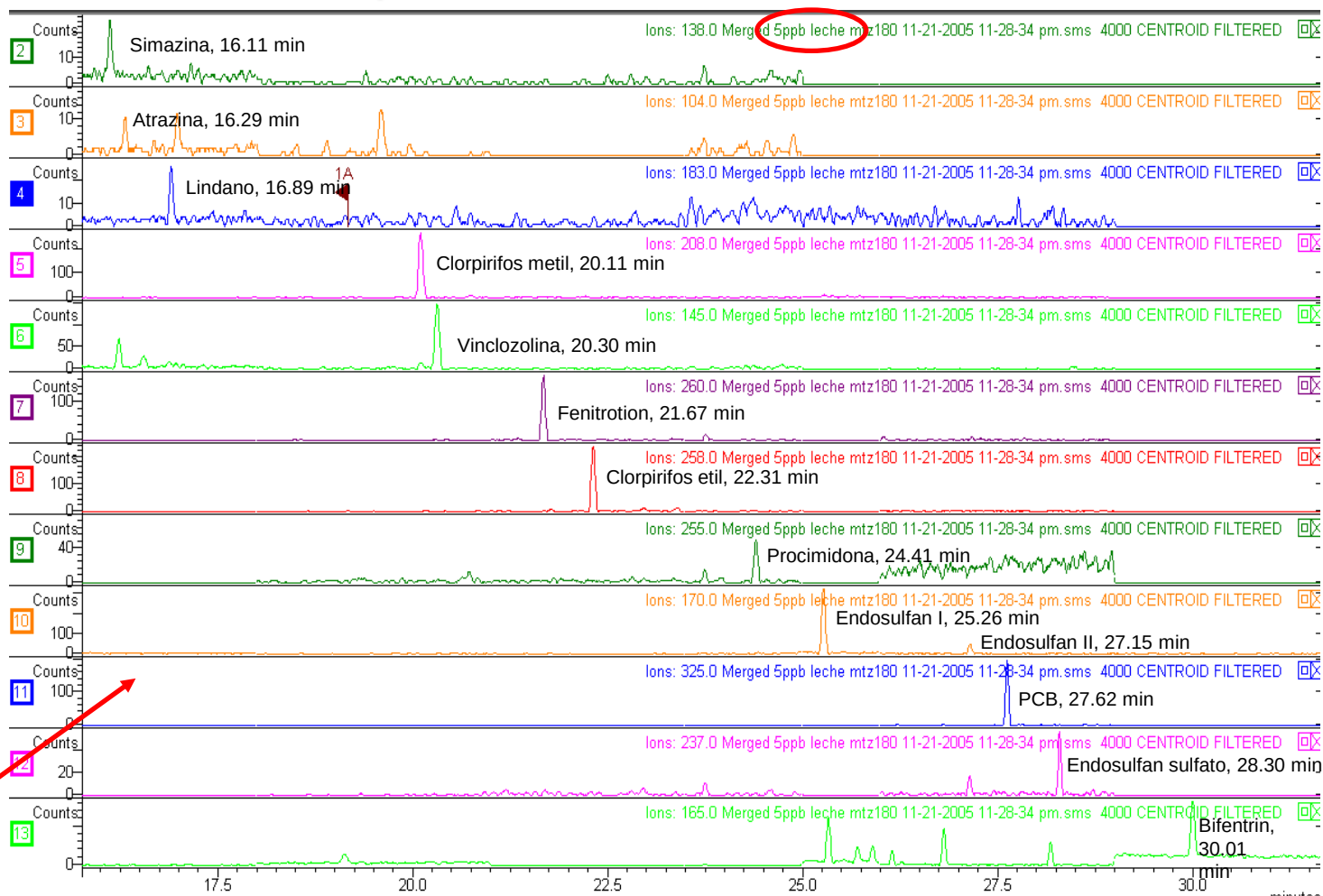
ASE



GC - ITD



DETERMINATION OF 12 PESTICIDES AND A PCB IN POWDER MILK BY PRESSURIZED LIQUID EXTRACTION - GC - MS *



* Mezcuca, M.; Repetti, M.R.; Agüera, A.; Ferrer, C.; García-Reyes, J.F.; Fernández-Alba, A.R.; Anal Bioanal Chem 389 (2007) 1833-1840.

