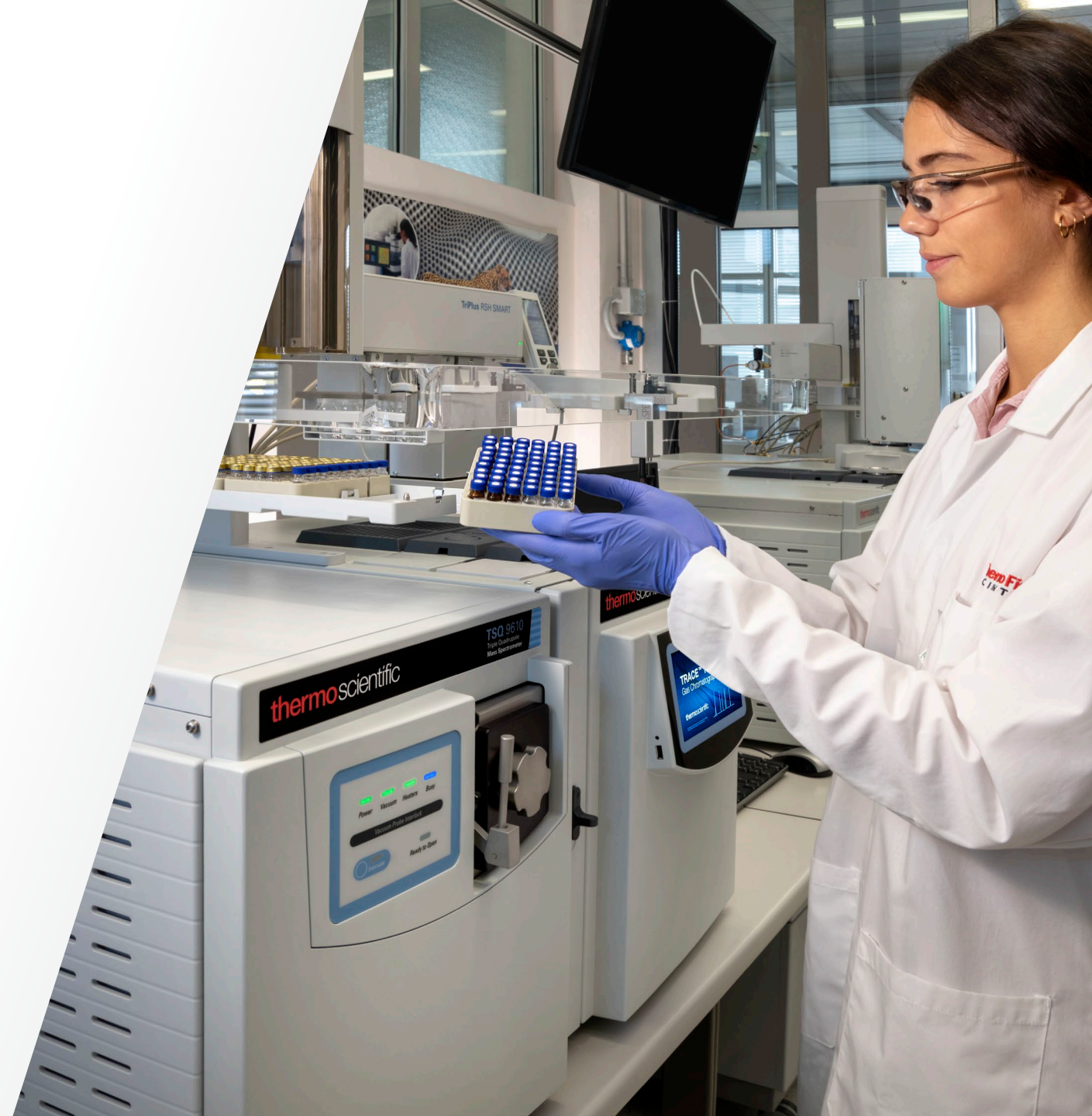


Implementing new GC-MS technology to stay ahead with your pesticides analysis

Łukasz Rajski

Product Application Specialist
Thermo Fisher Scientific

 The world leader in serving science



Overview

1 Introduction the new Thermo Fisher Scientific GCMS line up

2 Ehtylene oxide

3 Pesticides in baby food

4 Pesticides in black tea

5 Summary



New GCMS line up from Thermo Scientific

Thermo Fisher Scientific's GC and GC-MS Portfolio

- Thermo Scientific™ **Trace™ 1600/1610 GC**
 - A flexible, workhorse GC providing day-in, day-out performance
- Thermo Scientific™ **ISQ 7610™ – Single Quadrupole GC-MS**
 - Robust and reliable for routine mass spec analysis
- Thermo Scientific™ **TSQ 9610™ – Triple Quadrupole GC-MS/MS**
 - Sensitivity and selectivity for the most demanding research
- Thermo Scientific™ **Orbitrap™ Exploris™ GC**
 - High resolution, accurate mass for untargeted analysis and identification of unknowns
- **Autosamplers**
 - Thermo Scientific™ **AI/AS 1610 Liquid Autosampler**
Cost effective and simple solution for liquid sample injections
 - Thermo Scientific™ **TriPlus™ RSH SMART** for enhanced sampling techniques capability and automation for sample preparation workflows



TRACE 1610



ISQ 7610



TSQ 9610



Orbitrap Exploris GC

TRACE 1610 GC

Enhanced interaction

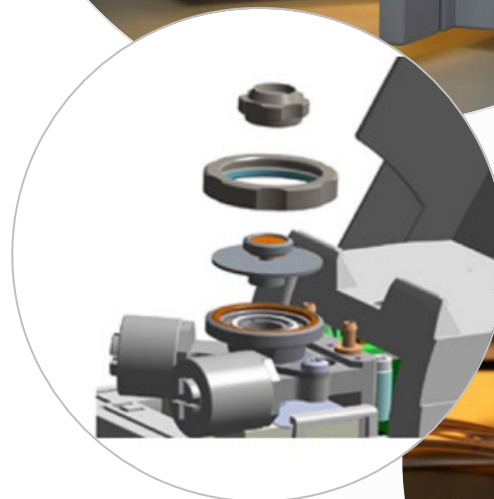
- Easy navigation through intuitive multi-function touchscreen interface
- Multi-language
- Instrument health icon always visible for status notification
- Consumables usage counters
- Automatic leak check
- Diagnostic information
- USB port for video uploads and software updates



TRACE 1610 GC

Simplified operations

- How-to videos instructions
- Tool-free iConnect Column Lock
- Illuminated GC oven
- Tubing-free inlet design
- Integrated backflush in the SSL and PTV injector for simplified pre-, mid-, post-column operation



AI/AS 1610 Liquid Autosampler

Simplified operations

- Illuminated syringe holder and magnifier lens
- Single cable connection with the AI/AS 1610
- Simplified dual-tower Gemini control and method setup
- Easy slide-in to quickly access to the inlet
- Color-coded status indicator on top of the tower
- Removable vial tray
- AI/AS 1610 control through the GC touchscreen



Introducing the new TSQ 9610 GC-MS/MS

The TSQ 9610 GC-MS/MS offer **unstoppable confidence** and allow your customer to **stay ahead** by:



Increasing instrument uptime



Maximizing sample throughput

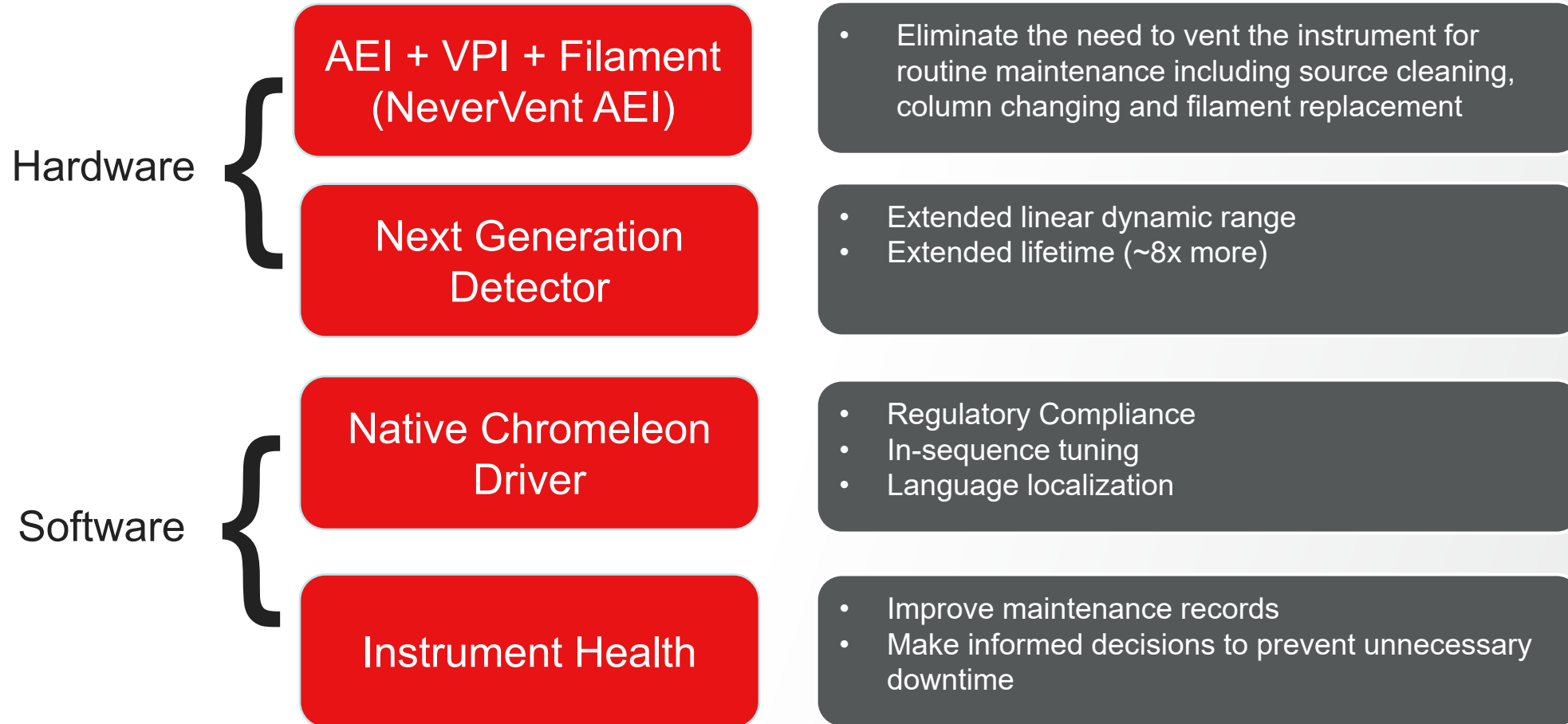


Providing a rapid ROI



TSQ 9610 GC-MS/MS

New Features



Increasing instrument uptime

NeverVent Technology



Thermo Scientific™ NeverVent™ technology allows analytical laboratories to perform maintenance without interrupting their workflow



