CHRONECT by TRAJAN

APPLICATION NOTE

Determination of MCPD and glycidyl ester in foodstuff

with the CHRONECT™ Workstation MCPD and the module ISO 18363-3

Introduction

This application note describes the fully automated determination of 2- and 3-MCPD and glycidol in fats and oils according to the official AOCS method Cd29a-13 - Acidic Transesterification using the CHRONECT™ Workstation MCPD. Glycidyl (GE), 2-monochloropropane-1,3-diol (2-MCPD) and 3-monochloropropane-1,2-diol (3-MCPD) fatty acid esters are carcinogenic and fruit-damaging food contaminants in edible fats and oils that are now part of the established analytical repertoire of commercial and routine laboratories. Glycidyl and 2- and 3-MCPD esters form under elevated temperatures in the presence of chlorine, e.g., during desodorization during the refining process. In addition, glycidol and 2- and 3-MCPD can already form during fruit growth (e.g., in palm), provided the plant grows on chlorine-containing soil. Many food manufacturers therefore already check the levels of glycidol and 2-/3-MCPD before and after the refining process.

There are several official methods for analyzing the three contaminants, including the AOCS Cd29a-13 method from the American Oil Chemist Society (AOCS). This was originally published by Ermacora and Hrncirik of the company Unilever in 2013. Hence the colloquial name: "Unilever method", which also corresponds to ISO 18363-3.

In this method, the glycidyl esters are initially converted to 3-monobromopropane-1,2-diol esters (3-MBPD-E) in the presence of bromide (Figure 1). Subsequently, all three ester-bound contaminants are cleaved from the fatty acids under acidic conditions and elevated temperature (40 °C). The free fatty acids are extracted in a subsequent step and the now free glycidol, 2- and 3-MCPD are derivatized with phenylboronic acid. The derivatives are extracted and injected into a GC-MS system. The corresponding ion traces for the three derivatives then provide a chromatogram as shown in Figure 2. In addition, for each analyte, a signal is also obtained for the deuterated variant, which is added at the beginning as an internal standard.

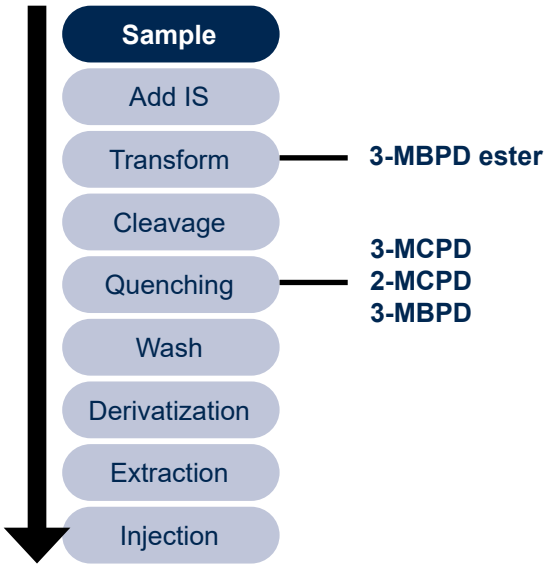

Figure 1. Schematic illustration of sample preparation according to the official AOCS Cd29a-13 method using the CHRONECT™ Workstation MCPD – Module ISO 18363-3.

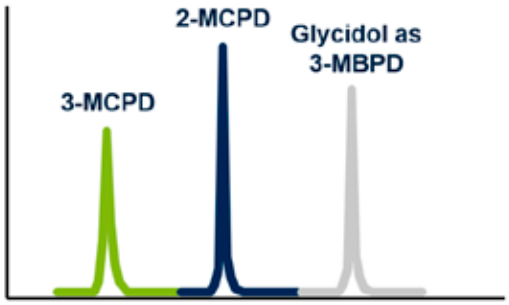

Figure 2. Schematic chromatogram with the ion traces for 2-MCPD, 3-MCPD and glycidol.

Figure 3. CHRONECT™ evaporation module on a 120 cm PAL3 with the configuration for the AOCS Cd29a-13 method.

