Automated determination of 3-monochloropropanediol, glycidol and their esters in foodstuffs with GC-MS/MS

Wenzel, K.[1], Uber, T.[2] , Nestola, M. [2], Becker, E.[1], Kirchhoff, E.[1], Berlin/D

[1]Institut Kirchhoff Berlin GmbH, Oudenarder Str. 16, 13347 Berlin/D

[2]Axel Semrau GmbH & Co.KG, Stefansbecke 42, 45549 Sprockhövel/D

Introduction

3-monochloropropanediol fatty acid esters (3-MCPD-FE) and glycidyl fatty acid esters (glycidyl-FE) as well as their free compounds belong to the process contaminants (food borne toxins) occurring in numerous foods. These compounds are formed during the manufacturing process of fatty and salty foodstuffs at high temperatures and the refining of fats and oils. Free 3-MCPD and glycidol have been classified by the International Agency for Research on Cancer (IARC) as "potentially carcinogenic to humans“[1]. In 2016, the European Food Safety Authority (EFSA) found out that 3-MCPD-FE and glycidyl-FE in the human organism are almost completely split into free compounds by digestion enzymes. For these substances, a Tolerable Daily Intake (TDI) of 2 µg per kilogram of body weight is defined by the EFSA [1]. Regarding the maximum levels in foodstuffs and food additives, limit values for free 3-MCPD in Regulation (EC) No 1881/2006 and in Regulation (EU) No 231/2012 are harmonized.

Analytics

Three indirect analytical methods are established for the determination of 3-MCPD, glycidol and their esters in routine. These three indirect methods are ISO norms: ISO norm 18636-1 (AOCS Cd 29c-13, DGF C-VI 18 (10)), ISO norm 18636-2 (AOCS Cd 29b-13, Kuhlmann “3 in 1“) and ISO norm 18636-3 (AOCS Cd 29a-13, “Unilever”). The principle of the methods is based on the cleavage of the fatty acid esters and the resulting release of the basic 3-MCPD, which is quantified by GC-MS.

In order to meet the labor-intensive manual preparation of the methods and a faster release of results, we established the automation of the ISO standard 18363-1 because of the short time of ester cleavage. The analysis is split into two assays. In assay A, the sum of bound 3-MCPD and glycidol and in assay B only the bound 3-MCPD is analyzed (Figure 1).