Available on the TSQ 9610 with the Thermo Scientific™ ExtractaBrite™ and Advanced Electron Ionization (AEI) source

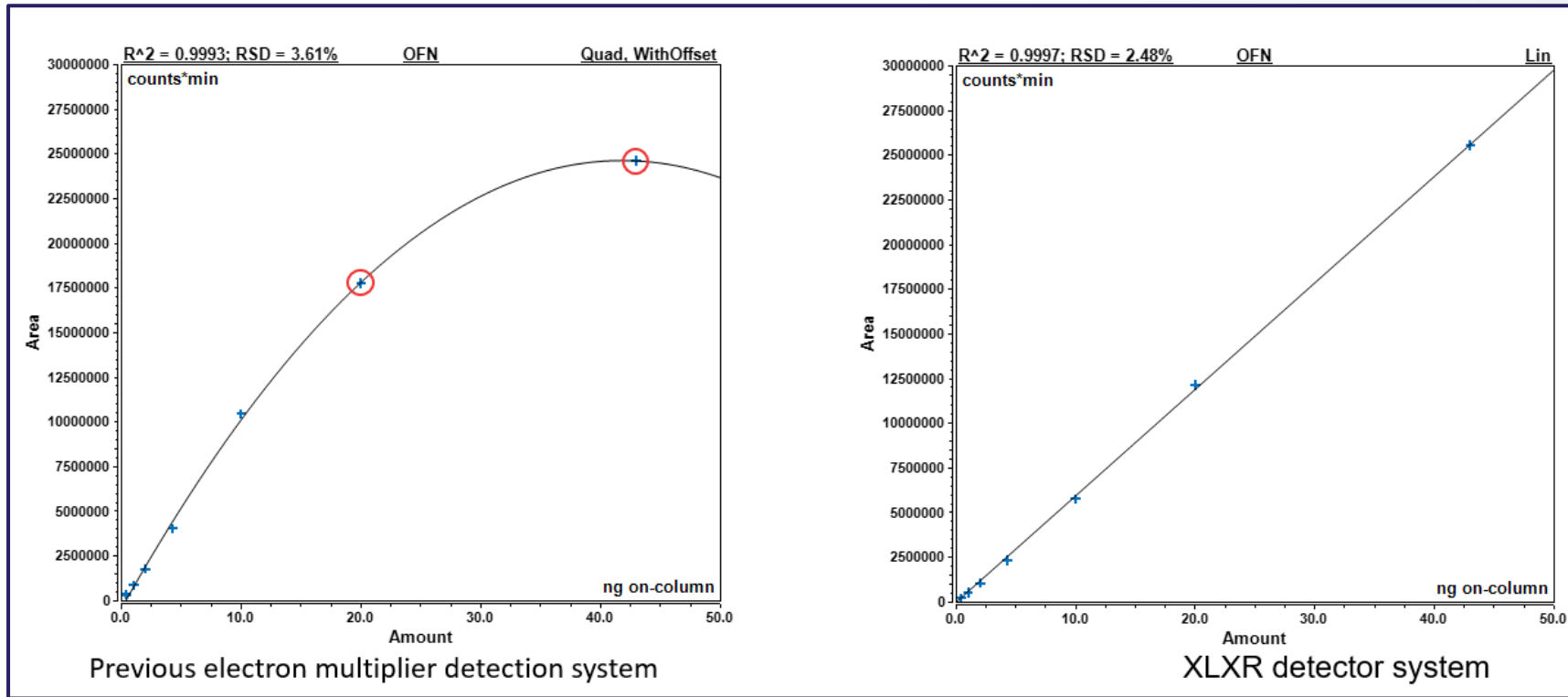
		Maintenance activity		
		Column change (hrs:mins)	Exchange ion source (hrs:mins)	Replace filaments (hrs:mins) (only available on NV-AEI)
Standard GC-MS	Requires vacuum system venting and pump down operations	4:35	4:00	4:00
NeverVent GC-MS	Venting and pump down not required	00:35	00:05	00:05
NeverVent time savings		87%	98%	98%

Maximizing sample throughput

Extended dynamic range detector



The XLXR detector provides extended dynamic range allowing extended calibration ranges



XLXR detector is not saturated at high concentrations

TSQ 9610 GC-MS/MS summary



NeverVent technology

- Available with ExtractaBrite and AEI
- Increases instrument uptime

Off-axis ion guide pre-filter

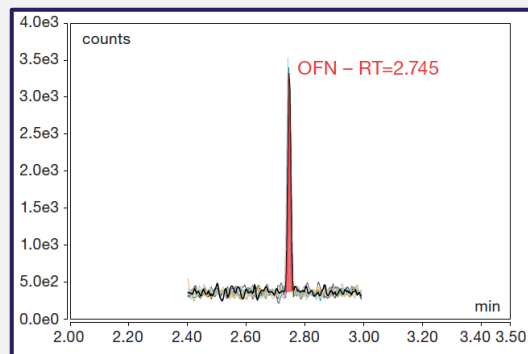
- Eliminates the neutral noise



Evo collision cell

- Allows analysis of more compounds
- Shortens runtimes without loss of signal

Class-leading sensitivity



8 x 1 fg on-column OFN injections with %RSD of 4.1%. IDL is 0.12 fg



XLXR detector as standard

- Extended dynamic range (2X more than previous model)
- Extended lifetime (7X more than previous model)



TRACE 1600 GC series

- Unique modular injector and detector design
- Easy-to-use touchscreen with real-time instrument monitoring and video guides

Software productivity tools

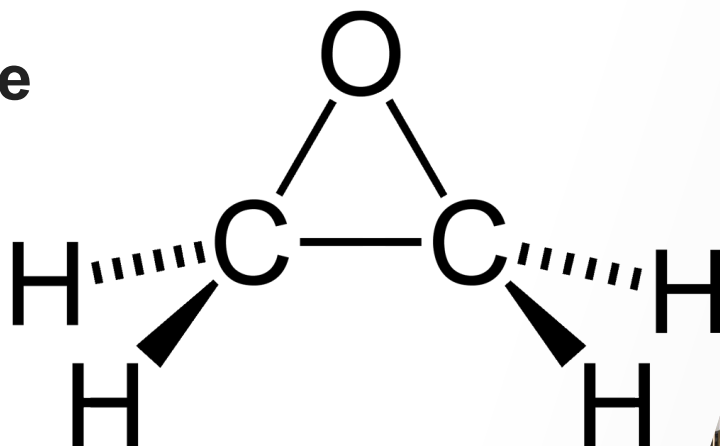
- Compliant-ready software
- Instrument health



Ethylene oxide

Uses of ethylene oxide

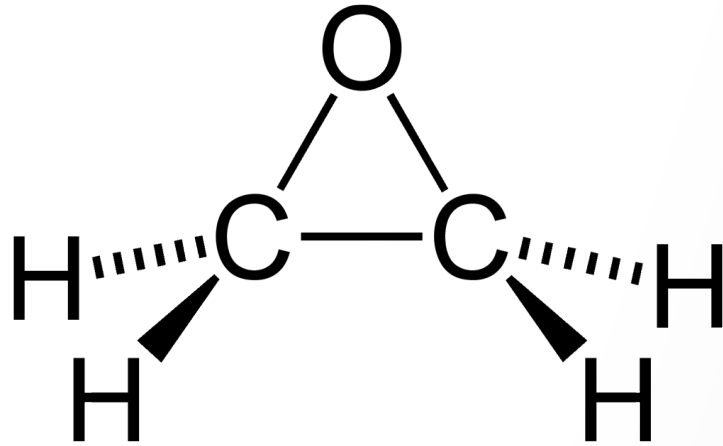
- Synthesis of polymers
- Synthesis of solvents
- Synthesis of adhesives
- Synthesis of detergents
- Synthesis of modified polysaccharides
- Sterilization of medical equipment
- Fumigation of dry food commodities



Ethylene oxide

Typical commodities fumigated with EO

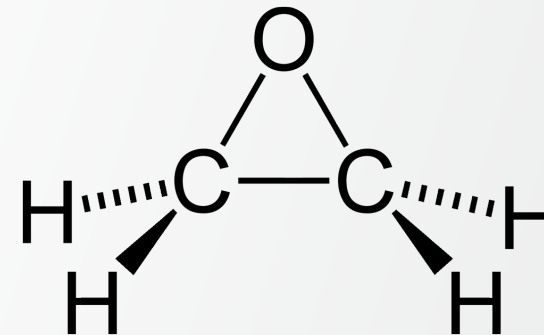
- Herbs
- Spices
- Nuts
- Dates
- Raisins
- Oily seeds
- Milled cereals
- Feed
- Milk powder



Ethylene oxide

107 RASFF notifications from 01.01.2022 to 15.06.2022

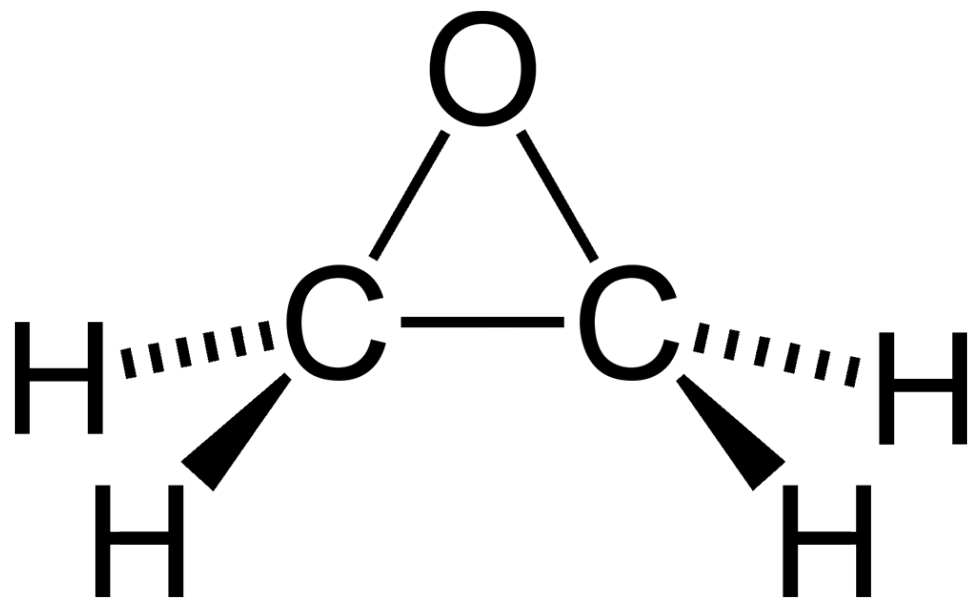
- Food supplements
- Crushed chilli
- Sesame seeds
- Animal feed
- Spice blends
- Ice cream
- Instant noodle
- Xanthan gum
- Locust bean gum
- Wheat protein
- Spice mix