Instrument setup

The CHRONECT™ Workstation MCPD - Module ISO 18363-3 includes everything needed for fully automated sample preparation. An important step in sample preparation according to the AOCS Cd29a-13 method is evaporation to change the solvent or for concentration before injection into the GC-MS. The CHRONECT Workstation MCPD - Module ISO 18363-3 includes an evaporation unit (Figure 3) to perform these evaporation steps fully automated. A pressure program is applied with the aid of additional gas control by CHRONOS™ to ensure efficient evaporation.

In addition to this module, the workstation includes modules such as a vortex mixer, agitator, quick wash station and holders for samples and solvents. Additionally, parking stations are in-stalled for the use of different syringes during sample preparation.

With the additional integrated dilutor module, up to six different solvents are available. The CHRONECT Workstation MCPD - Module 18363-3 can be configured in different sizes according to the sample volume.

Measurement parameters and results

An important criterion for the automation of manual sample preparation is the appropriate sensitivity and robustness of the system. For this purpose, a calibration of glycidol as well as 2- and 3-MCPD in a range from 25 µg/kg to 2500 µg/kg has been established in a first step, as shown in Figure 4. The linearity of all components is clearly evident with a correlation coefficient of > 0.99 for at least nine data points in the measurement range.

To achieve a detection strength with limits of quantification of 25 µg/kg, a correspondingly low blank value is required. Figure 5 shows that all blank values measured on five consecutive days are below 11 µg/kg. Especially 2-MCPD and glycidol show very low blank values (< 5 µg/kg).

One criterion for the robustness of a sample preparation is the analysis of a sample on several consecutive days. Figure 6 shows the analysis of such a spiked olive oil sample for 500 µg/kg glycidol, 2- and 3-MCPD on six consecutive days. The relative standard deviation of all components over the period was less than 2.9 % in each case, with recoveries between 95 and 101 %.

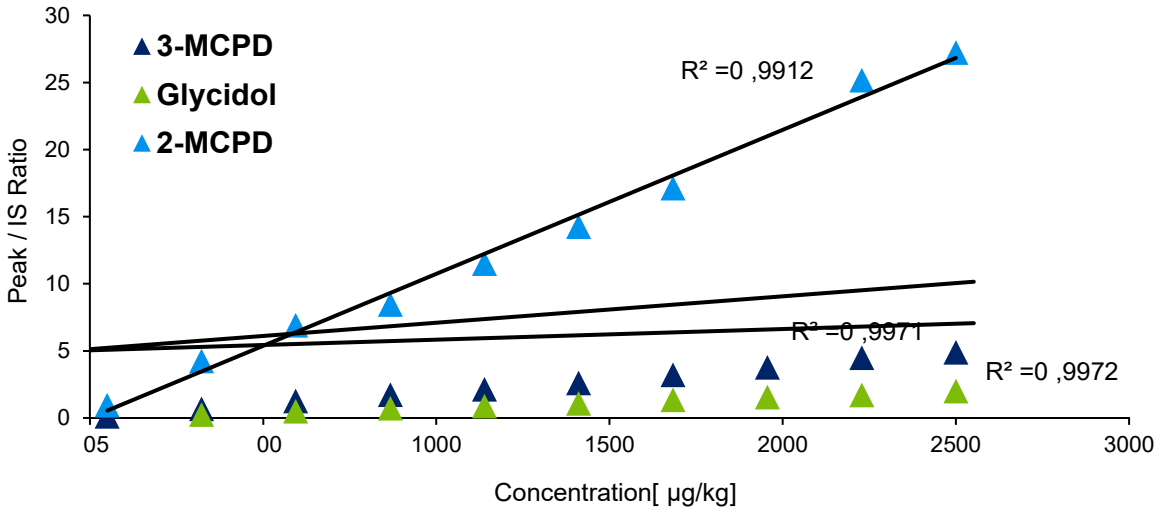

Figure 4. Calibration lines for the three components 2-/3-MCPD and glycidol over a concentration range from 25 µg/kg to 2500 µg/kg.