MILK

VALIDATION PARAMETERS – ASE, GC-MS

COMPOUND	Recoveries % 5 µg/kg	Repeteability (n=10) 1 µg/kg	Reproducibility (n=6) 1 µg/kg	Linearity Range: LOQ – 5 µg/kg	LOD (µg/kg)	LOQ (µg/kg)
Simazine	93	9	9	0.9113	0.500	1.600
Atrazine	96	6	13	0.9868	0.500	1.600
Lindane	87	9	7	0.9825	0.800	2.600
Chlorpyrifos Me	50	6	11	0.9997	0.020	0.006
Vinclozolin	48	4	10	0.9945	0.070	0.200
Fenitrothion	56	5	7	0.9979	0.060	0.200
Chlorpyrifos Et	83	9	12	0.9977	0.005	0.010
Procymidone	53	6	7	0.9076	0.200	0.600
Endosulfan I	93	4	12	0.9113	0.030	0.100
Endosulfan II	97	4	17	0.9986	0.120	0.400
PBC 153	29	6	7	0.9901	0.009	0.030
Endosulfan Sulf.	110	3	9	0.9999	0.210	0.700
Bifenthrin	71	5	11	0.9999	0.080	0.260

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CEREAL-BASED BABY FOOD

PROCESSED CEREAL
+
OTHERS COMPONENTS



CEREAL	LIPIDS	STARCH	BRUT FIBER	SOLUBLE FIBER	WATER	PROTEINS
OAT	5.7	42.5	1.56	22.8	13	12.6
WHEAT	2.2	59.2	2.0	10.1	13.2	11.7
MAIZE	3.8	62.6	2.2	8.4	12.5	9.2
RICE	2.4	70.4	0.7	5	13.1	7.4
BARLEY	2.1	52.2	1.5	19.6	11.7	10.6

ROLLED OAT

COMMERCIAL ROLLED OAT

grinded



QuEChERS method



UPLC

GC



ROLLED OAT (GRINDED)

QuEChERS method - Optimization

➤ SAMPLE:

2.5 g and 5 g

5 g of sample

➤ SOAKING PROCEDURE:

different times

4 hours of soaking

➤ Buffered - Unbuffered

Unbufferized QuEChERS method

➤ ULTRASONIC EXTRACTION

➤ CLEAN-UP:

