Monitoring of chlorates in milk and milk powders

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Chlorate background

- Chlorate (ClO_3^-) is a substance that is no longer approved as a pesticide (CD 2008/865/EC).
- ClO_3^- is formed as a by-product when using chlorine, chlorine dioxide or hypochlorite for the disinfection of drinking water, water for food production and surfaces coming into contact with food.
- WHO guideline of 0.7 mg/L (700 PPB) for ClO_3^- in drinking water.

Chlorate Legislation

Reg. 396/2005

- Covers ~1100 pesticides currently used, formerly used in agriculture in or outside the EU
- MRLs are listed for some 315 fresh products
- A default MRL of 0.01 mg/kg (10 ppb), where a pesticide is not specifically mentioned.
- MRLs also apply to the same products after processing, adjusted to take account of dilution or concentration during the process.

EFSA Monitoring Data 2014

- Chlorate residues are present at levels that frequently exceed the default MRL of 10 ppb and that the levels vary depending on the source and the product.

- These findings indicate that even if good hygiene practices are used, in order to ensure an adequate hygiene of food products, it is currently not possible to achieve levels compliant with the current MRL of 10 ppb.

Proposed Temporary MRL

- 200 ppb for chlorate in milk (includes sodium, potassium and magnesium chlorate expressed as chlorate).

- The default MRL of 10 ppb applies to infant formula “as consumed”.

  Article 10 (1) of CD 2006/141

CD 2006/141/EC

Point 16

"Therefore, as far as foodstuffs for particular nutritional uses intended for infants and young children are concerned, it is appropriate to adopt a very low common limit for all pesticides. This very low common limit should be fixed at 0.01 mg/kg (10 ppb) which normally is in practice the minimum detectable level."

CD 2006/141/EC

Article 10 (1)

"Infant formulae and follow-on formulae shall not contain residues of individual pesticides at levels exceeding 0.01 mg/kg (10 ppb) of the product as proposed ready for consumption or as reconstituted according to the instructions of the manufacturer".

Interpretation for IF

MRL for Reconstituted IF = 0.01 mg/kg

Reconstituted IF = 25.2 g powder + 180 mL H_2O

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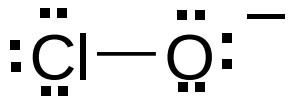
Dilution factor (w/w) = (25.2g + 180 g)/25.2 g = 8.14

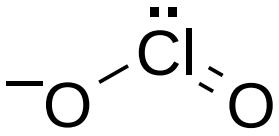
10 ppb Recon. IF ~ 81.4 ppb IF

Methodology for chlorate analysis

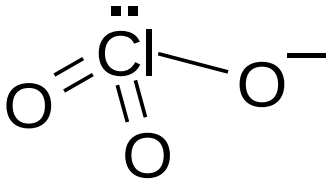
Chlorate Chemistry



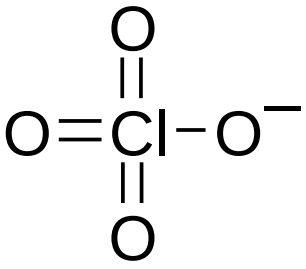
Hypochlorite



Chlorite



Chlorate



Perchlorate

Analytical problem

- Very small polar molecules, which make it difficult to achieve selective analysis.
- Need selective detection i.e. MS or MS/MS to achieve low levels of detection.
- Due to high water solubility speciality chromatographic columns or ion chromatography are required.

Analytical methods

- Very few published methods available for milk or dairy powders
- Most methods use Ion chromatography coupled to mass spectrometry.
- EURL method available using an alternative Hypercarb LC column.
- The best methods are unpublished.

EPA Methods Perchlorate in Water

Technique	EPA	MDL in Water	LCMRL ppb	Column(s)
IC-Suppressed Conductivity	314.0 / 9058	1 ppb	n/a	AS16 or AS20
IC-Suppressed Conductivity Matrix Rinse-Elimination Primary and Confirmation Columns	314.1	0.030 ppb	0.150	AS16 + AS20
2-D IC Suppressed Conductivity Matrix Rinse-Elimination Primary and Confirmation Columns	314.2	0.06 0.005	0.19 ---	4 mm AS16 + 2 mm AS20 with TAC-ULPC 4 mm AS16 + 0.4 mm AS20 with MAC-200
IC-MS SIM 99 and 101 m/z	332.0 / 6860	0.010 ppb	0.050	AS16 or AS20
IC-MS/MS MRM 99/83 and 101/85 m/z	332.0 / 6860	0.005 ppb	0.020	AS16 or AS20
LC-MS SIM 99 and 101 m/z	6850	0.010 ppb	0.050	AS21
LC-MS/MS MRM 99/83 and 101/85 m/z	331.0 / 6850	0.005 ppb	0.020	AS21

