Fully automated sample preparation for the determination of plasticizers in PVC from food contact materials and toys

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Introduction

Food contact materials (FCM) made from PVC, such as e.g. gaskets of metal lids or cling films, may release plasticizers into the packed food. Such migration repeatedly exceeded legal limits or non-authorized plasticizers have been used. In a European enforcement campaign on migration from gaskets into oily foods in 2011, for example, legal limits were exceeded in 24% of the 308 samples analyzed [1]. The EU also banned the use of certain phthalates as plasticizers for toys and childcare products, whereas its content is limited to below 0.1 % [2]. Furthermore the directive 2011/65/EU will restrict "certain hazardous substances in electrical and electronic equipment", including the same group of phthalates [3]. Plasticizers are analyzed and quantified by GC-FID or MS, if detection limits lower than 0.1 % are required. So far up to 40 different plasticizers were found and quantified in FCM and toys.

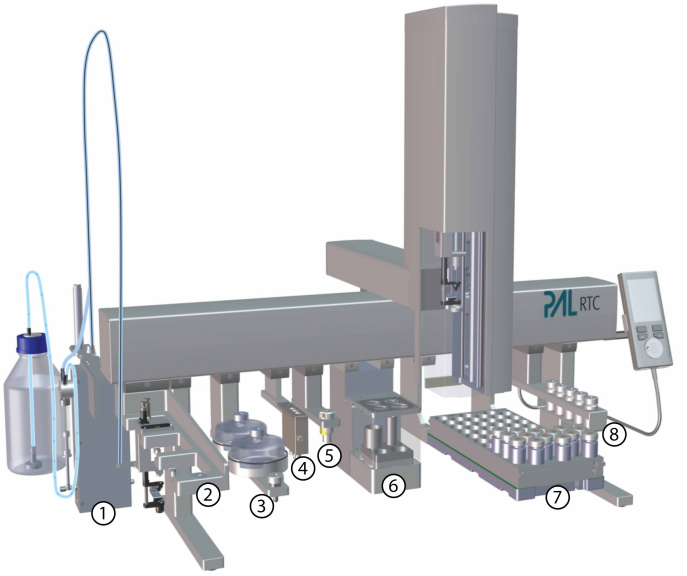


Figure 3: 1: dilutor (dosage of solvents and solutions), 2: park station, 3: large wash module (container for ethoxide/ethanol solution), 4: LCMC wash module (outside rinsing of syringe of dilutor), 5: MHE tool (pressure release of sample and derivatization vials), 6: vortex mixer module, 7: tray holder, 8: standard wash module

Analytical method

A piece of the PVC is solved in tetrahydrofuran and precipitated with ethanol. The supernatant is analyzed directly as well as after transesterification to ethyl esters. Transesterification enables the detection of epoxidized soybean oil (ESBO), epoxidized linseed oil (ELO) and polyadipates (PA), but also confirm the identifications of the direct analysis through the transesterified products [4]. Furthermore, after transesterification phthalates may be determined as sum parameter.

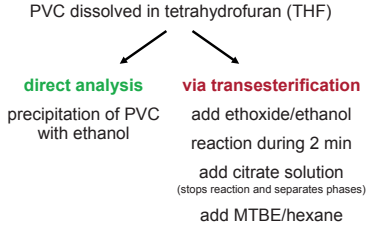


Figure 1: Procedure of the sample pretreatment. Two analysis of one sample are preformed by either GC-FID or MS.

Example: test mixture

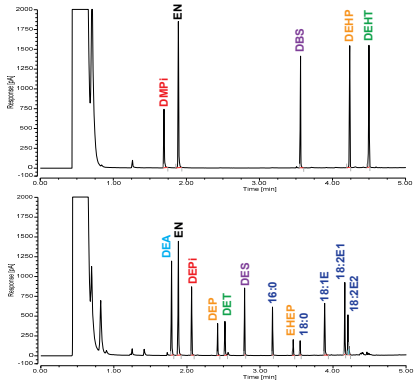


Figure 2: GC-FID chromatograms of test mixture, analyzed before and after transesterification: DMPi dimethyl pimelate, EN 1-ethyl naphthalene, DBS dibutyl sebacate, DEHP di-(2-ethylhexyl) phthalate, DEHT di-(2-ethylhexyl) terephthalate, DEA diethyl adipate, DEPi diethyl pimelate, DEP diethyl phthalate, DET diethyl terephthalate, EHEP 2-ethylhexyl ethyl phthalate, 16:0-18:2E (epoxidized) fatty acid ethyl esters from ESBO

- *Internal standards:* transesterification yield and onset saponification is monitored by comparing the peak areas of the inert internal standard **EN** with **DMPi** transesterified to **DEPi** (verification).
- *Polyadipates:* quantified after transesterification via **DEA**, calibrated by certain types of polyadipates.
- *ESBO, ELO:* quantified after transesterification via sum of fatty acid ethyl esters (**FAEE**) or selected FAEE, calibrated on ESBO or ELO.
- *Verification of identity:* **DBS** by **DES**; **DEHP** by **DEP**, **DEHT** by **DET**.
- *Sum parameter:* quantification of **DEP** (complete transesterification required), screening for absence of phthalates, e.g. <0.1 %, calibrated on the largest phthalate to be detected.

