Talanta 182 (2018) 505–522

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Effect of the cleaning procedure of Tenax on its reuse in the determination of plasticizers after migration by gas chromatography/mass spectrometry

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ARTICLE INFO

Keywords:
Tenax
Plasticizers
Benzophenone
PTV-GC/MS
PARAFAC
Migration test

ABSTRACT

This paper presents the simultaneous determination of a UV stabilizer (benzophenone (BP)) together with four plasticizers (butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)) in Tenax by gas chromatography/mass spectrometry and PARAFAC, using DiBP-d_4 as internal standard.

Regulation (EU) No. 10/2011 establishes Tenax as food simulant E for testing specific migration from plastics into dry foodstuffs. This simulant must be cleaned before its use to eliminate impurities. Tenax is expensive, so its reuse would save costs.

A two-way ANOVA was used to study some parameters affecting the cleaning and the extraction of Tenax. The most adequate conditions were chosen taking the values of the coefficient of variation and the average recovery rates of spiked Tenax samples into account.

A study to determine if some analytes remain in Tenax when it is reused and the effect that the cleaning procedure may have in the adsorption capability of Tenax was proposed. This study led to the conclusion that Tenax could not be reused in this multiresidue determination.

All the analytes were unequivocally identified in all the stages of this work and trueness was verified at a 95% confidence level in all cases. A calibration based on PARAFAC provided the following values of capability of detection (CCβ): 2.28 $\mu g\,L^{-1}$ for BHT, 10.57 $\mu g\,L^{-1}$ for BP, 7.87 $\mu g\,L^{-1}$ for DiBP, 3.04 $\mu g\,L^{-1}$ for DEHA and 124.8 $\mu g\,L^{-1}$ for DiNP, with the probabilities of false positive and false negative fixed at 0.05.

The migration of the analytes from a printed paper sample into Tenax was also studied. The presence of BHT in the food simulant was confirmed and the amount released of this analyte from the paper was 2.56 $\mu g\,L^{-1}$.

1. Introduction

The migration of chemicals from food contact materials into food is an important issue in food safety to ensure the protection of human health and the interests of consumers. Food contact materials are all materials and articles intended to come into contact with food such as plastics, paper, ceramic, metals and ink used in food packaging, food containers, etc.

General requirements for all food contact materials are laid down in Framework Regulation (EC) 1935/2004 [1]. The main principle of this Regulation is that any material or article intended to come into contact directly or indirectly with foodstuffs must be sufficiently inert so as not to transfer substances to food in quantities which would: i) endanger human health, ii) bring about an unacceptable change in the composition of the food or iii) bring about a deterioration in the organoleptic properties of the food. The group of materials and articles listed in Annex I of [1] should be manufactured in compliance with the general and detailed rules on good manufacturing practice described in Regulation EC 2023/2006 [2].

However, no food contact material is completely inert, and foodstuffs can be aggressive products that may interact with these materials. Therefore, it is possible that the chemical constituents of food contact materials may migrate into the packaged food [3,4].

Regulation (EU) No 10/2011 [5] establishes poly (2,6-diphenyl-p-phenylene oxide), which is better known under its trade name Tenax®, as food simulant E for testing specific migration from plastics into dry

Abbreviations: BP, Benzophenone; BHT, butylated hydroxytoluene; DiBP, diisobutyl phthalate; DEHA, bis(2-ethylhexyl) adipate; DiNP, diisononyl phthalate; CCβ, capability of detection, EURL-FCM, European Reference Laboratory for Food Contact Materials; ILC, interlaboratory comparison; IS, internal standard; SMLs, specific migration limits; RASFF, Rapid Alert System for Food and Feed; EI, electron impact; SIM, single ion monitoring; ANOVA, analysis of variance; CCα, decision limit; CORCONDIA, core consistency diagnostic; LS, linear least squares; α, probability of false positive; β, probability of false negative; H_0, null hypothesis; H_a, alternative hypothesis; TIC, total ion chromatogram