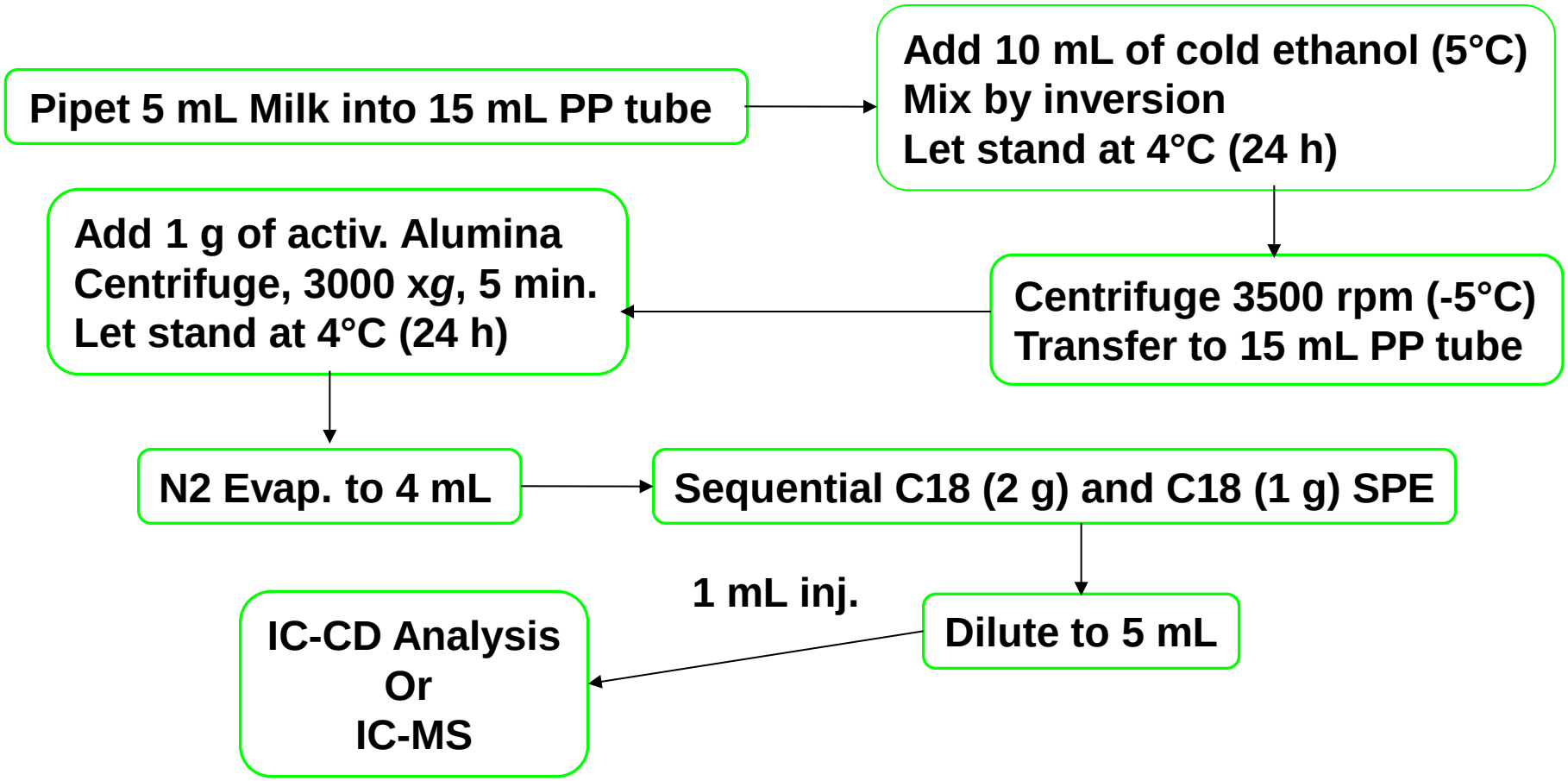
SIM = Single Ion Monitoring MRM = Multiple Reaction Monitoring LCMRL = Lowest Concentration Method Reporting Limit

