Metrohm Australia

White Paper IC BC-0001-092017

Determination of iodide in milk and milk powder via ion-chromatography with pulsed amperometric detection applying in-line stopped flow dialysis.

Keywords

IC / Metrohm 930 Professional IC / Metrosep A SUPP 3-250/4.0 / Milk / Iodide / In-line stopped flow dialysis / Pulsed amperometric detection (PAD)

Background:

Iodine is an essential trace element for humans development.

It is a component of the thyroid hormone thyroxin, which regulates the body's metabolic state and the growth and development in children. Iodine deficiency is an important health problem throughout much of the world. The dietary uptake of sufficient trace amounts of iodide is therefore necessary for mental and physical development. Important sources of Iodide are seafood, dairy products, iodized table salt and processed foods like iodized bread. As with many other essential nutrients, intakes in excess of physiological requirements can produce adverse effects.

For infants, the only source of iodide is milk or infant formula. Hence, it is of vital importance that the iodide levels in milk are strictly monitored.

Iodine tends to be supplemented at farm level in the expectation of increasing cow health and fertility. In addition to that, iodine is commonly used to disinfect the cow teats prior to the milking process.

As there are many sources of iodine in the milk production process, many of them on farms outside of the final production control, there is a concern that such practices may result in high fluctuations of milk iodide.

Furthermore, fluctuations in milk will affect the ingredients composition for infant formulas. For traceability throughout the supply chain, a simple and robust method is required to monitor iodide levels in milk.

Summary

The objective of this study was to develop and validate a fast and reliable method for the quantification of low-level iodide in milk. Limited sample preparation requirements was an additional desire to ensure short turnaround time for results.

Many of the analytical techniques such as IC and ICP require purification steps to eliminate fats and proteins. Microwave digestion, alkaline extraction, acid digestion or precipitation with methanol/acetonitrile followed by ultracentrifugation are commonly used to prepare samples. The method developed here applies in-line, stopped flow dialysis, which reduces the manual handling required. Consequently, the total error is also significantly reduced.

The ion chromatographic determination was carried out on a medium capacity anion exchanger utilizing a nitric acid mobile phase followed by pulsed amperometric detection (PAD). The PAD detector is equipped with a wall jet cell on a silver working electrode and a silver/silver chloride reference electrode. A great deal of attention was given to finding the right volt-amperometric settings and measuring potential in order to have a robust method. Eliminating time-consuming electrode polishing procedures is a key consideration in selection of evaluation conditions. (Refer to addendum 4)

A multistep, short period, reduction potential was applied in order to optimize the cleaning efficiently without the formation of hydrogen gas. The method turns out to be extremely sensitive and reproducible and has a linear range from 0.1 to 20 ppb.

Samples

Commercially available full cream milk.

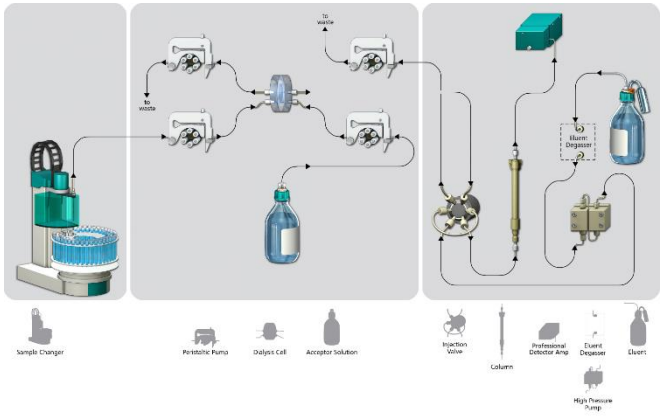
Instruments

930 Compact IC Flex Oven/ChS/PP/Deg	2.930.2360
850 PAD detector	2.850.9110
858 Professional Sample Processor	2.858.0020

Accessories

Metrosep RP2 Guard	6.1011.030
Metrosep A Supp 3 - 250/4.0	6.1005.320
Ag working electrode, 3 mm	6.1257.720
Ag/AgCl reference electrode	6.1257.740
Dialysis Membrane 0,1	JVWP04700

Instrument diagram



Reagents and accessories

- Nitric acid concentrate : 0.1 M HNO3 in water (0.1N), eluent concentrate for IC, 16355 Sigma Aldrich
- Iodide Standard for IC, TraceCERT®, 1000 mg/L iodide in water, 41271
- Sodium chloride, ultra-pure, 99.999%, 204439 Sigma Aldrich
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)
- Dialysis membrane: Omnipore ™ 0.1µm ; Hydrophilic Polytetrafluoroethylene (PTFE), Millipore JVWP04700