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https://doi.org/10.1016/j.talanta.2018.02.011
Received 12 December 2017; Received in revised form 1 February 2018; Accepted 4 February 2018
Available online 08 February 2018

foodstuffs. This regulation also indicates the specifications that must fulfil this simulant: particle size of 60–80 mesh and a pore size of 200 nm. Cereals, sugar, dried or dehydrated fruits and vegetables, milk powder including infant formula, cocoa powder, coffee, spices and seasonings in the natural state such as cinnamon, powdered mustard, pepper, vanilla, saffron, salt and dry pasta such as macaroni and spaghetti are examples of dry foodstuffs according to [5].

The European Reference Laboratory for Food Contact Materials (EURL-FCM) has organised several interlaboratory comparison (ILC) exercises related to the identification, migration and quantification of potential migrant substances into food simulant E. In 2012, the EURL-FCM published a report [6] concerning the results of one of the ILCs whose general aim was to evaluate the laboratory performance and precision criteria of the harmonised method for the extraction and quantification of the model substances from Tenax and also for the migration test from a fortified plastic film into this simulant. Then, in 2013, the EURL-FCM performed another ILC [7] about the identification and quantification of unknown substances spiked in Tenax. Regarding the identification of the unknown substances, 48% of the national reference laboratories could identify correctly all the substances, whereas 76% of the laboratories identified correctly all the substances in a follow-up study [8] which reflects the complexity of the analysis.

Tenax is a porous polymer with high adsorption capacity as bulk powder material that efficiently traps volatiles [9,10]. This product presents several advantages such as high thermal stability and high adsorption capacity [10]. In addition, it is reusable many times after its cleaning according to some works [10,11]. However, as far as the authors are aware, there are no studies on the effect that the extensive cleaning of Tenax by Soxhlet may have on its adsorption capability [11,12]. On the other hand, Tenax is expensive [10,11] and difficult to manage [6] since it is a fine and light powder prone to static electricity. The cleaning of Tenax is extremely important since it contains impurities when is sold in bulk, so it must be cleaned prior to its use, even in its first use [9]. Tenax can be cleaned up, for example, by extraction with isooctane [11], diethyl ether [13], etc.; or by Soxhlet extraction using different solvents such as acetone [6,9], diethyl ether [10], acetonitrile [12], methanol and hexane [14].

Apart from plastics, printed paper and board are the most commonly used food packaging materials [15] that can be in contact with food directly or indirectly [16]. These materials are listed in Annex I of the Framework Regulation [1] as a type of material that should be covered by specific harmonised rules. However, they are not currently covered by specific European legislation. This is the reason why the present work followed the requirements laid down in [5] although this regulation is specific for plastic materials.

The migration testing conditions for materials and articles not yet in contact with food are specified in the Commission Regulation (EU) 2016/1416 [17] which amends the ones established in [5]. The sample shall be placed in contact with the food simulant for a test contact time and at a test contact temperature which should be selected in such a way that they represent the worst foreseeable conditions of use [17].

The migration behaviour of components from paper, cardboard and/or board into Tenax has been compared to the migration into dry foodstuffs such as, for example, fresh fruits [18,19], vegetables [18], cereals, rice [12], salt and sugar [20]. These studies concluded that the food simulant tends to overestimate migration values in comparison with food, so the results obtained with the simulant have a safe margin for consumer protection. In fact, Zurfluh et al. [21] stated that Tenax is a much stronger adsorbent than dry foodstuffs.

In this work, Tenax was used for the determination of four plasticizers (butylated hydroxytoluene (BHT), diisobutyl phthalate (DiBP), bis(2-ethylhexyl) adipate (DEHA) and diisononyl phthalate (DiNP)) together with benzophenone (BP), which is an ultraviolet (UV) stabilizer, by gas chromatography/mass spectrometry and PARAFAC using DiBP-d_4 as internal standard (IS). Specific migration limits (SMLs) have been set for these analytes in [5].