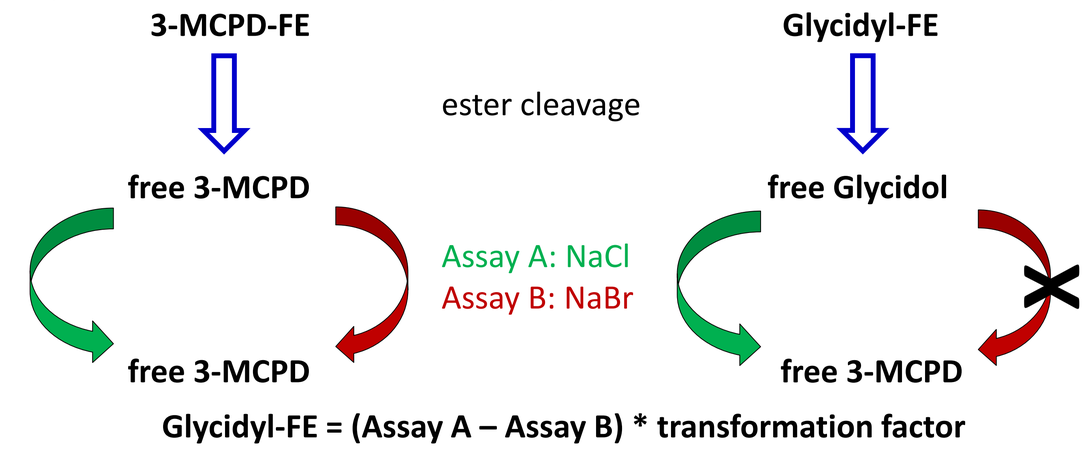

Figure 1: Principle of analysis of the ISO norm 18636-1

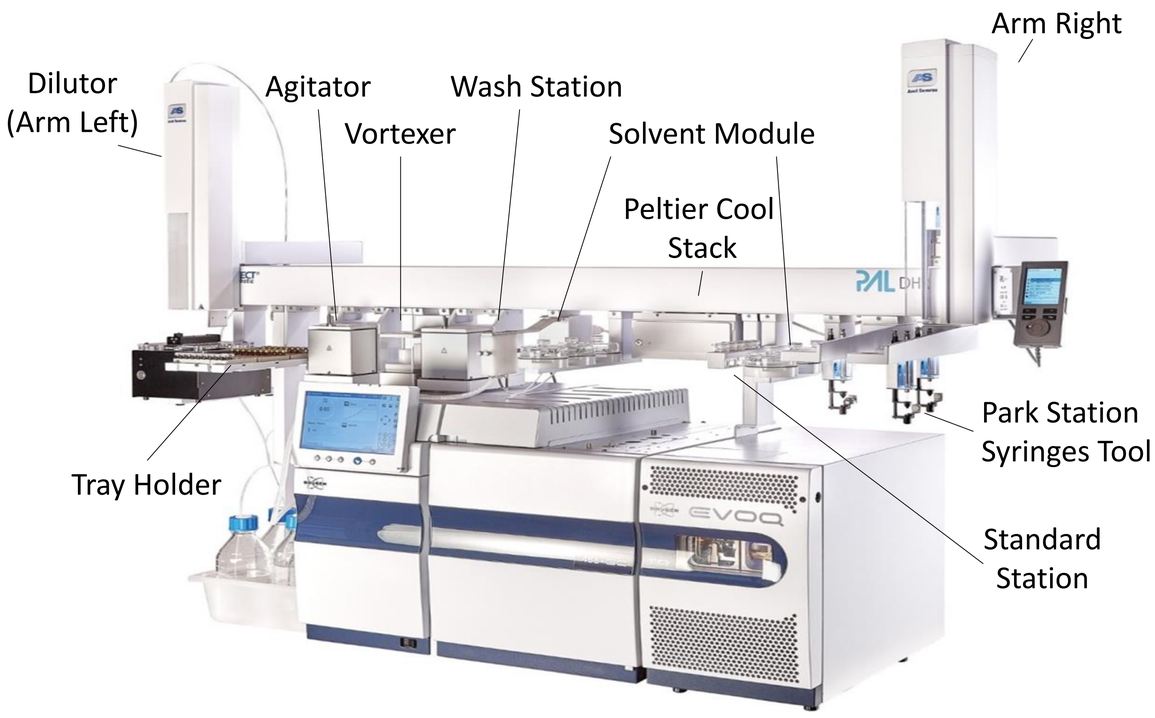

Figure 2: MCPD Workstation

The fully automated determination of 3-MCPD- and glycidyl fatty acid esters in fats and oils as well as in fatty foods is carried out with the MCPD Workstation (Figure 2). The system automates the entire sample preparation, starting from the sample dissolution to the detection with GC-MS/MS (Figure 3).

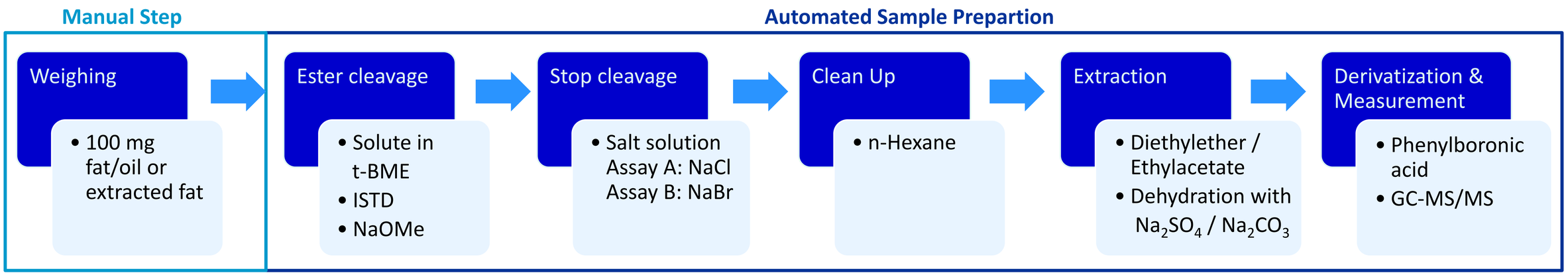

Figure 3: Workflow of the sample preparation

Validation

The coupling of a Dual-Head-System of CHRONECT Robotic to a GC-MS/MS enables a significant time saving, which allows a higher sample throughput. Furthermore, the automated determination is characterized by a minimization of the risk of contamination. The quantification limit and detection limit were determined by 6-fold spiking of free matrix (Figure 4). To determine the precision, correctness and linearity, a 3-fold spiking was carried out on 3 concentration levels (1, 2, 5 mg/kg). The validation data for various matrices demonstrated that the automation is sensitive, precise, correct and robust (Table 1).

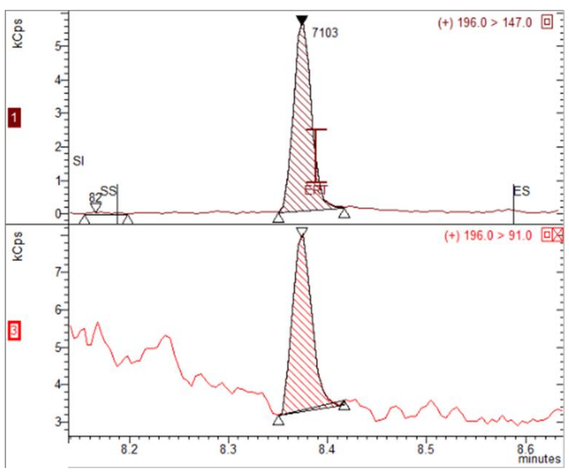

Figure 4: Limit of quantification (0.05 mg/kg fat)

Matrices	Linearity		Recovery		Repeatability		Measurement uncertainty*	
Fat/Oil	Assay A Assay B	4.2% 3.9%	Assay A Assay B	95% 88%	Assay A Assay B	3.9% 2.8%	Assay A Assay B	20% 25%
Biscuit with chocolate	Assay A Assay B	4.3% 2.9%	Assay A Assay B	102% 98%	Assay A Assay B	4.3% 3.6%	Assay A Assay B	20% 20%
Milk Powder	Assay A Assay B	3.4% 5.0%	Assay A Assay B	101% 98%	Assay A Assay B	4.2% 5.7%	Assay A Assay B	20% 25%

Table 1: Validation data for various matrices (*expanded measurement uncertainty, k=2)

Reference:
[1] EFSA Journal 2016;14(5):4426: Risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food, EFSA Panel on Contaminants in the Food Chain (CONTAM)

www.institut-kirchhoff.de