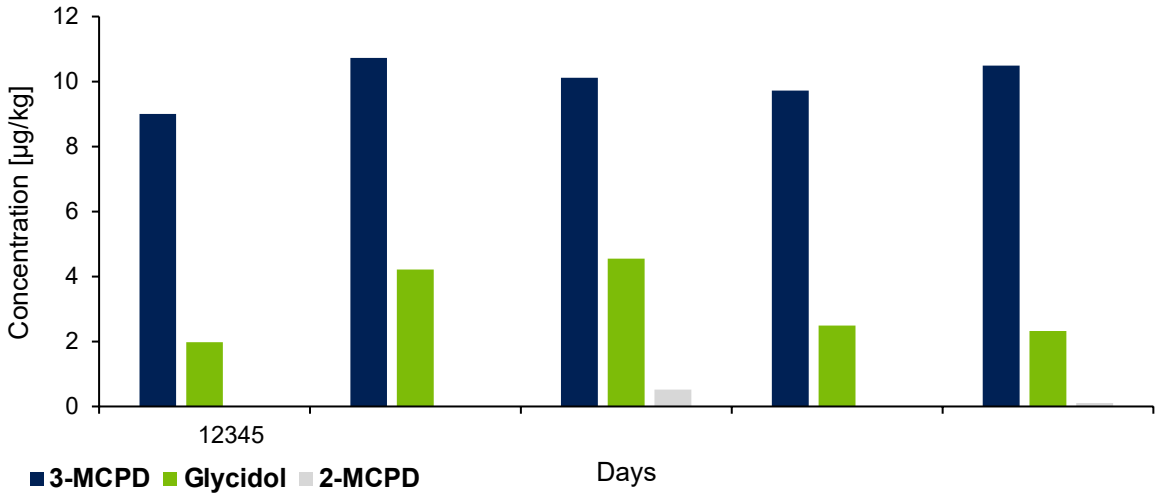

Figure 5. Blank values (n = 5) measured using an olive oil for five consecutive days.

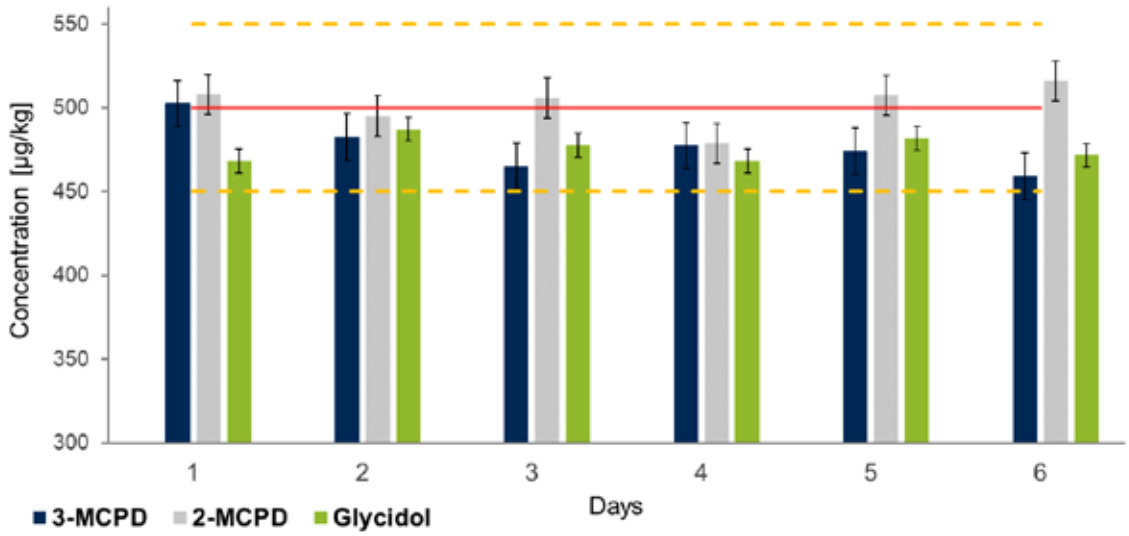

Figure 6, Recovery and reproducibility for six consecutive days for 2-/3-MCPD and glycidol with spiked olive oil (500 µg/kg).