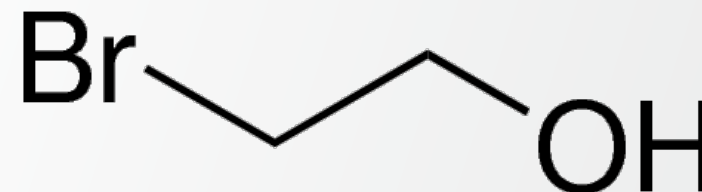
RASFF
Rapid Alert System for Food and Feed

Ethylene oxide

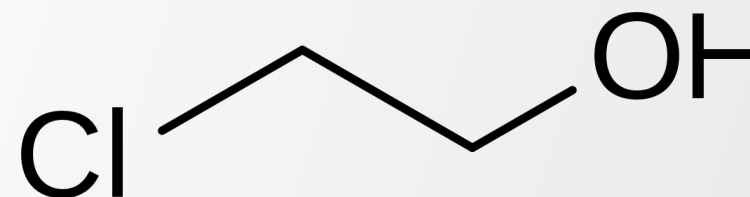
EO and its degradation products



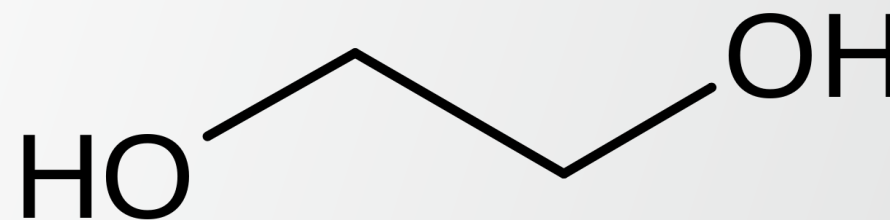
Ethylene oxide



2-bromoethanol



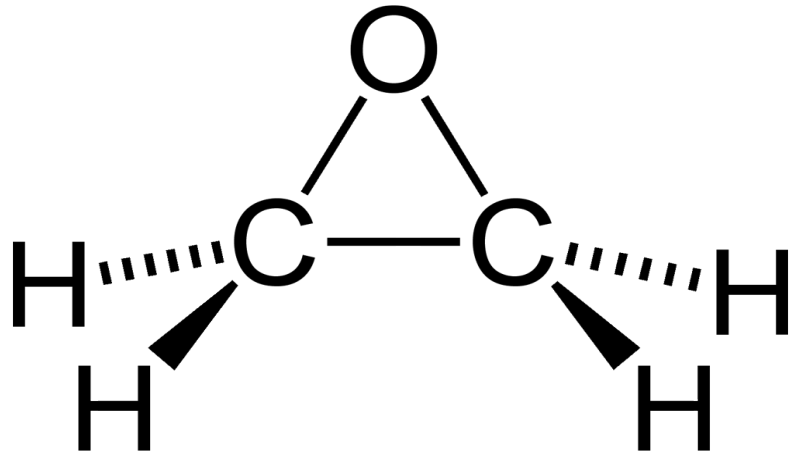
2-chloroethanol



Ethylene glycol

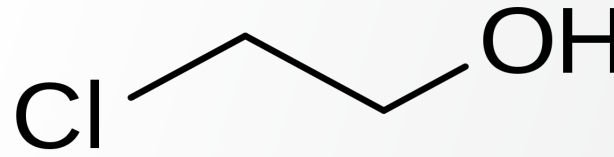
Ethylene oxide

EO and its degradation products



Ethylene oxide

+



2-chloroethanol

Ethylene oxide residue definition in the EU:

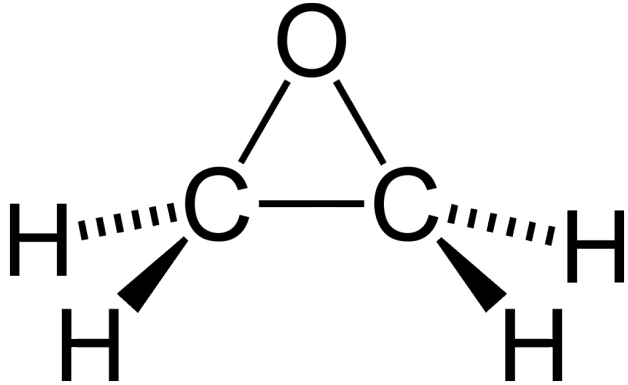
sum of ethylene oxide and 2-chloro-ethanol expressed as ethylene oxide

Reg. (EU) 2015/868



Ethylene oxide

Physicochemical properties

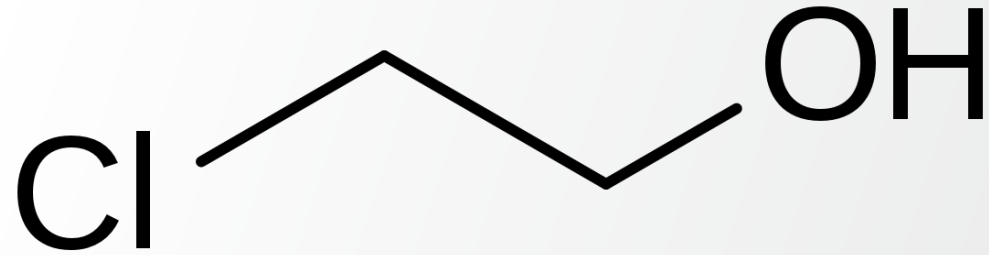


Formula C_2H_4O

Boiling point $10.4\text{ }^\circ\text{C}$

Vapor pressure 146 atm ($20\text{ }^\circ\text{C}$)

Molecular mass 44 Da



Formula C_2H_5ClO

Boiling point $130\text{ }^\circ\text{C}$

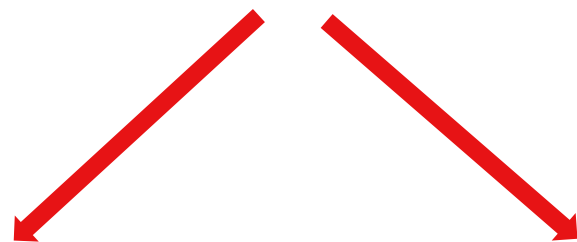
Vapor pressure 0.007 Pa ($20\text{ }^\circ\text{C}$)

Molecular mass 80 Da

Ethylene oxide

Analytical challenges

Low boiling point



Losses
in the
extraction

Poor retention
in the
chromatographic
column

Low molecular mass



Non-selective transitions

Dry matrices



Dirty extracts

Interferences

Robustness
problems

Ethylene oxide



GC MS/MS method

- **TRACE 1610** gas chromatograph,
- **TSQ 9610** GC triple quadrupole
- **TriPlus RSH** autosampler
- **TG-624SiIMS** (30m x 0.25mm x 1.40um)
- **GuardGOLD** Capillary Columns (5m x 0.25mm)



Injector

Use this inlet

Temperature Settings

Enable temperature control
 Temperature: 90 [0..450 °C]

Inlet Parameters

Operating mode: Split

Split flow control
 Split flow: 5.0 [5.0..1250.0 ml/min]
 Split ratio: 5

Purge flow control
 Purge flow: 5.000 [0.500..50.000 ml/min]

Constant septum purge
 Stop purge for: [0.00..999.99 min]
 Surge pressure: [5.00..1000.00 kPa]
 Surge duration: [0.00..999.99 min]

Vacuum compensation
 Enable gas saver mode
 Gas Saver Flow: 50.0 [5.0..500.0 ml/min]
 Gas saver time: 1.50 [0.00..999.99 min]

Enable backflush
 Backflush Start Time: [0.00..999.99 min]

Enable Custom Duration
 Custom Duration: [0.00..999.99 min]

Set default values

PTV Ramp Settings

Pressure [5..1000 kPa]	Rate [0.1..14.5 °C/s]	Temp [0..450 °C]	Time [0..999.99 min]	Flow [5..1250 ml/min]	Back flush
			0.80	50.0	
			12.0	250	10.00

Injection: [] [] [] [] [] []

Evap: [] [] [] [] [] []

Transfer: [] [] [] [] [] []

Cleaning: [] [] [] [] [] []

Enable evaporation phase
 Enable clean phase
 Enable pressure ramps

Transfer delay time: 0.00 [0.00..999.99 min]

Post cycle temperature: Maintain

Display phase program plot

Utilities

Vapour volume calculator
 Column flow calculator
 Retention time alignment tool

Oven program

No	Retention time [min]	Rate [°C/min]	Target value [°C]	Hold time [min]
1	0.000	Run		
2	2.000	0.00	45.0	2.00
3	4.100	50.00	150.0	0.00
4	16.000	100.00	300.0	10.40
5		New Row		
6	16.000	StopRun		

Transfer line 250°C

Ion source temperature 270 °C

Mass transitions

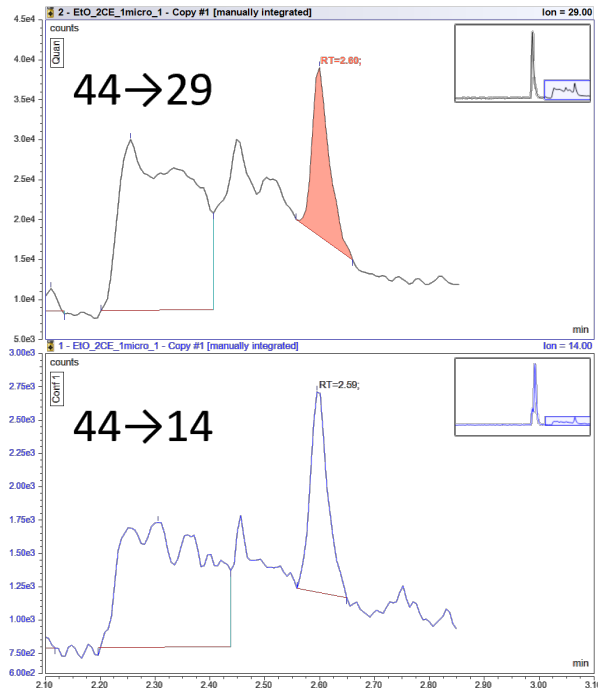
Compound	CE	Transition
EtO	20	44 -> 14
EtO	5	44 -> 29
2CE	5	80 -> 31
2CE	5	80 -> 43
2CE-d4	5	84 -> 33
2CE-d4	5	86 -> 33