different combinations and sorbents

Clean-up: 150 mg PSA
+ 50 mg C₁₈

ROLLED OAT (GRINDED). Some results

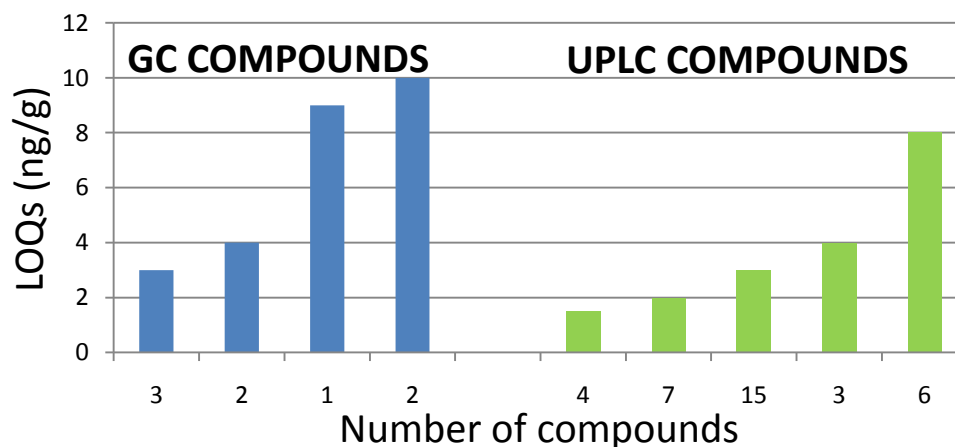
➤ Recoveries

GC compounds: **63-129 %**

UPLC compounds: **58-123 %**

RSD < 20 %

➤ LOQs

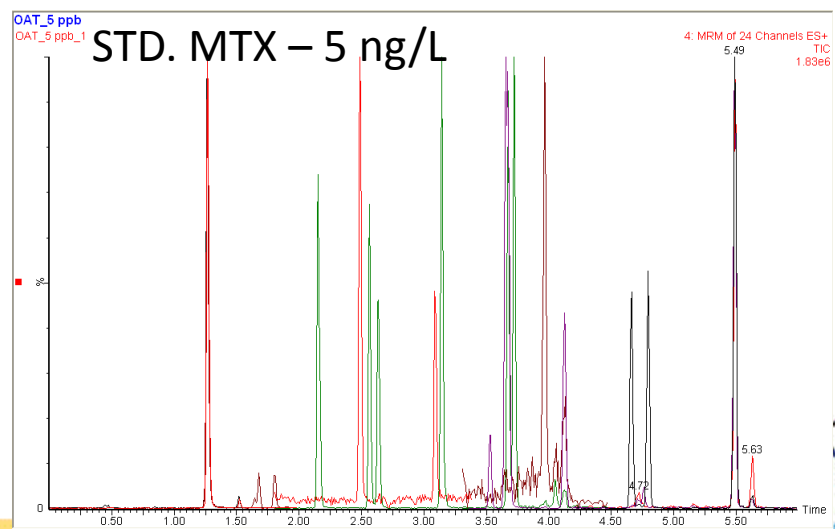
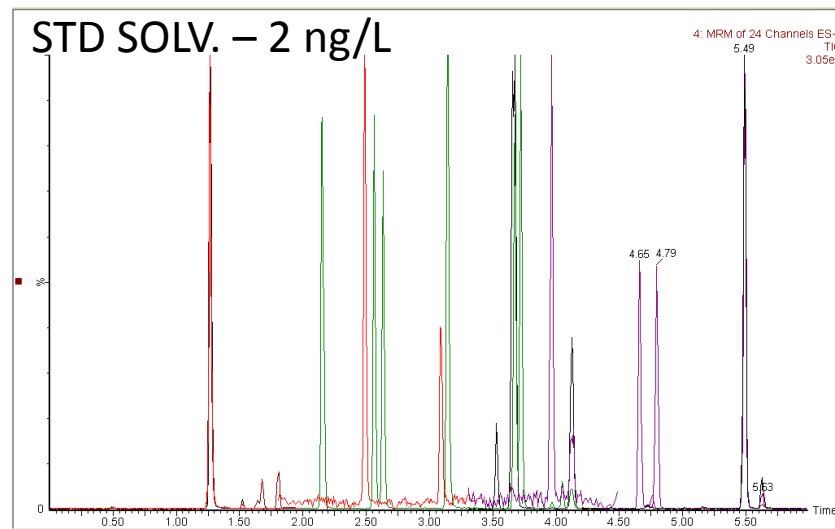


ROLLED OAT (GRINDED).

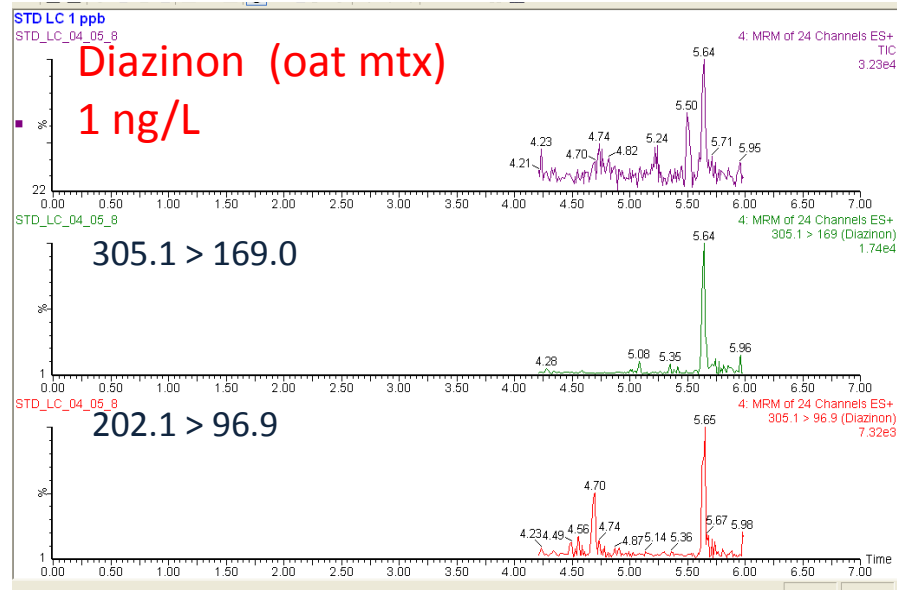
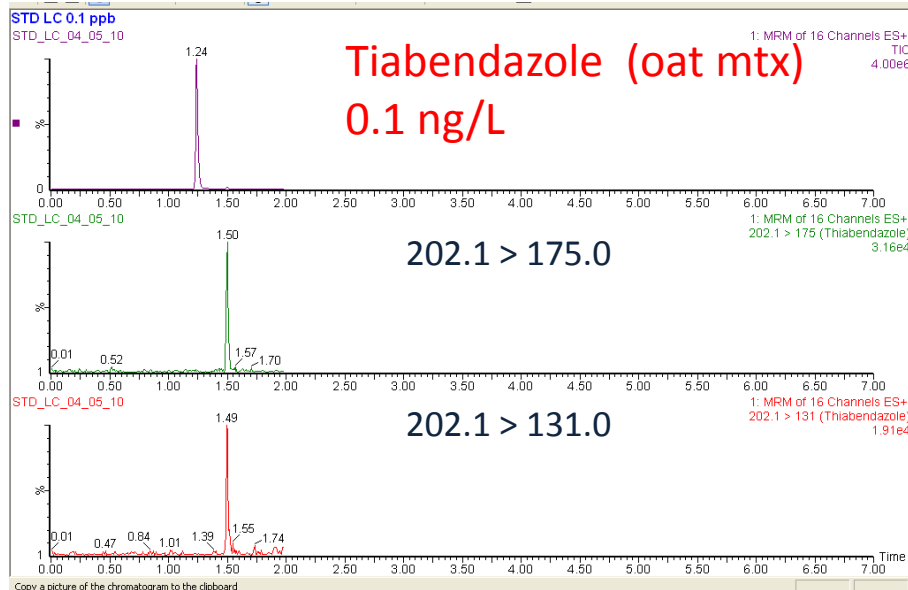
QuEChERS extract