Finally, the comparability of the results from the automated sample preparation is compared with results from samples of two different ring tests. For this comparison, two materials from FAPAS ring test trials (T2649 and T2658) were selected. As can be seen in Figure 7, the results agree very well (RSD < 5 %) with those from the interlaboratory test and are within the z-range of 2 around the determined values of FAPAS from the interlaboratory tests.

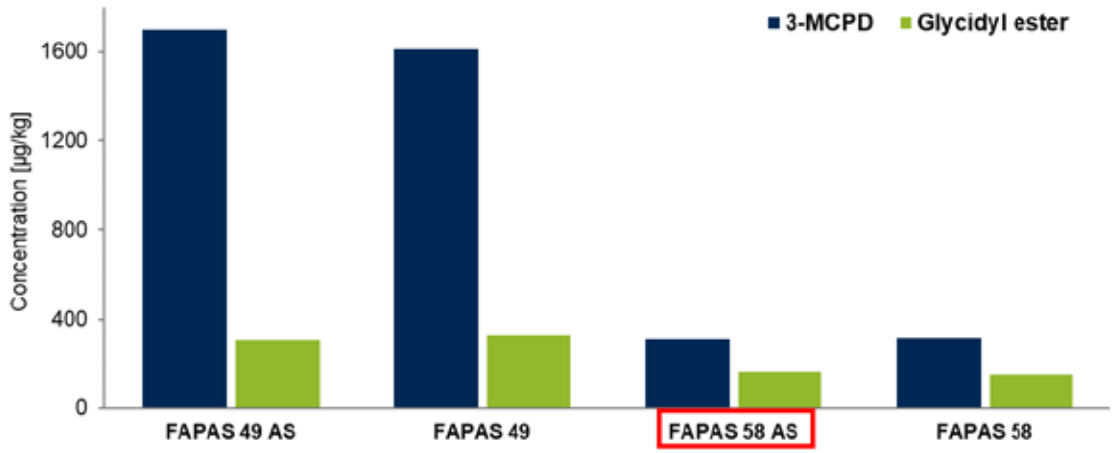

Figure 7. Comparison of automated results of CHRONECT™ Workstation MCPD – Module ISO 18363-3 (AS, red) with ring test results.

Evaluation of the results

The very good linearity in the measured concentration range from 25 µg/kg to 2500 µg/kg coupled with the excellent reproducibility and recovery for glycidol, 2-MCPD and 3-MCPD show that from an analytical point of view nothing prevents you from switching to automated sample preparation. The only manual step in sample preparation is the weighing of fat/oil samples. The subsequent preparation runs fully automatically, including injection into a GC-MS system, and can also prepare several samples simultaneously. Since the values obtained from the automated sample preparation also agree very well with the values obtained from the manual sample preparation, a consistent quality of the data in the automated process is ensured.

With a transesterification time of at least 16 hours for the official AOCS Cd29a-13 method, it is additionally possible to perform other operations such as standard dilutions or further sample preparation in the unused time of the autosampler.

The CHRONECT™ Workstation MCPD - Module ISO 18363-3 is an excellent addition to your laboratory in a routine environment with reliable data. The method presented has the advantage that a sample can be analyzed for 2- and 3-MCPD and glycidol in a single run. Due to the flexible CHRONECT robot autosampler platform, it is also possible to perform sample preparation using the "DGF Fast & Clean" method. In addition, the workstation can be extended to include the other official AOCS methods Cd29b-13, AOCS Cd29c-13 and AOCS Cd29d-20 by a minor modification.

For more information visit www.trajanscimed.com or contact techsupport@trajanscimed.com

The MCPD Workstation with Module ISO 18363-3 is a development by Trajan.
Subject to technical changes.