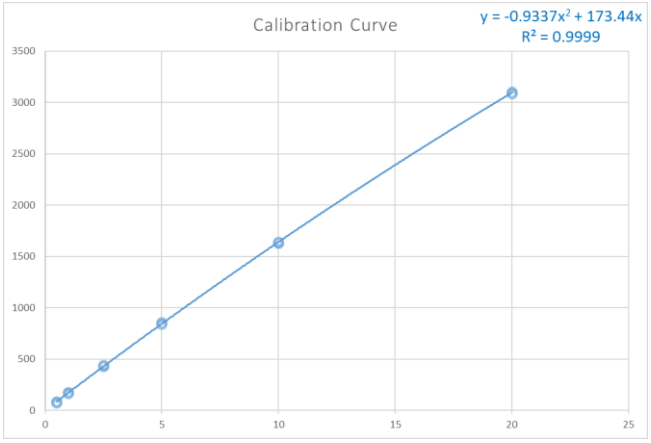
Solutions

Eluent	15 mM HNO_3 in ultrapure water
Receptor solution	Ultra-pure water
Diluent solution	10 mg/l NaCl

Standard solution and Calibration

The standards are made up from a 1000 µg/l Iodide solution, further diluted in ultra-pure water containing 10 mg/l NaCl. (Refer to comments) Every standard was injected in duplicate to make up the whole calibration.

Conc. (µg/l)	1	2	3	4	5	6
β Iodide	0.5	1	2.5	5	10	20



Sample preparation

The samples were diluted 50 times with ultrapure water to make the concentration fit in the calibration range.

Analysis

The analysis was carried out fully automated and controlled via MagICNet 3.2

Parameters

Dialysis

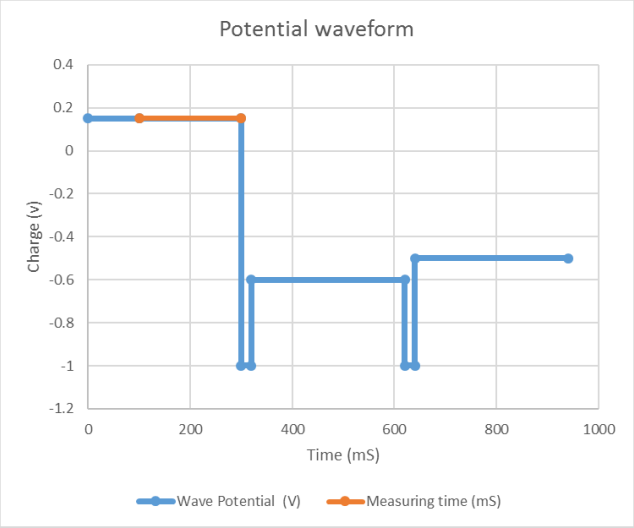
Sample volume	10 ml
Dialysis time	300 sec
Transfer time	80 sec

Separation

Column temperature	45 °C
Flow Mobile phase	1.0 ml/min
Injection volume	20 µl

Detection:

Detector temperature	35 °C
Cycle duration	940 ms
Measuring duration	200 ms
Range	2mA
Potential profile	
300 ms	+0.15 V
20 ms	- 1.00 V
300 ms	- 0.60 V
20 ms	-1.00 V
300 ms	-0.50 V



Results:

The results below represent the concentrations in the undiluted sample.

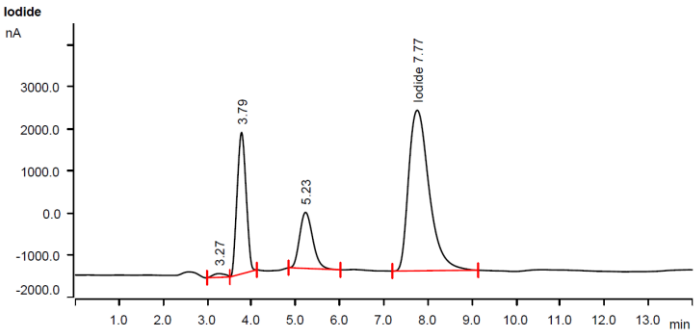
Determination	Full Cream milk Spike	
	0 ppb	250 ppb
	β Iodide [µg/l]	β Iodide [µg/l]
1	635	910
2	637	885
3	650	902
4	644	893
5	651	891
6	656	908
7	649	892
8	654	893
9	655	894
10	661	897
Av.	649	896
Rel. Std %	1.3	0.9
Spike recovery %		**98.9**

Calculation

Calculation automatically by MagICNet 3.2 based on peak area.