Automatization

The PAL RTC autosampler and its ability of exchanging e.g. diluting and injection tools offers the possibility to fully automate all steps of sample preparation and derivatization. The automatization not only eliminates lab work, it also allows an automated elaboration of optimized conditions for transesterification.

Modules of automated method

The sample pretreatment consists of three parts; automation starts after weighing of e.g. 50 mg of PVC into a 10 ml autosampler vial.

1 Dissolution
2 Direct analysis
3 Analysis after transesterification

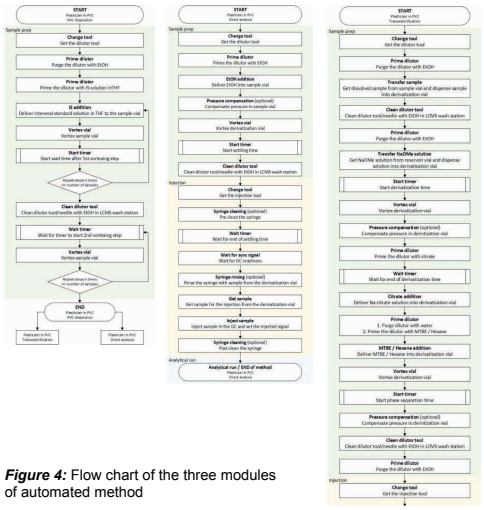
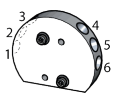


Figure 4: Flow chart of the three modules of automated method



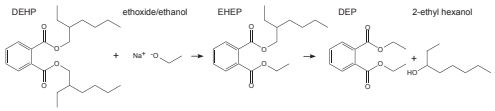
1 Tool
2 Water (Waste)
3 Ethanol
4 Sodium ethylate solution
5 MTBE / Hexane (4+6)
6 Disodium citrate solution

Figure 5: Up to 5 different solvents and solutions may be dispensed by the dilutor tool.

GC conditions, instrumentation

Injection:	0.5-2 µl, injection with band formation, split injection, split flow 20 ml/min, 250 °C
Injector liner:	packed with glass wool
Separation column:	20 m x 0.25 mm i.d., 0.15 µm 100 % dimethyl PS
Carrier gas:	Hydrogen (FID), helium (MS) 60-80 kPa const. press.
Oven temp. program:	60 °C (0.5 min), 30 °/min to 110 °C, 50 °/min to 300 °C
Instrumentation:	PAL RTC, CTC Analytics, Trace 1310, DSQ II, Thermo Scientific

Transesterification



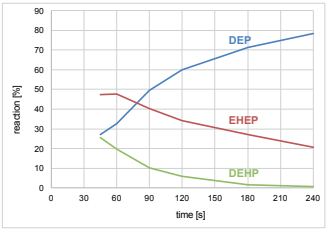


Figure 6: Example, conversion of DEHP to DEP via EHEP.

Verification

The transesterification reaction must be stopped by adding a citrate buffer after complete reaction before onset saponification. The precise reaction time is established by running a test sample under different conditions. The yield of transesterification and the start saponification is monitored by comparing an inert standard (EN) with a standard (DMPi) which is transesterified.

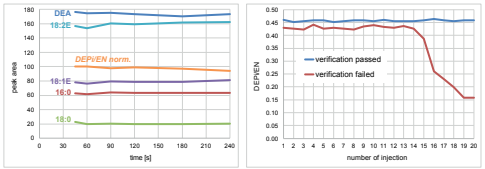


Figure 7: Incomplete transesterification or saponification results in a lower ratio of DEPi/EN. Left graph: comparison of the verification ratio (normalized to 100) with the transesterification products of PA and ESBO; complete transesterification already after 45 s, no significant saponification up to 240 s. Right graph: example of failed verification; during the second series of 20 samples (red line) derivatization failed after sample #14 due to less ethoxide added (partially blocked tube).

Summary

- Comprehensive analysis of plasticizers
- Automatization provides:
  - constant derivatization conditions
  - less lab work
- Derivatization monitored by verification standard
- Fast GC: 10 min cycle time

References

[1] G. McCombie, A. Harling-Vollmer, M. Morandini, G. Schmäschke, S. Pechstein, W. Altkofer, M. Biedermann, S. Biedermann-Brem, M. Zurfluh, G. Suter, M. Landis, K. Grob Eur Food Res Technol 235 (2012) 129–137.
[2] Directive 2005/84/EC of the European parliament and of the council, Dec. 14th 2005
[3] Directive 2011/65/EU of the European parliament and of the council, June 8th 2011
[4] S. Biedermann-Brem, M. Biedermann, K. Fiselier and K. Grob Food Additives and Contaminants 22 (2005) 1274-1284.

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