Ethylene oxide

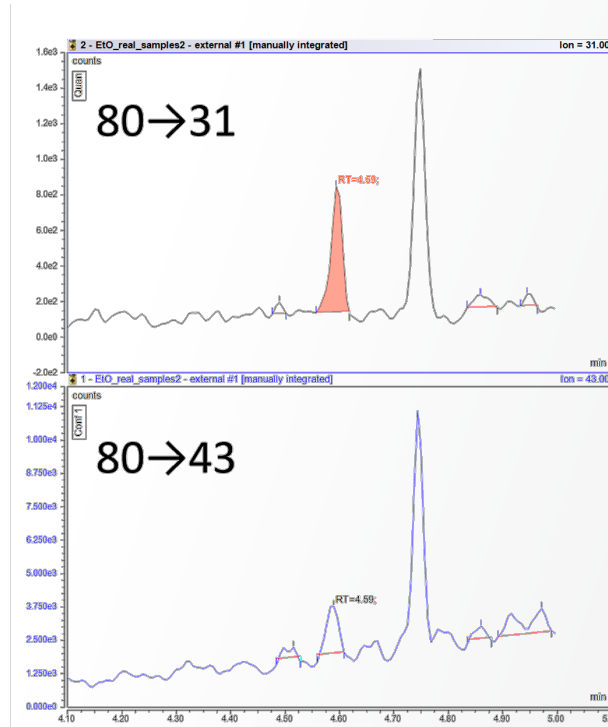
Sensitivity

Concentration: 2 mg/L

Injection volume: 1 μ L



Ethylene oxide

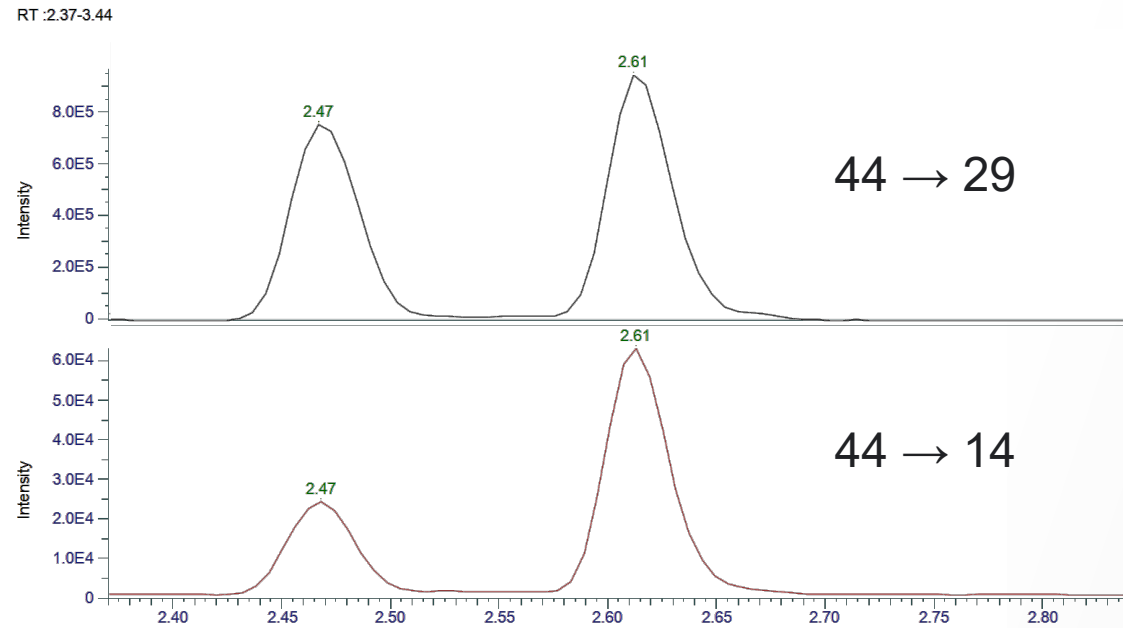


2-chloroethanol



Ethylene oxide

Selectivity- separation from acetaldehyde



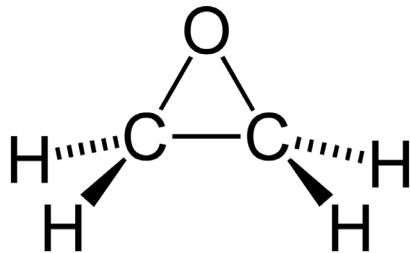
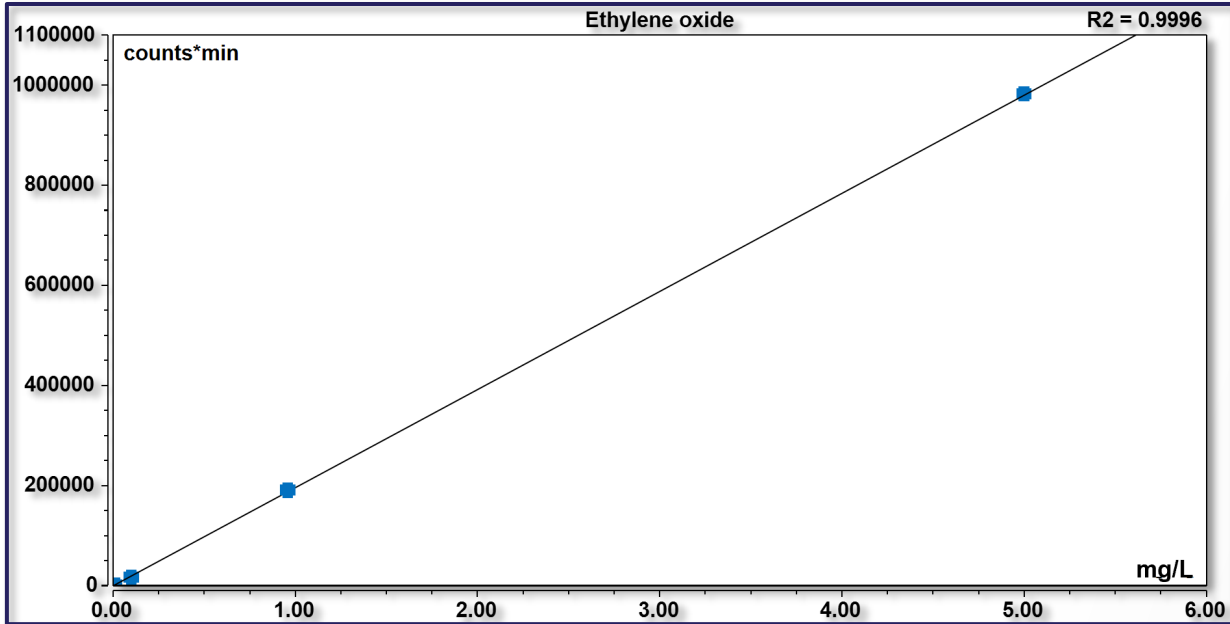
Acetaldehyde

Ethylene
oxide



Ethylene oxide

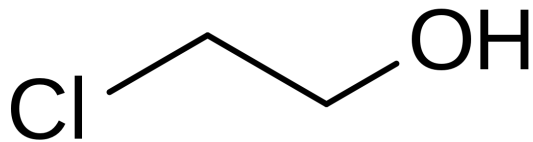
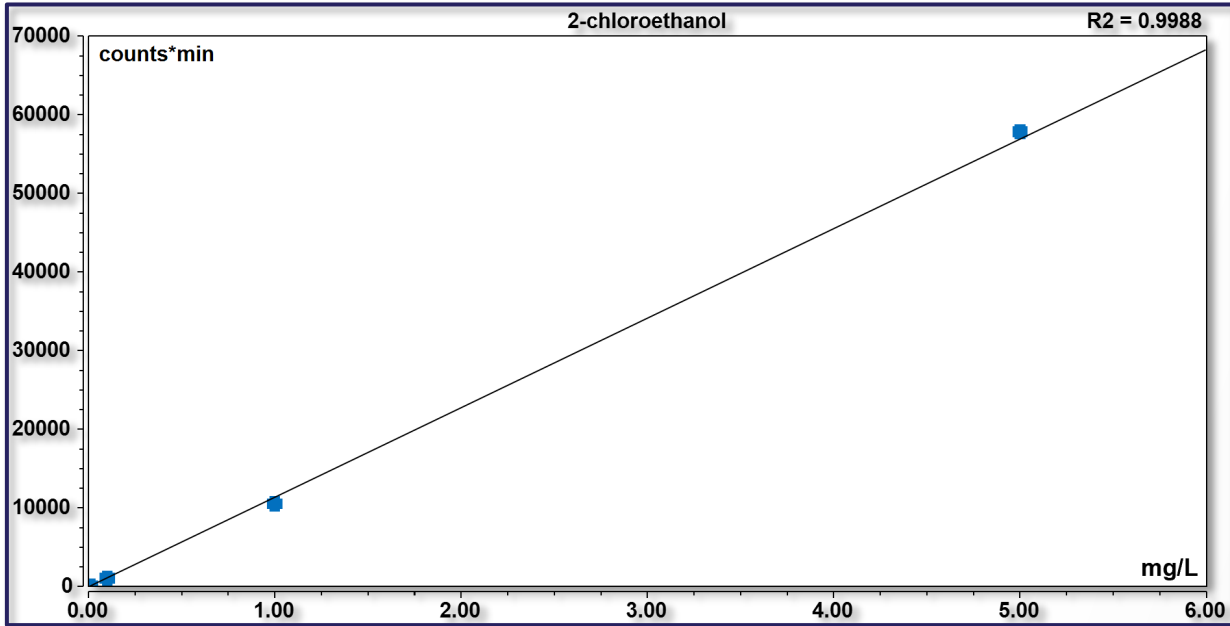
Linearity



Theoretical concentration	Peak area	Calculated concentration	Deviation of back calculated concentration	Ion ratio
[mg/L]	[counts · min]	[mg/L]	[%]	[%]
0.002	249	0.002	18	7.52
0.005	831	0.005	7	6.86
0.010	1499	0.009	-13	7.50
0.100	16883	0.087	-13	7.17
1.000	199845	1.025	0	6.78
5.000	982577	5.013	0	6.53