Example determination

Milk sample diluted 1/50 in ultrapure water



Comments

The standards are prepared in a 10 ppm sodium chloride solution as low electrolyte concentrations show insufficient ionic transfer over the dialysis membrane.

It is assumed that extreme low concentrations of polarizable ions such as iodide adhere to the surface of the membrane. This effect is eliminated by increasing the ionic strength of the standard solutions.

Conclusion

This method has demonstrated to be a robust and selective detection technique for the quantification of iodine in dairy products. Good recoveries are obtained after applying in-line stopped flow dialysis.

Appendix

- Appendix 1: Sample chromatogram
- Appendix 2: Overlay of sample determinations
- Appendix 3: Cyclic voltammograms on silver electrode against silver/silver chloride reference electrode.

References

- Irish Journal of Agricultural and Food Research 52(2):209-216; December 2013
- Determination of iodine in human milk and infant formulas ,Luisa Maria Fernandez-Sancheza,, Pilar Bermejo-Barreraa , Jose Maria Fraga-Bermudezb , Joanna Szpunarc , Ryszard Lobinskic L.M. Fernandez-Sanchez et al. / Journal of Trace Elements in Medicine and Biology 21 (2007)
- Nutrient Reference Values for Australia and New Zealand ; https://www.nrv.gov.au/nutrients/iodine
- Metrohm Monograph: Sample preparation techniques for ion chromatography, Metrohm AG, Herisau, Switzerland, 8.025.5003.

Date

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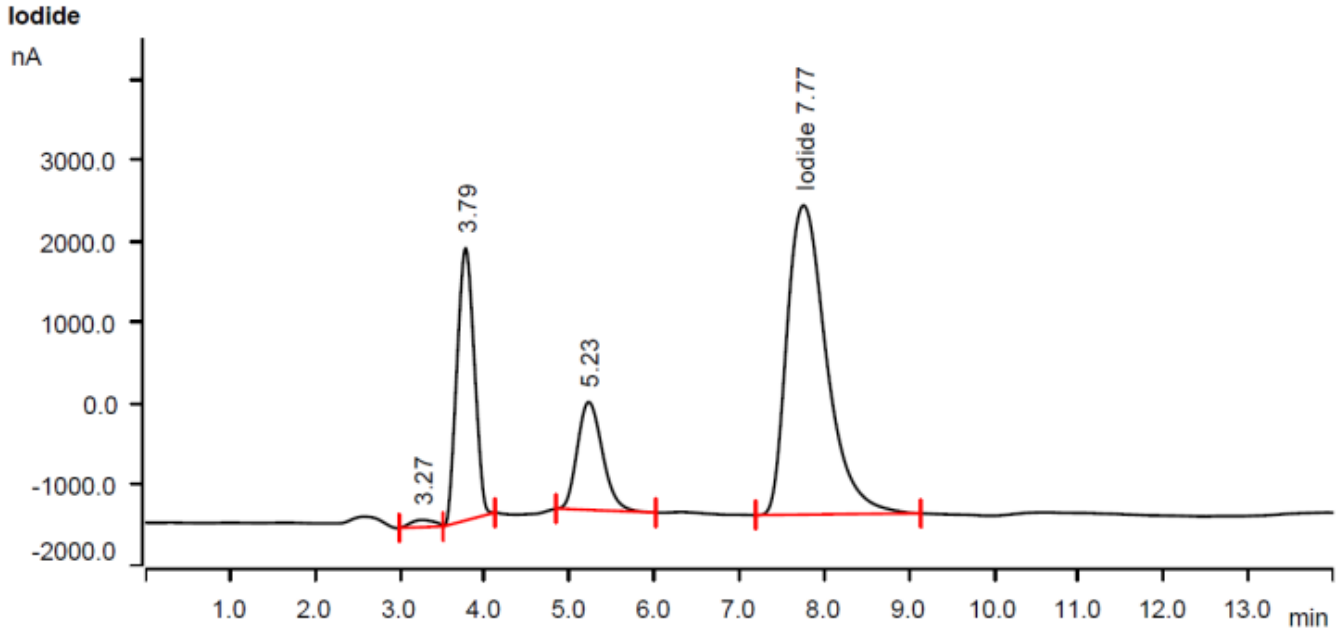
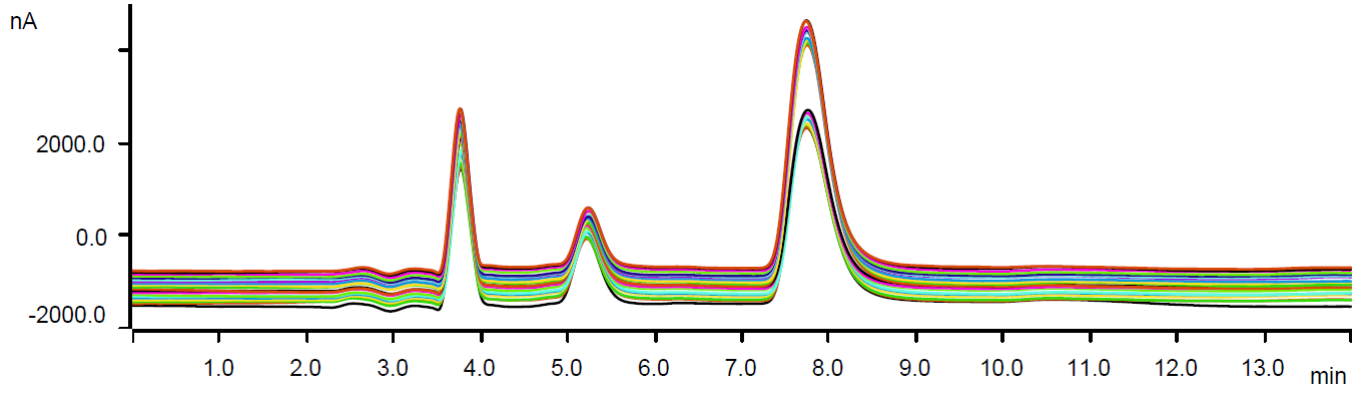
Appendix 1: Sample chromatogram