ThermoFisher SCIENTIFIC

Teagasc Agriculture and Food Development Authority

The Irish Agriculture and Food Development Authority

Kirk Perchlorate Method



LOD: 0.5 ppb

QuPPe LC-MS/MS Conditions

Column: Hypercarb 2.1 x 100 mm 5 µm

Pre-column: Hypercarb 2.1 x 10 mm 5 µm

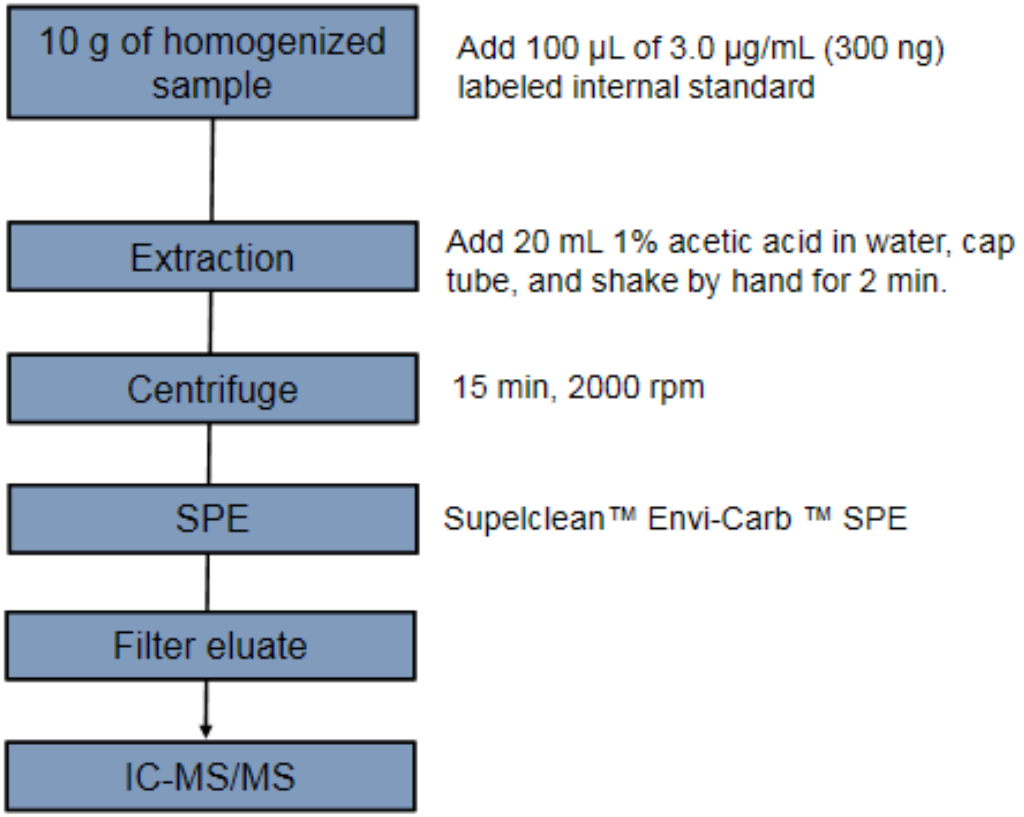
Mobile phase : (A) 1% Acetic Acid + Methanol (95:5, v/v)

(B) Acetic Acid + Methanol (1:99, v/v)

