Determination of fluoride in food using Ion-Selective Electrodes

X. Maurer, M. Anastassiades, M. Wieland, A. Wachtler
E-Mail: Michelangelo.Anastassiades@cvuas.bwl.de

Introduction

Besides being a natural component in food, fluoride also appears as a residue in food following fumigations with sulfuryl fluoride (SF). SF is applied for disinfection, e.g. before transportation of dry food commodities. SF is approved as an A.S. within the EU and its use is authorized in several member states. Separate MRLs for SF and fluoride ion, are established with the latest revision taking place in July 2022 (Reg. (EC) 2022/1321) with the MRLs of several dry commodities (e.g. in raisins, cereals, flour, nuts, tea and spices) being raised. These new MRLs shall apply after February 21st 2023. For the determination of fluoride in water, methods employing ion-selective electrodes (ISE) are often used. For dry commodities microdiffusion is sometimes employed to achieve enrichment of fluoride prior to its determinative analysis [1]. In this study, we aimed at checking whether ISE, alone or in combination with microdiffusion, may be employed for controlling the fluoride MRLs in food.

Methods

Two different measurement approaches for the analysis of fluoride residues were tested**,** the **direct ISE-measurement in QuPPe extracts** and **ISE measurement following microdiffusion-assisted enrichment.**

In **microdiffusion**, the dry sample is weighed into the outer area of the diffusion vessel and 1 mL 0.1 M NaOH is added into the central cavity as a trapping solution. The sample is then covered with 4 mL perchloric acid (5M saturated with hexamethyldisiloxane) to initiate HF diffusion to the trap. After closing the vessel (using vaseline for sealing), the diffusion is conducted for 5 h at 50 °C. Afterwards 1 mL TISAB II solution is added to the trap solution prior to ISE measurement.

For **direct measurement**, the sample is processed according to the QuPPe method [2]. Before measurement with the electrode, the sample extract is also diluted in a ratio of 1:1 with TISAB II solution.

Microdiffusion

Various microdiffusion conditions were tested to check the efficiency of the enrichment step. Figure 1 shows the ISE-determined levels of incurred fluoride in wheat and infant formula, following microdiffusion under varied conditions. Diffusion yields of fluoride increased with time and diffusion was accelerated by heating. Satisfactory yields and recoveries were achieved after 48 h at room temperature or 5 h at 50 °C. Following microdiffusion at 50 °C for 5 h, the recovery of spiked fluoride on oats (at 2 mg/kg), was determined at 96% using an external calibration. Moreover, drying homogenates of samples with high water content (cucumber) prior to microdiffusion was also tested in terms of practicability and recovery. Here, recovery rates at 109% in spiked homogenate at 2 mg/kg were achieved.

