Application Note AN-P-085

Iodine monitoring in natural sources

Superior method for iodide analysis by IC and amperometry

Dairy products are amongst the top three natural sources of iodine—the other two being seafood and eggs [1,2]. Iodine is an essential mineral for human health, where it is necessary for e.g., the production of thyroid hormones [1–3]. These hormones are especially important for brain and neural development in infancy. However, excessive intake of this trace element may also cause health issues [1–3]. Therefore monitoring iodine intake for humans as well as its content in natural sources are of major interest.

The presented method describes the determination of free iodide in milk samples using Metrohm Low Volume Inline Dialysis for automated sample preparation prior to injection into an ion chromatograph (IC) and subsequent amperometric detection in direct current (DC) mode. An automatic cleaning cycle using a dedicated flexiPAD method was applied to guarantee continuous and reproducible results when using DC mode.

Inline Dialysis reduces the time required for manual sample preparation which helps increase sample throughput, labor efficiency, and repeatability via automation.

SAMPLES AND SAMPLE PREPARATION

Three different commercially available milk samples were analyzed for their iodide content. The milk samples were manually diluted with ultrapure water with a dilution factor of 20 prior to analysis.

EXPERIMENTAL

Metrohm Low Volume Inline Dialysis was used as an automated sample preparation technique. The analyte of interest (i.e., iodide, I^-) can pass through the dialysis membrane (0.2 µm, cellulose acetate), whereas larger molecules (e.g., proteins and enzymes which are present in milk) cannot pass through and are transferred to the waste.

The Metrohm IC Amperometric Detector in DC mode was used for electrochemical detection of iodide. A silver working electrode was used in a thin layer cell together with an Ag/AgCl reference electrode.

Historically, the detection of iodide with IC using DC mode has resulted in low reproducibility during longer sample series due to signal reduction caused by passivation of the working electrode over time. Thus, an additional flexiPAD method was developed for this situation and applied to automatically clean the working electrode after each determination to avoid electrode fouling. The reproducibility of the results is guaranteed, even for longer sample series.

RESULTS

Three different milk samples were analyzed for their iodide content (Tables 1–3). The natural iodide concentration in the samples ranged from below the detection limit of the method up to 141 µg/L. A study with three different spiking concentrations was performed for all three samples, where the recoveries were in the range of 94–107%.

Recovery values were calculated using the following formula:

$$R = \frac{[100 \cdot c_f]}{[c_u + c_a]}$$

R recovery [%]
c_f concentration of fortified sample [µg/L]
c_u concentration of unfortified sample [µg/L]
c_a concentration of analyte added to the sample [µg/L]

Table 1. Results of the spiking study of organic whole milk. The sample was spiked with 50, 100, and 200 µg/L iodide.

Sample 1	I^- concentration (µg/L)	Recovery (%)
Natural [I^-]	141	–
Sample spiked with 50 µg/L I^-	189	99
Sample spiked with 100 µg/L I^-	251	104
Sample spiked with 200 µg/L I^-	363	106

Table 2. Results of the spiking study of regular whole milk. The sample was spiked with 50, 100, and 200 µg/L iodide.

Sample 2	I^- concentration (µg/L)	Recovery (%)
Natural [I^-]	105	–
Sample spiked with 50 µg/L I^-	157	101
Sample spiked with 100 µg/L I^-	200	98
Sample spiked with 200 µg/L I^-	304	100

Table 3. Results of the spiking study of another brand of organic whole milk. The sample was spiked with 50, 100, and 200 µg/L iodide.

Sample 3	I^- concentration (µg/L)	Recovery (%)
Natural [I^-]	<LOD	–
Sample spiked with 50 µg/L I^-	78.4	107
Sample spiked with 100 µg/L I^-	124	100
Sample spiked with 200 µg/L I^-	210	94