LC-MS/MS system: Agilent 1200 with ABSciex 5500 Qtrap

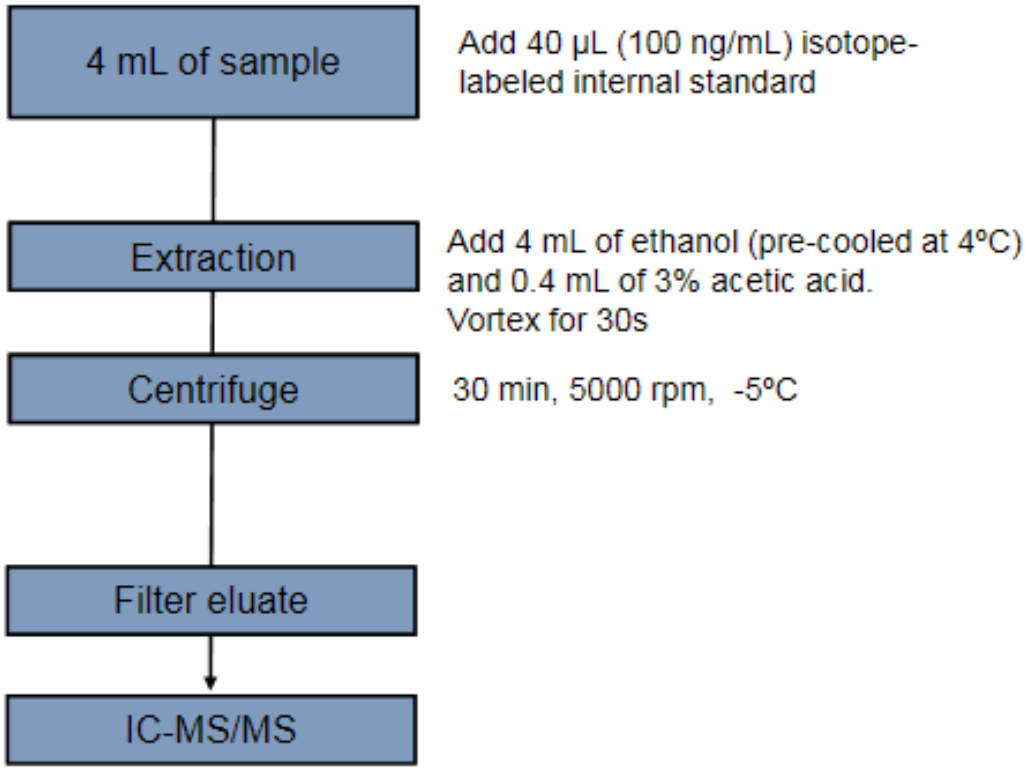
Analyte	**Transitions *(m/z)***
Chlorate	83 > 67, 85 > 69
Chlorate-$^{18}O_3$ (IS)	89 > 71
Perchlorate	99 > 83, 101 > 85
Perchlorate-$^{18}O_3$ (IS)	107 > 89

Extraction of Perchlorate from Food



Note:
SPE needed,
adds complexity

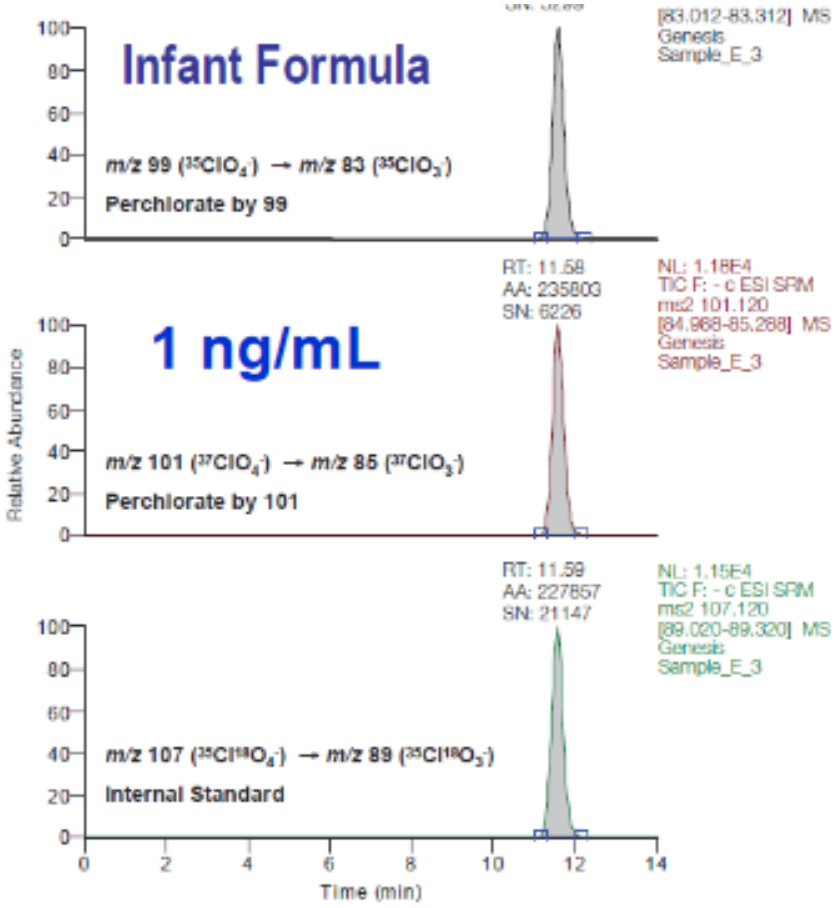
Perchlorate in IF and Milk



Thermo Scientific Application Note: AN533 Analysis of Perchlorate in Infant Formula by Ion Chromatography-Electrospray-Tandem Mass Spectrometry (IC-ESI-MS/MS)