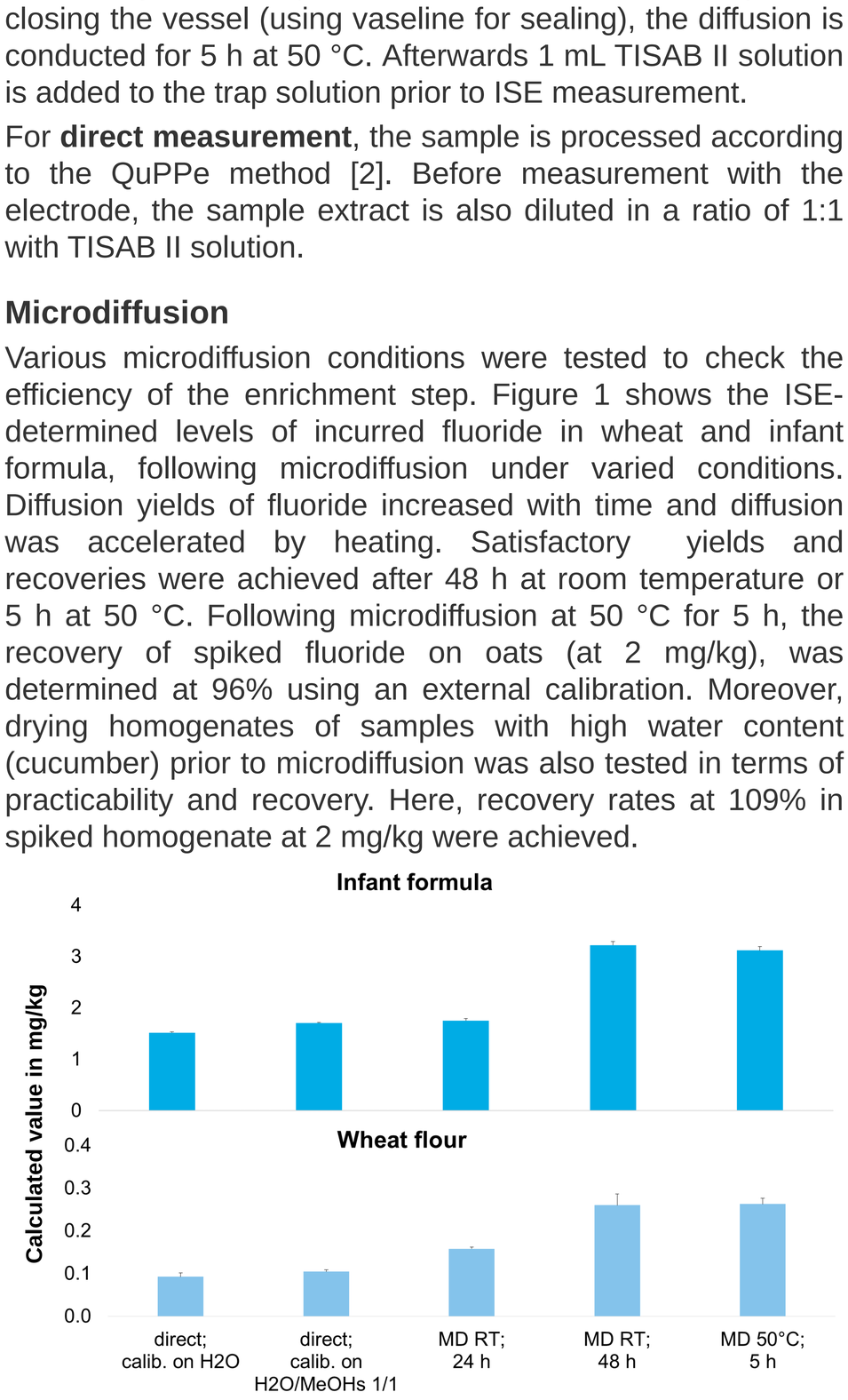


Figure 1: Comparison of results with different conditions of microdiffusion (MD) to results with direct measurement.

Matrix Effects

To examine matrix effects during direct measurement, calibration curves prepared in QuPPe extracts of various matrices and in solvent (methanol containing 1% formic acid/H_2O 1/1) were compared (see Figure 2). In this experiment matrix effects were negligible.

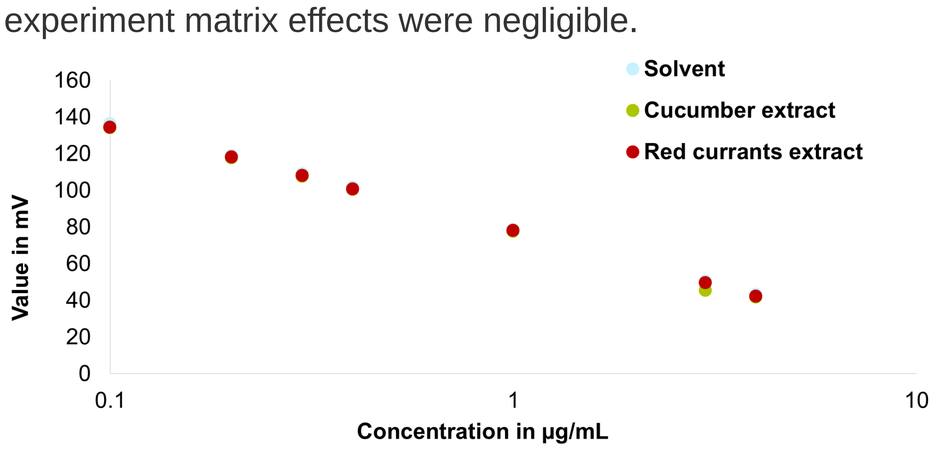
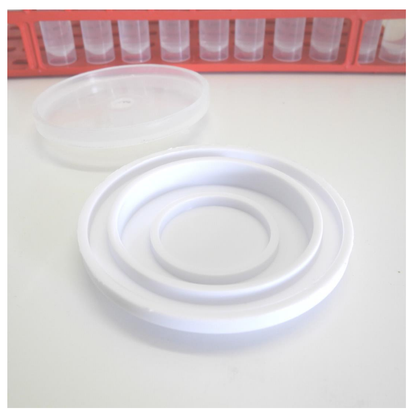


Figure 2: Calibration curves in different matrix extracts.

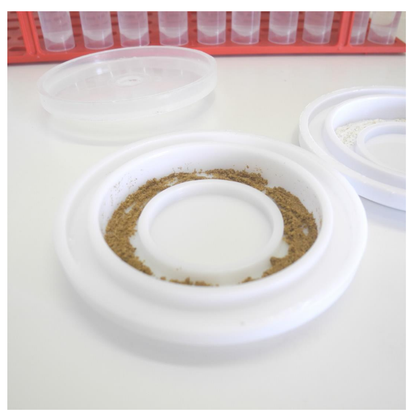


Comparison of fluoride contents in vegetables

Fluoride is present as a trace element in all food commodities. Table 1 shows background levels in different cucumber samples indicating that the MRL of 0.2 mg/kg is exceeded in the majority of the samples.