Ethylene oxide

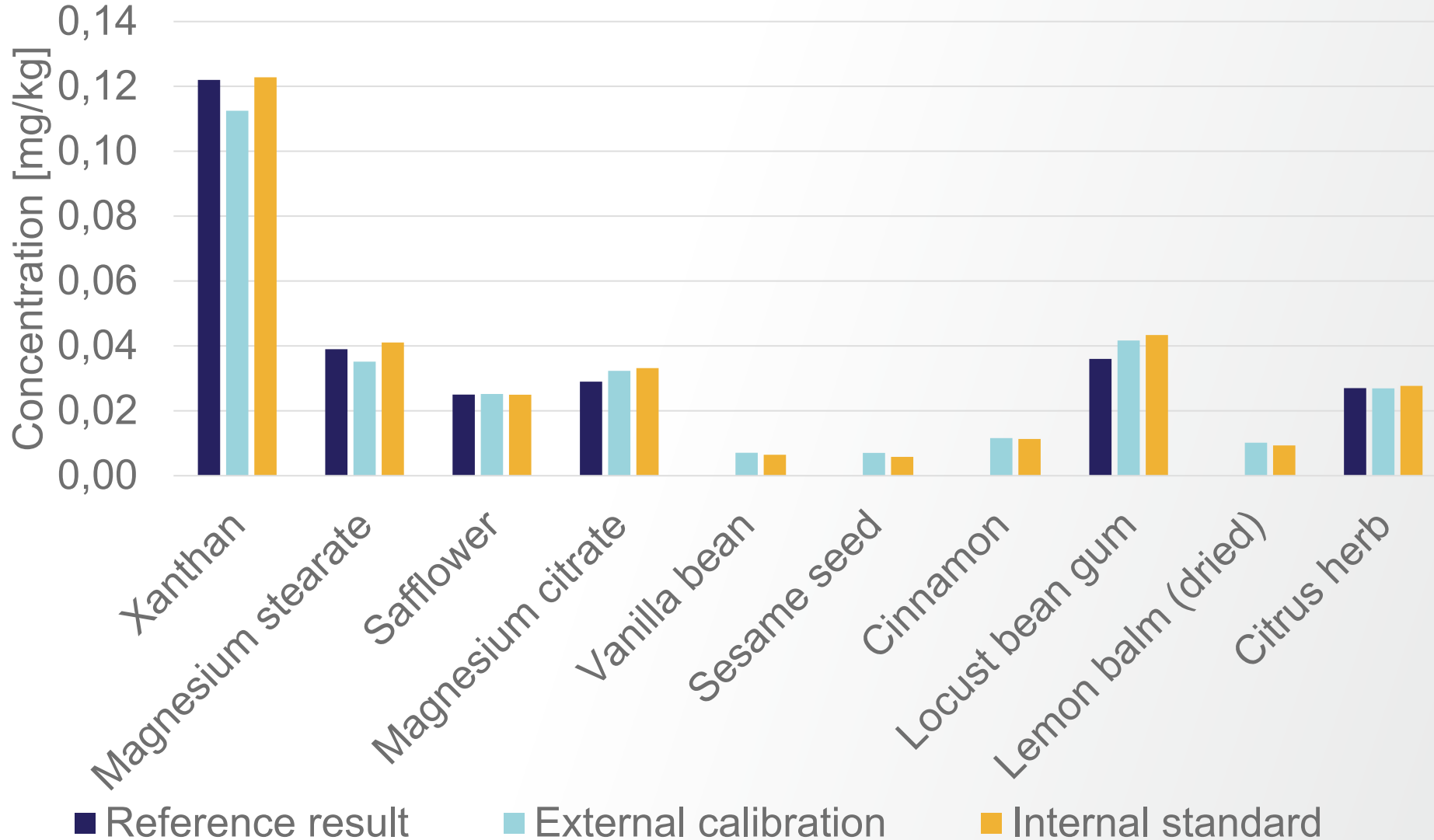
Linearity



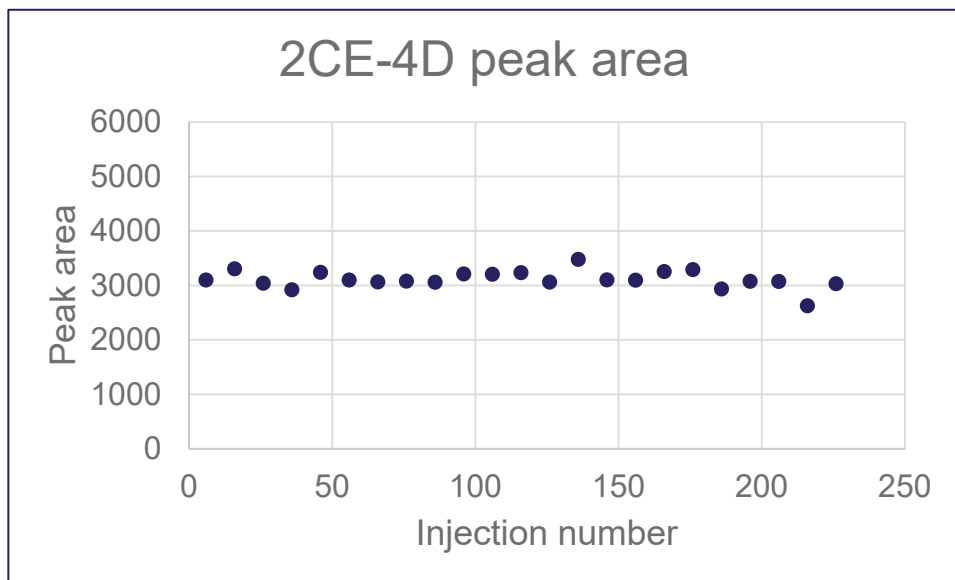
Theoretical concentration	Peak area	Calculated concentration	Deviation of back calculated concentration	Ion ratio
[mg/L]	[counts · min]	[mg/L]	[%]	[%]
0.002	16	0.002	7	111
0.005	56	0.006	13	117
0.010	98	0.009	-7	91
0.100	1049	0.093	-7	106
1.000	10531	0.926	-7	105
5.000	57839	5.081	2	98

Ethylene oxide

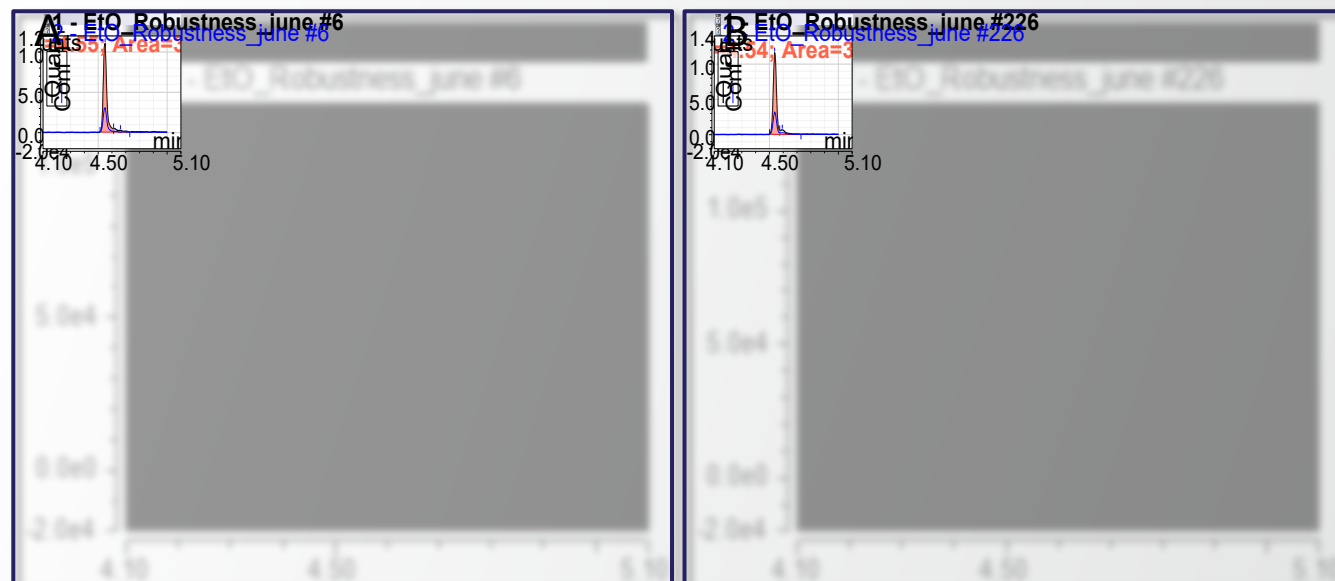
Real samples



Robustness of the analysis



The system was stable during a three-day long sequence (figure shows every 10th injection)



2CE-4D in sesame seed sample; A beginning of the sequence; B end of the sequence

Summary of results

- Chromatography: the chromatographic method provided a very good retention of the analytes and separation from the matrix interferences
- The quantitation at MRL was easily achieved, even with 1 μL injection volume showing excellent sensitivity
- The XLXR detector facilitates quantitation in a broad range on concentration showing good linearity between 0.007 – 16.5 mg/kg in the samples
- Robustness: the system provided stable results during a 3-days long unattended sequence

Sample preparation with QuEChERS

10 g
baby
food

10 mL
ACN

Shake
(4 min)

Add :
4gr MgSO_4 (4g),
NaCl (1g),
 $\text{Na}_3\text{Citrate}\cdot 2\text{H}_2\text{O}$
(1g),
 $\text{Na}_2\text{Citrate}\cdot 1,5\text{H}_2\text{O}$
(0,5g)

Shake
(4 min)

Centrifuge
(4000
rpm,
5 min)

Take 1 mL
supernatant and
add:
 MgSO_4 (750 mg)
PSA (125 mg)

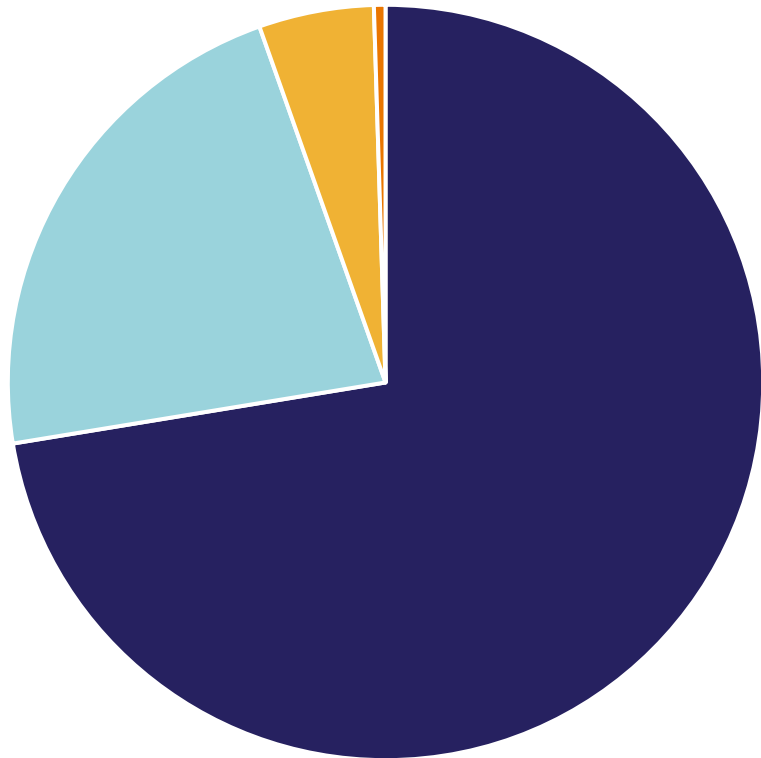
Vortex
(30s)