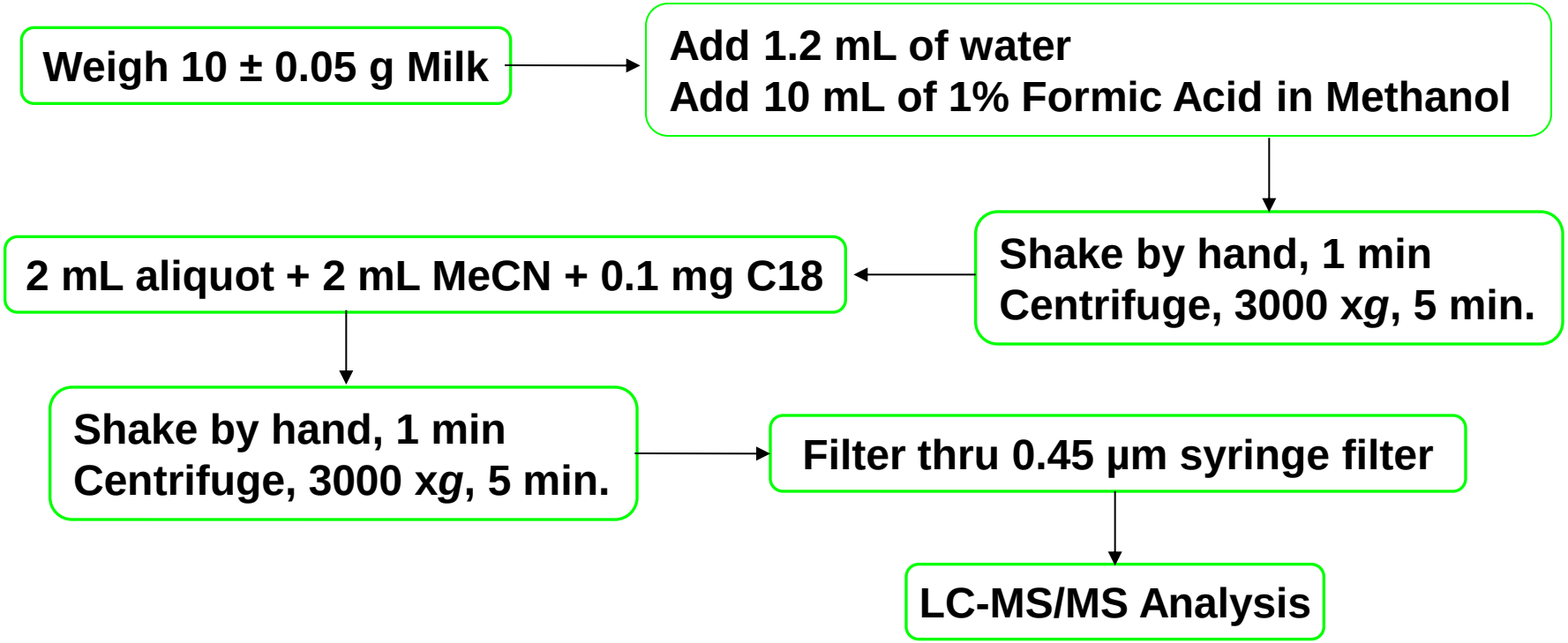
- Recoveries: 103-114 %
- RSDs: < 5% (1 ng/mL)
- LODs: 5 pg/mL
- Calibration: 0.02-10 ng/mL

Thermo Scientific™ Dionex™ ICS 5000 with Thermo Scientific TSQ Quantum Access MAX™ triple-stage quadrupole MS



QuPPe-AO-Method

Developed by EURL in Germany



LOQ: 20 ppb for chlorate in milk

Teagasc Method

- What method? → LC-MS/MS Method (LOQ 10 ppb)
- When? → Initial Method April 2016
- Sample throughput → 150 samples/week
- Cost → To be discussed