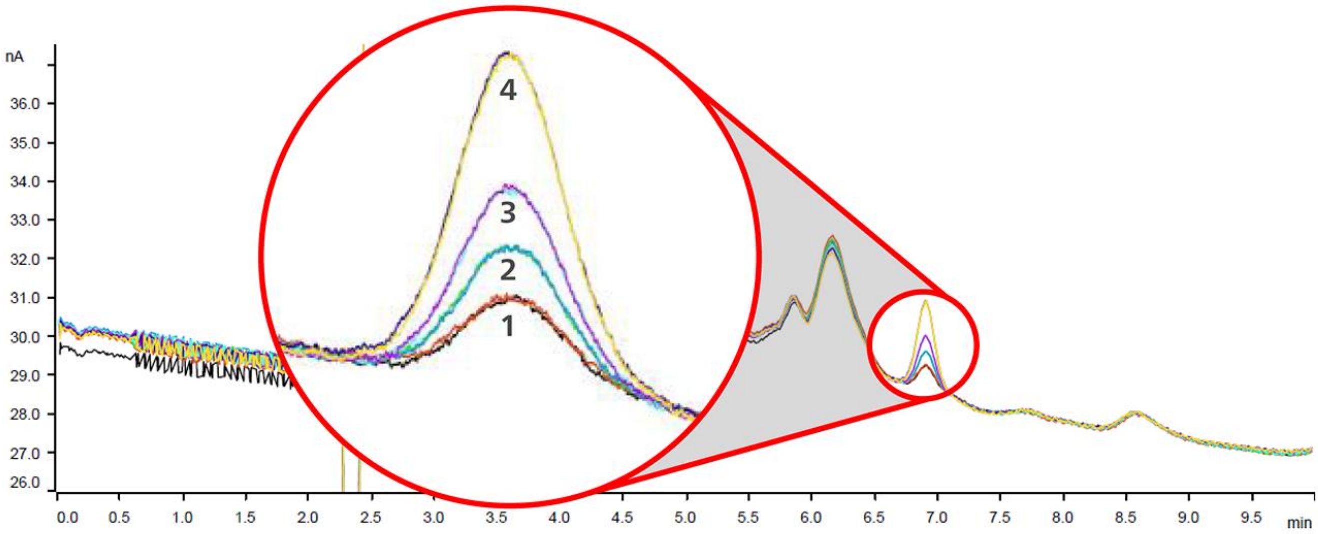

Figure 1. Overlay of chromatograms from the spiking tests performed on Sample 2. Iodide analyses were performed with a 930 Compact IC Flex equipped with dialysis. Separation was performed on a Metrosep A Supp 17 - 150/4.0 column. Inlay: 1) The sample was measured and the natural iodide concentration was determined to be 105 µg/L. 2) The sample was spiked with 50 µg/L iodide and the determined concentration was 157 µg/L. 3) The sample was spiked with 100 µg/L iodide and the determined concentration was 200 µg/L. 4) The sample was spiked with 200 µg/L iodide and the determined concentration was 304 µg/L.

The limit of detection (LOD) for this method was determined according to the signal-to-noise ratio and also in accordance with DIN 32645. LOD was calculated as 36 µg/L (S/N) and 27 µg/L (DIN 32465), respectively.
The following formula was used for the calculation of the LOD according to the signal-to-noise ratio:

$$LOD = \frac{CONC}{\frac{HGT}{3 \cdot Noise}}$$

LOD Limit of detection [µg/L]
CONC Analyte concentration [µg/L]
HGT Height of the analyte [nA]
Noise Noise of the determination [nA]

CONCLUSION

This IC method offers a straightforward, fast, and sensitive solution for reproducible analysis of the iodide concentration in milk. The utilization of an automated cleaning method for the working electrode reduces electrode fouling and increases sample throughput without any additional manual work. Low Volume Inline Dialysis enables automatic sample preparation, increasing the overall method efficiency while considerably reducing the analysis costs.

REFERENCES

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2. van der Reijden, O. L.; Zimmermann, M. B.; Galetti, V. Iodine in Dairy Milk: Sources, Concentrations and Importance to Human Health. *Best Pract Res Clin Endocrinol Metab* **2017**, *31* (4), 385–395.
3. Gunnarsdottir, I.; Dahl, L. Iodine Intake in Human Nutrition: A Systematic Literature Review. *Food & Nutrition Research* **2012**.

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CONFIGURATION

IC equipment: Low Volume Inline Dialysis

Accessory set for rapid Inline Dialysis. For use with the 858 Professional Sample Processor and an additional two-channel peristaltic pump.

858 Professional Sample Processor – Pump

The 858 Professional Sample Processor – Pump processes samples from 500 µL to 500 mL. The sample transfer takes place either with the installed bidirectional two-channel peristaltic pump or with an 800 Dosino.

Metrosep A Supp 17 - 150/4.0

The Metrosep A Supp 17 - 150/4.0 separation column is the column of choice for anion determinations that require good separating efficiency and short separation times at room temperature. The maximum flow rate of 1.4 mL/min then also makes it possible to optimize the determination. The Metrosep A-Supp-17 columns convince with their good price-performance ratio.