Centrifuge
(4000
rpm,
5 min)

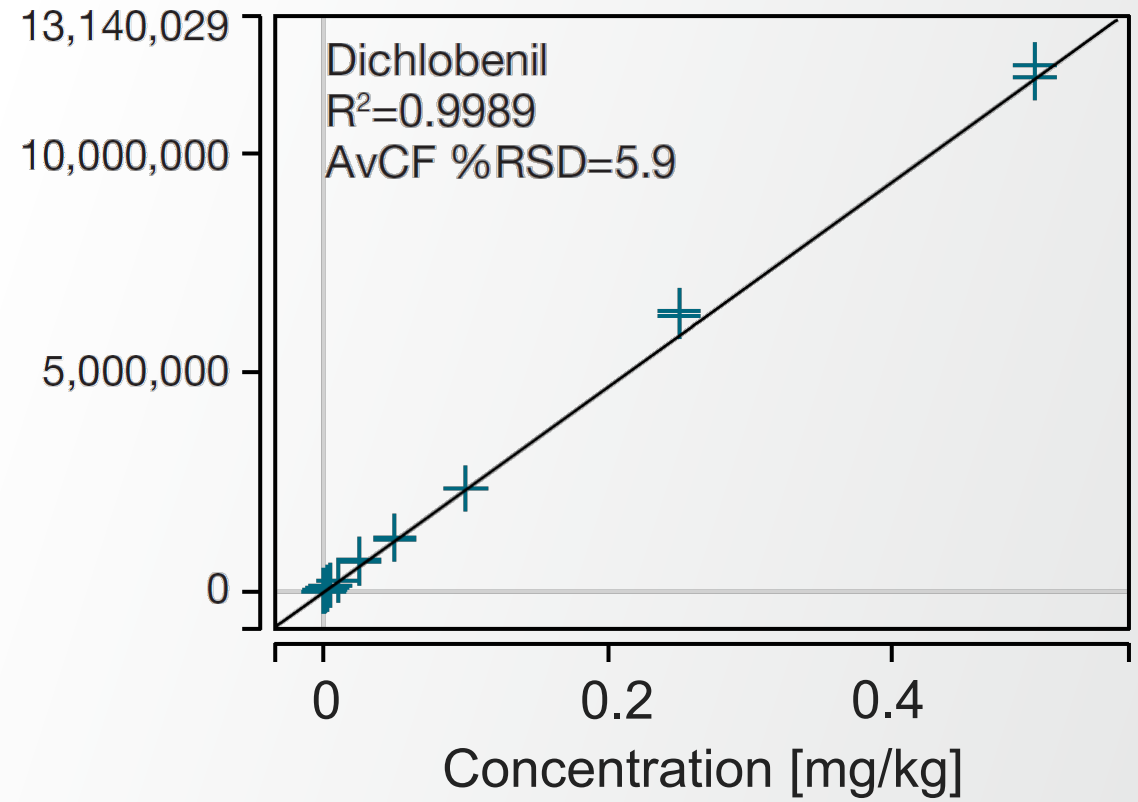
Take 4 mL
supernatant and
acidify with 40 μl of
5% formic acid in
ACN (v/v)

Linearity

Linearity range

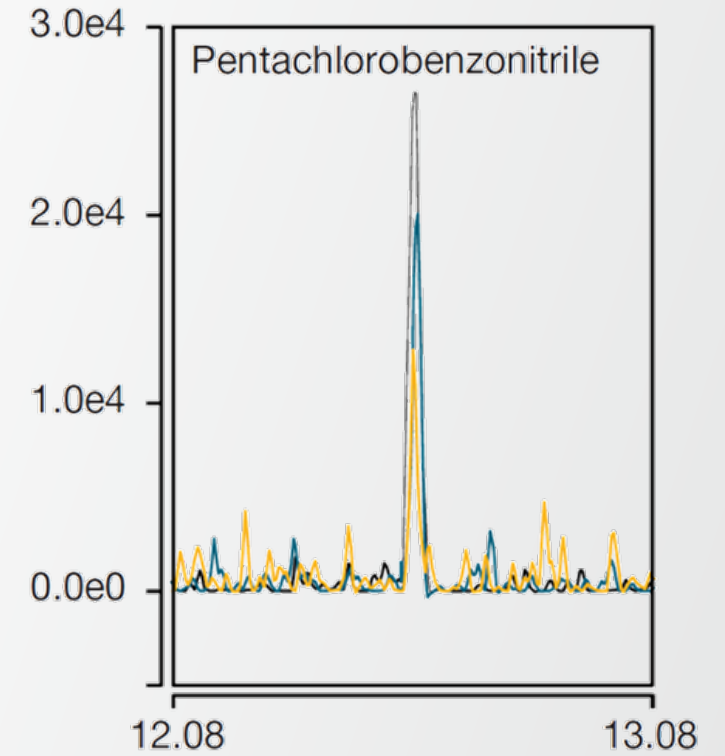
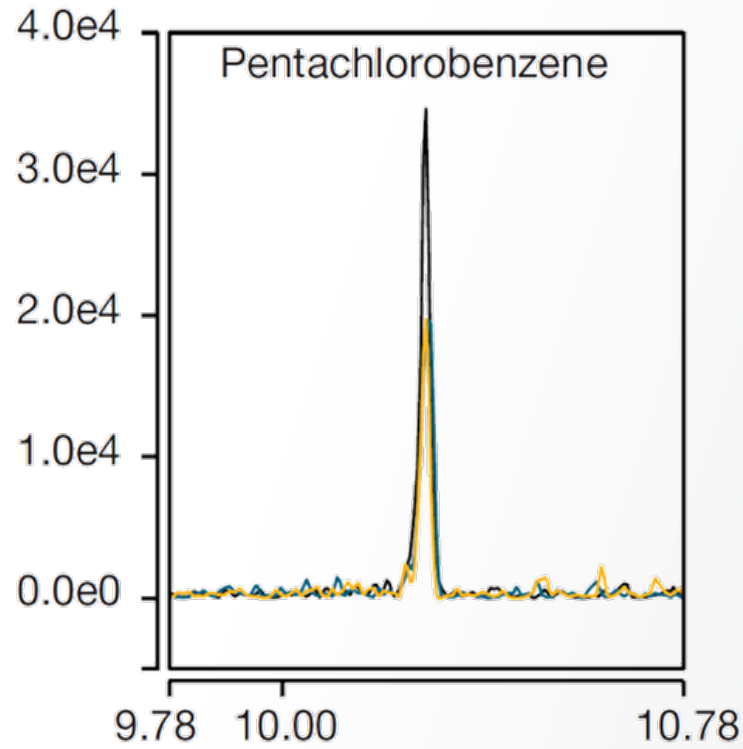
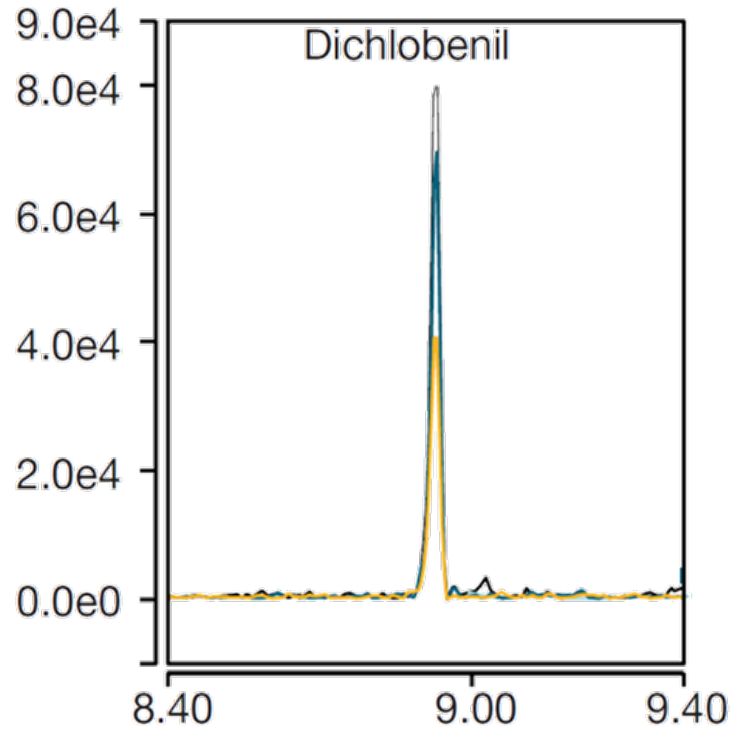


■ 0.00005-0.500 mg/Kg ■ 0.0005-0.500 mg/Kg ■ 0.001-0.500 mg/Kg ■ 0.001-0.100 mg/Kg