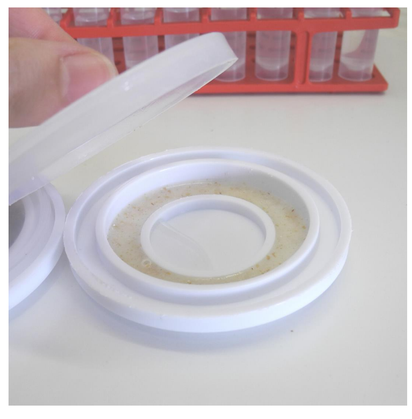
Table 1: Fluoride content in cucumber samples (direct ISE-measurement in QuPPe extracts).

Fluoride in mg/kg	Origin
0.367	Germany
0.201	Germany
0.195	Germany
0.179	Germany
0.211	Spain
0.292	Spain



Method Validation

Validation was performed at 1 mg/kg (n = 5) using both approaches. With the background levels laying between 0.1 and 0.2 mg/kg, validation at lower spiking levels would not fulfill the AQC criteria. Measurement repeatability was checked by repeated measurement (n = 10) of cucumber extracts spiked at 1 mg/kg. RSD was as low as 1.4%.



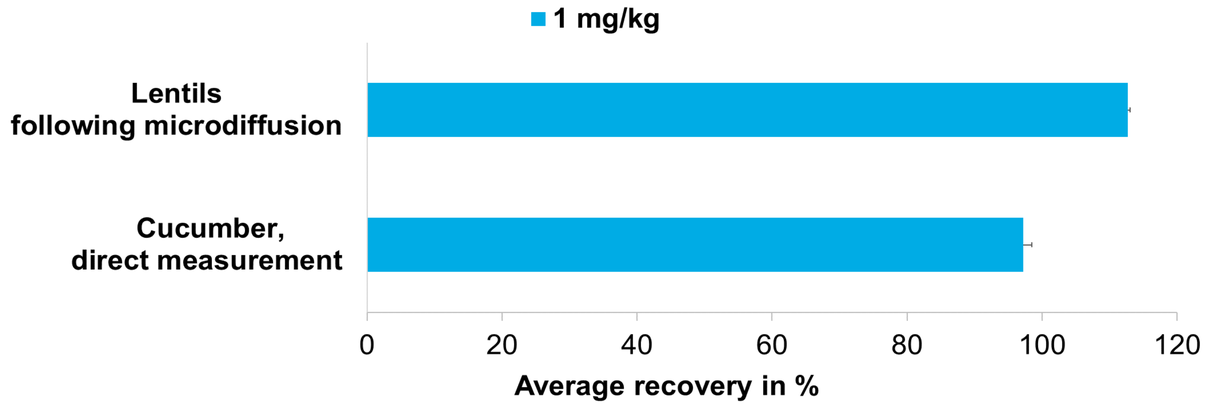


Figure 3: Validation results in cucumber (using the direct approach) and in lentils (using the microdiffusion approach).

Summary

For the determination of fluoride levels in food two approaches were tested: Direct ISE measurement in QuPPe extracts and ISE measurement following microdiffusion. The latter was mainly used for dry samples. Heating at 50 °C helped to reduce microdiffusion duration from 48 h to 5 h with nearly quantitative recoveries. In direct measurement, matrix effects were negligible opening the way for external calibrations. Natural background levels in food, unfortunately hampered AQC-conform validation at low levels. The procedures using direct measurement and microdiffusion were successfully validated at 1 mg/kg in cucumber and lentils respectively. Furthermore, measurement of background levels of fluoride in various samples suggests that many MRLs set at the LOQ (e.g. at 0.2 mg/kg) would need to be revised to avoid unnecessary MRL-violations and to facilitate analysis.

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[1] T. Tomori; H. Koga; Y. Maki; Y. Takaesu: Fluoride analysis of foods for infants and estimation of daily fluoride intake; 10.05.2004 Bull. Tokyo dent. Coll., Vol. 45, No. 1, pp 19-32

[2] M. Anastassiades; A.-K. Wachtler; D. I. Kolberg; E. Eichhorn; H. Marks; A. Benkenstein; S. Zechmann; D. Mack; C. Wildgrube; A. Barth; I. Sigalov; S. Görlich; D. Dörk; G. Cerchia: Quick Method for the Analysis of Highly Polar Pesticides in Food Involving Extraction with Acidified Methanol and LC- or IC-MS/MS Measurement (22.07.2021);www.eurl-pesticides.eu/userfiles/file/EurlSRM/EurlSrm_meth_QuPPe_PO_V12.pdfpesticides(07.09.2022)