UPLC - TQD



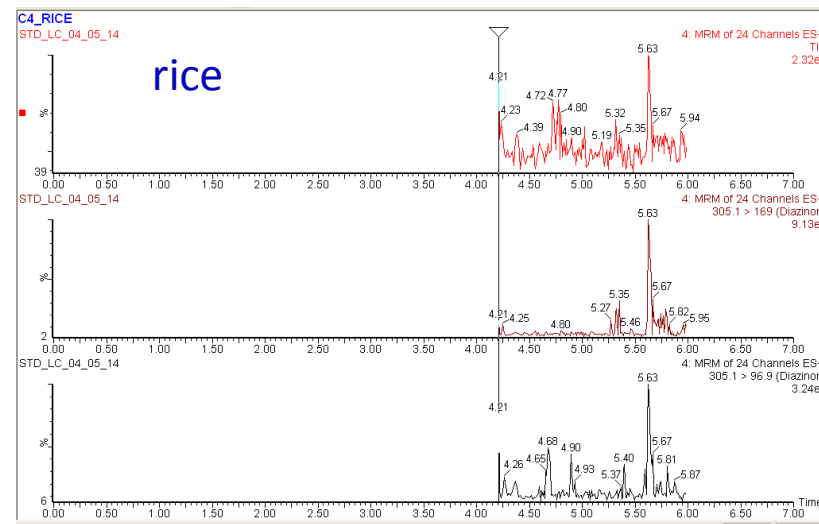
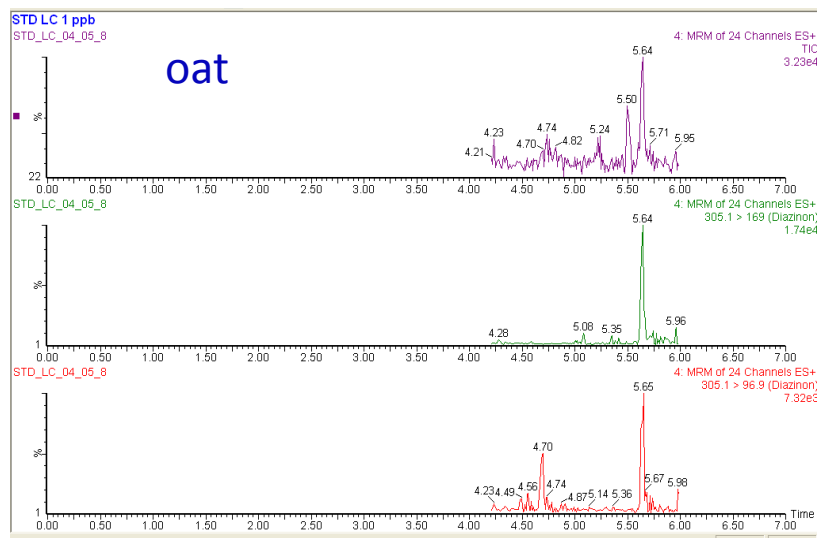
ROLLED OAT (GRINDED) – UPLC-MS/MS



CEREAL-BASED BABY FOOD

- ✓ OAT
- ✓ RICE
- ✓ WHEAT
- ✓ BARLEY

BASED BABY FOOD



DIAZINON RECOVERIES

1 ng/kg

CONCLUSIONS

- QUECHERS VERSION USED WAS SUITABLE FOR SELECTED MATRICES AND COMPOUNDS EVALUATED
- FURTHER EXTENSION TO MIXED INFANT FORMULAS AND ENHANCEMENT OF THE SCOPE OF PESTICIDES ARE IN COURSE

Acknowledgments



- Universidad Nacional del Litoral –UNL- for research support
- AGENCIA Agencia Nacional de Promoción Científica y Tecnológica APCyT - SECYT- Argentina for research and equipment support



MANY

THANKS

FOR YOUR

ATTENTION !