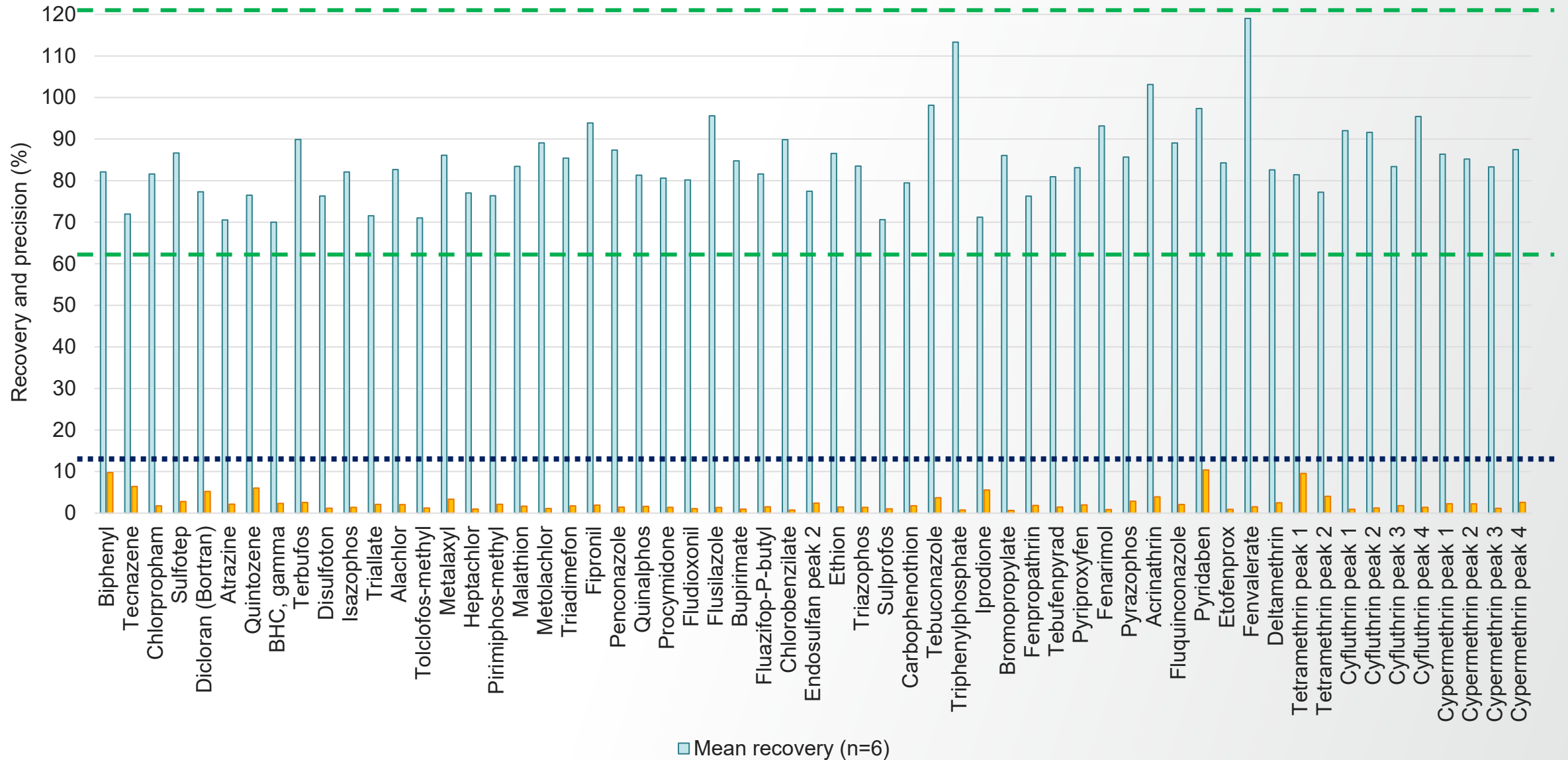
Sensitivity

Pesticides at 0.00005 mg/kg (0.05 ppb)



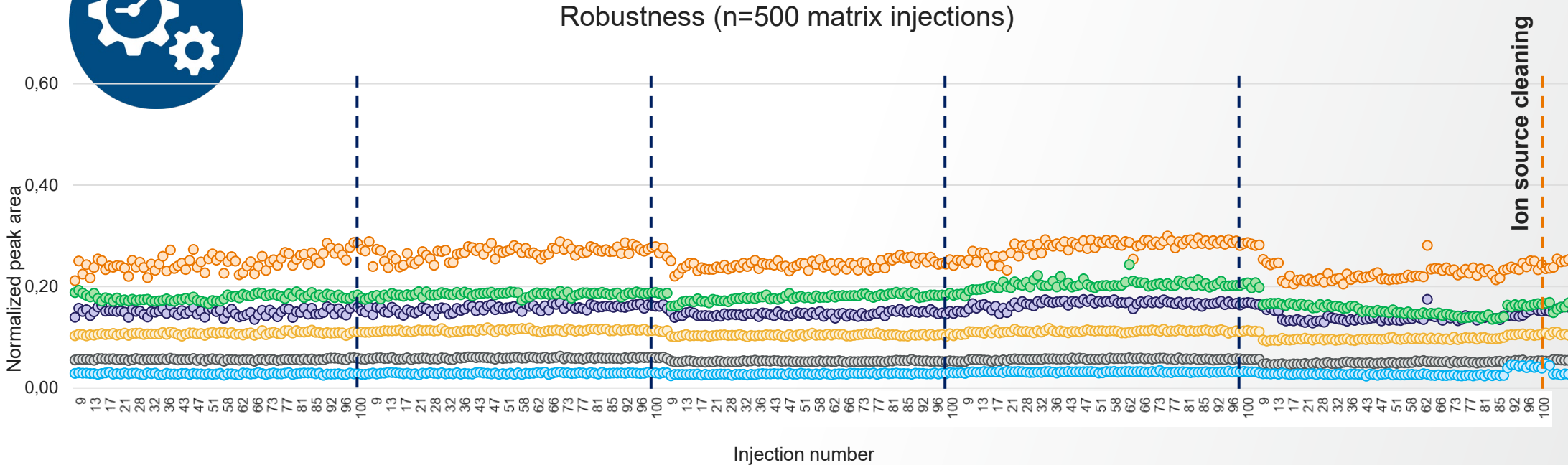
Recovery and precision in baby food

Recovery and repetability(0.003 mg/kg)



Increasing instrument uptime: Assessment of robustness

Consistent results at low levels



○ BHC, Alpha (%RSD=7)

○ Hexachlorobenzene (%RSD=9)

○ Aldrin (%RSD=6)

○ Isodrin (%RSD=6)

○ Triflumizole

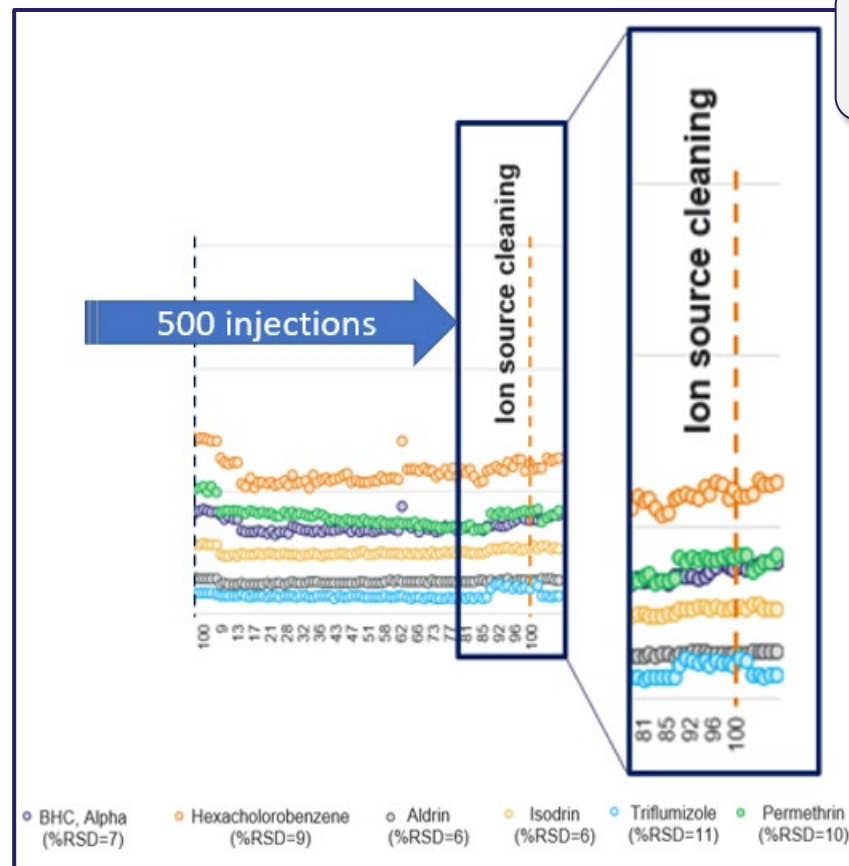
○ Permethrin peak (%RSD=10)

Increasing instrument uptime

Consistent results and NeverVent Technology



Even when maintenance is performed on the ionization source, the instrument produces consistent results at low levels