Plasticizers are used as additives to improve the flexibility of plastic materials, especially in PVC articles. The most commonly used plasticizers are phthalates which are endocrine disruptors since they interfere with the endocrine and hormone system [22]. In addition, phthalates may be involved in autism spectrum disorders, asthma's pathogenesis and cancer in humans [23]. Certain phthalates are ubiquitous in the environment even in the laboratory due to their widespread use. The problem of the ubiquity of DiBP by a non-constant leaching process in the laboratory was detected and overcome in the determination of plasticizers in a previous work [24]. Phthalates can also easily migrate into food [25]. Therefore, considering their toxicity and ubiquitous presence, reliable analytical methods that allow their identification and quantification should be developed.

The use of antioxidants and UV-absorbers are important to protect plastic materials against degradation [22]. BHT is an antioxidant used in food packaging to slow the degradation from exposure to UV light [26], while benzophenone is widely used as a photoinitiator to cure inks and varnishes with UV light for the printing of packaging materials used in food applications [12] such as printed paper and board.

Different EU countries have transmitted to the Rapid Alert System for Food and Feed (RASFF) [27] several notifications in relation to the migration of BP, DiBP, DEHA and DiNP from food contact materials and the presence of BHT in food and feed over the last years. RASFF has reported 5 notifications for BHT, 23 for BP, 2 for DiBP, 13 for DEHA and 42 for DiNP from 24/08/2004 to 29/06/2017. Some notifications for BP have been transmitted through RASFF due to the migration of this compound from carton boxes containing cereal products. An alert about the migration of BP from ink on cartons containing bags with milk powder and cinnamon powder from Turkey was also sent. The amounts of BP found in this case were 428 $\mu g\, kg^{-1}$ for the milk powder and 50.2 $mg\, kg^{-1}$ for the cinnamon powder.

This work deals first with the study of the effect of some parameters that affect the cleaning and the extraction of Tenax on the recovery of the analytes. Then, another study to determine if Tenax could be reused in this multiresidue determination was carried out. Tenax is an expensive simulant (100 g costs around 3500 euros), so reusing Tenax could be important to avoid high costs in the analyses.

Migration tests were also performed on a printed paper sample intended to come into contact with dry foodstuffs using the polymeric powder Tenax as food simulant.

Up to the authors' knowledge, this is the first time that the PARAFAC decomposition has been carried out with data from analyses of Tenax as food simulant.

2. Material and methods

2.1. Chemicals

Tenax TA (refined), particle size 60–80 mesh, was obtained from Supelco (Bellefonte, USA) and cleaned up prior to use. All the Tenax used in this work came from the same batch.

Diisobutyl phthalate (CAS no. 84-69-5), diisobutyl phthalate-3,4,5,6-d_4 (CAS no. 358730-88-8; analytical standard), diisononyl phthalate (CAS no. 28553-12-0; ester content ≥ 99%, mixture of C_9 isomers), 2,6-di-tert-butyl-4-methyl-phenol (CAS no. 128-37-0), bis(2-ethylhexyl) adipate (CAS no. 103–23-1) and benzophenone (CAS no. 119-61-9; purified by sublimation), all of 99% or higher purity, were purchased from Sigma-Aldrich (Steinheim, Germany). Acetone (CAS no. 67-64-1; for liquid chromatography Lichrosolv®) and n-hexane (CAS no. 110-54-3; for liquid chromatography Lichrosolv®) were obtained from Merck KGaA (Darmstadt, Germany).

2.2. Standard solutions

Stock solutions of DiBP, DEHA and DiNP at 2000 $mg\, L^{-1}$, of BHT and BP at 1000 $mg\, L^{-1}$, and of DiBP-d_4 at 700 $mg\, L^{-1}$ were prepared