Milk sample, diluted 1/50 in ultrapure water



Appendix 2: Overlay of sample determinations

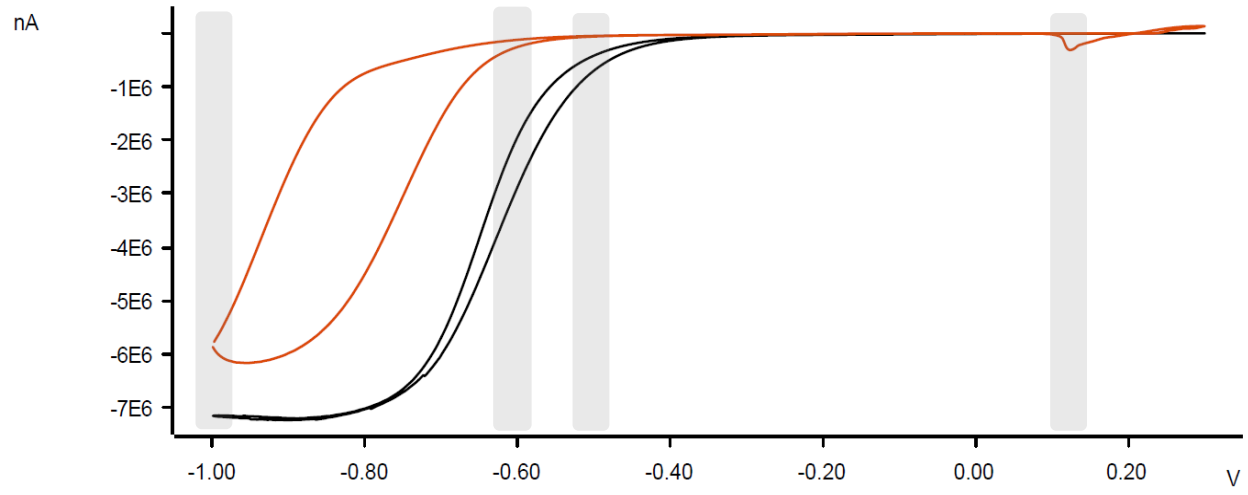
Ten milk samples in combination with ten spiked milk samples. A 250 ppb iodide spike was added to the raw milk sample, which equates to 5 ppb in the diluted, measured sample.



Appendix 3: Cyclic voltammograms on silver electrode against silver/silver chloride reference electrode.

To identify the optimal voltage settings for the determination of iodide, two cyclic voltamograms were run:

- *Cyclic voltammogram of 15 mM HNO_3 mobile phase*
- *Cyclic voltammogram of 15 mM HNO_3 mobile phase with 100 ppb iodide*



Reductive Cleaning Potential	Conditioning potentials	Detection Oxidative potential
-1.00 V	-0.60 V / -0.50	+0.15 V
AgI (S) ⇔ Ag (S) + I^-		Ag (S) + I^- ⇔ AgI (S)