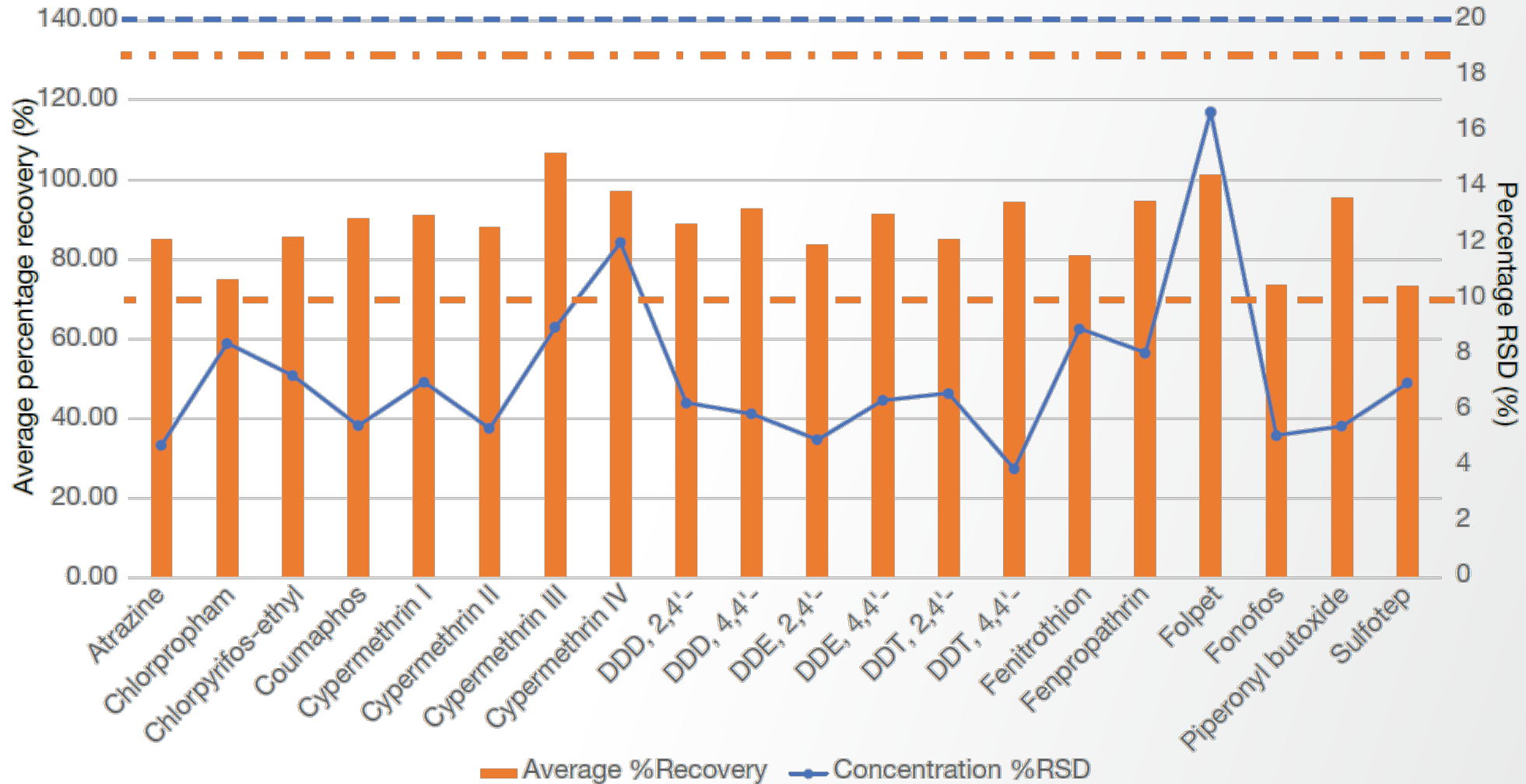


Maintenance performed to demonstrated stability after source clean



Instrument delivering consistent results again in under 2 hours

Recovery and precision in black tea

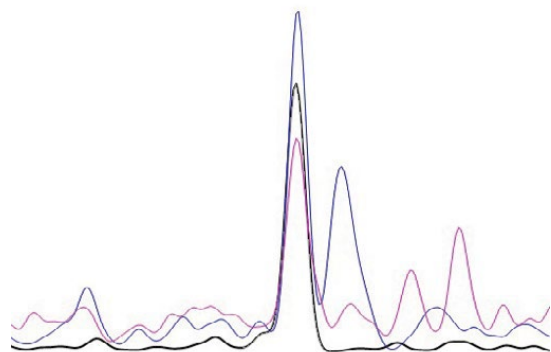


Recovery and precision in black tea

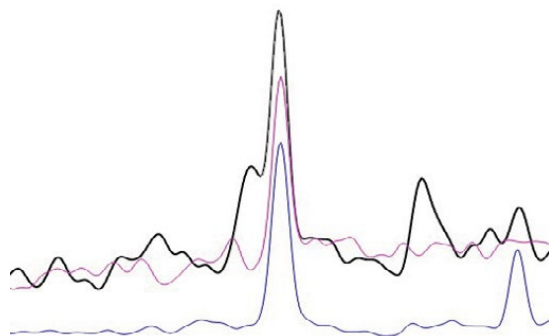
Compound	RSD [%]			Recover [%]		
	0.01 mg/kg (n=6)	0.25 mg/kg (n=6)	0.050 mg/kg (n=6)	0.01 mg/kg (n=6)	0.25 mg/kg (n=6)	0.050 mg/kg (n=6)
Atrazine	3.4	4.1	5.5	83.3	84.5	85.5
Chlorpropham	7.8	7.0	2.5	77.7	78.7	74.3
Chlorpyrifos-ethyl	4.7	6.0	3.5	84.0	78.9	81.5
Coumaphos	6.1	6.5	5.5	91.3	92.0	91.1
Cypermethrin I	8.0	3.4	4.1	92.9	91.5	91.3
Cypermethrin I	5.0	3.4	3.7	88.3	89.6	89.2
Cypermethrin I	9.7	4.1	3.6	101.2	91.6	90.7
Cypermethrin I	7.7	5.9	6.2	88.9	87.9	90.1
DDD, 2,4'-	3.4	5.0	2.2	93.3	91.8	91.3
DDD, 4,4'-	3.1	5.7	2.6	97.0	95.3	93.6
DDE, 2,4'-	3.8	4.7	2.2	86.1	83.4	81.6
DDE, 4,4'-	5.8	4.2	3.5	94.5	88.4	85.6
DDT, 2,4'-	3.8	4.4	3.8	89.6	90.2	87.6
DDT, 4,4'-	3.6	3.0	4.2	96.9	92.7	89.3
Fenitrothion	9.8	7.7	3.8	83.2	93.0	90.9
Fenpropathrin	6.0	7.5	5.0	99.1	92.2	92.6
Folpet	20.6	10.3	6.6	107.6	86.2	61.1
Fonofos	4.4	3.8	6.1	76.0	73.2	72.6
Piperonyl butoxide	4.8	3.6	4.3	98.5	95.7	95.0

Pesticides in black tea

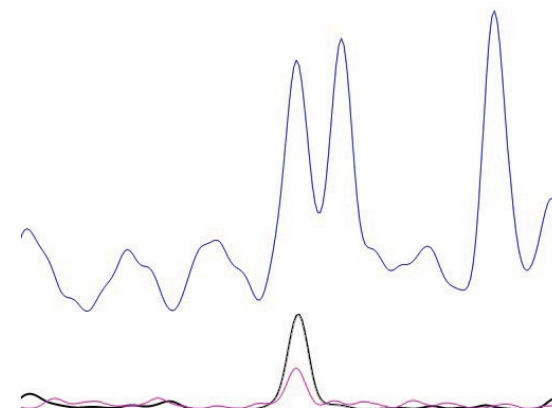
Chromatograms at 0.0005 mg/L (0.5 ppb)



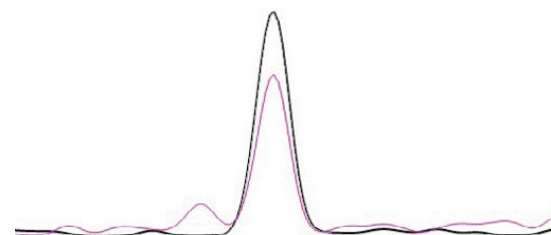
Atrazine



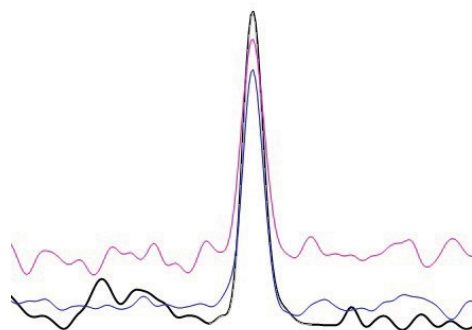
Chlorpopham



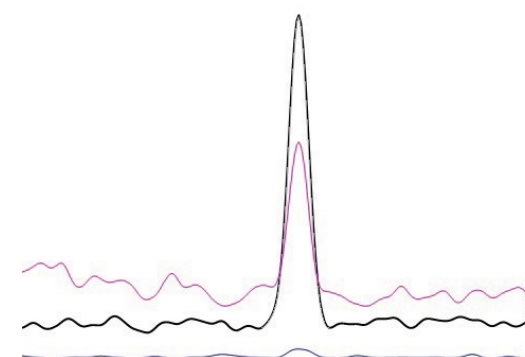
Chlorpyrifos-ethyl



Fonofos



Piperonyl butoxide



DDT, 4,4'

Application note | 001186



ThermoFisher
SCIENTIFIC

Food analysis

Analysis of ethylene oxide and 2-chloroethanol residues in food using GC-MS/MS

Authors
Łukasz Rajski¹ and Adam Ladak²
¹Thermo Fisher Scientific, Bremen, Germany
²Thermo Fisher Scientific, Hemel Hempstead, UK

Goal
The aim of this application note is to demonstrate the utility of the Thermo Scientific™ TRACE™ 1610 GC system and the Thermo Scientific™ TSQ™ 9610 triple quadrupole GC-MS/MS for the analysis of ethylene oxide and 2-chloroethanol residues in food samples.

Introduction
Ethylene oxide (EO) is a colorless and flammable gas with a broad spectrum of applications, including the preservation of dry food products, such as seeds, milled cereals, spices, herbs, nuts, milk powder, and raisins. However, upon consumption, ethylene oxide can negatively affect human health, with potential adverse effects on the central nervous system, mucous membranes, and mutagenic and carcinogenic effects.^{1,2} Residues of EO and its derivative products therefore need to be monitored closely. The importance of the EO analysis is highlighted by the high number of notifications published in the Rapid Alert System for Food and Feed (RASFF). Between January 1 and April 30, 2022, there were 96 alerts related to the detection of EO in food.³

Ethylene oxide is a challenging analyte, as the molecule is small and highly volatile with a boiling point of only 10.7 °C. This means that special precautions must be taken during the preparation of the sample to avoid analyte losses through evaporation. In the chromatographic column, the molecule is weakly retained and elutes just after the void time. Furthermore, EO is converted into 2-chloroethanol (2CE), 2-bromoethanol, and ethylene glycol through chemical reactions with the substances present in the

Keywords
Food, ethylene oxide, gas chromatography, pesticides, single-residue method, triple quadrupole

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Application note | 000437



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Food safety

Confident analysis of ultra-trace pesticides residues in baby food using triple quadrupole GC-MS

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Goal
The aim of this application note is to demonstrate the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer coupled to the Thermo Scientific™ TRACE™ 1610 GC equipped with programmable temperature vaporizing injector (PTV) for the determination of trace level pesticide residues in baby food.

Introduction
Pesticides are commonly used in agriculture to control various pests during cultivation, storage, and transportation.¹ The application of pesticides can result in residues at detectable concentrations in food. To ensure food safety for consumers and protect the environment, many organizations and countries around the world have established maximum residue limits (MRLs), which for the majority of pesticide-commodity combinations are set at the default level of 10 µg/kg.^{2,3} However, the European Union (EU) has established LOD MRLs between 3–8 µg/kg for specific pesticides prohibited in baby foods.⁴

The main challenge of pesticide analysis relates to the sensitivity required to meet strict regulatory limits. Moreover, analytical testing laboratories need to have multiclass, multiresidue methods that can be applied for the analysis of a large number of diverse pesticides in a high number of different sample types. These laboratories must also ensure high sample throughput, fast turnaround, and a low cost of analysis to offer a competitive service to their customers.

Keywords
Pesticides, baby food, gas chromatography-mass spectrometry, GC-MS, triple quadrupole, TSQ 9610 mass spectrometer, NeverVent Advanced Ionization Ion source (AEI), TRACE 1610 GC, programmable temperature vaporizing injector, PTV, AI/AS 1610

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Application note | 000560



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Mass spectrometry

Unstoppable analysis of pesticides residues in black tea using triple quadrupole GC-MS

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Goal
The aim of this application note is to demonstrate the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer coupled to the Thermo Scientific™ TRACE™ 1610 GC for trace level determination of pesticide residues in black tea.

Introduction
Products of botanical origin, including black tea, have become an increasingly prevalent part of the worldwide health culture with their global market forecast to reach more than \$230 billion by 2027. Manufacturers must ensure that these botanicals are safe for consumption, which requires routine/robust trace analysis of pesticide residues. Pesticides are chemicals used for crop protection against a variety of pests such as weeds, fungi, rodents, and insects. Because of their extensive use, pesticides can be found in the air, soil, water, and ultimately in the food chain. Despite their use being highly regulated, misuse of pesticides can lead to unwanted contamination of food and have possible impacts on both human and environmental health.

Keywords
Pesticides, tea, gas chromatography-mass spectrometry, GC-MS, triple quadrupole, TSQ 9610 mass spectrometer, NeverVent Advanced Ionization Ion source (AEI), TRACE 1610 GC, AI/AS 1610

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