Migration kinetics of primary aromatic amines from polyamide kitchenware: Easy and fast screening procedure using fluorescence

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ABSTRACT

Primary aromatic amines, PAAs, and their derivatives constitute a health risk and control of their migration from food contact materials is the subject of permanent attention by the authorities. 25.1% of notifications made by Rapid Alert System for Food and Feed in the European Union between 2010 and 2015 concerned PAAs, polyamide cooking utensils being a common source. It is thus useful to have fast and efficient analytical methods for their control.

In this work a non-separative, easy, fast and inexpensive spectrofluorimetric method based on the second order calibration of excitation-emission fluorescence matrices (EEMs) was proposed for the determination of aniline (ANL), 2,4-diaminotoluene (2,4-TDA) and 4,4′-methylenedianiline (4,4′-MDA) in polyamide cooking utensils. The procedure made it possible to identify unequivocally each analyte. Trilinearity of the data tensor guarantees the uniqueness of the solution obtained through parallel factor analysis (PARAFAC), so the factors of the decomposition match up with the analytes. The three analytes were unequivocally identified by the correlation between the pure spectra and the PARAFAC excitation and emission spectral loadings. The recovery percentages found were, 82.6%, 112.7% and 84.4% for ANL, 2,4-TDA and 4,4′-MDA respectively. The proposed method was applied to carry out a migration test from polyamide cooking utensils, using a 3% (w/v) acetic acid in aqueous solution as food simulant. Detectable levels of 4,4′-MDA were found in food simulant from some of the investigated cooking utensils. Finally, a kinetic model for the migration of 4,4′-MDA has been fitted to experimental data obtained in the migration test. Thanks to the selectivity of PARAFAC calibration, which greatly simplifies sample treatment avoiding the use of toxic solvents, the developed method follows most green analytical chemistry principles.

1. Introduction

PAAs are a group of compounds that have been used, for many decades, as raw materials and intermediates in a wide variety of production processes, including pesticides, textiles, and paints (azo-dyes), polymers, pharmaceuticals and cosmetics [1]. As a consequence, many industrial sectors use PAAs. According to the Ref. [2] this use can be distributed as: 25% in the chemical industry, 14% in the industry of polymers and rubber, 8% in agriculture, 9% in adhesives and paintings, 7% in the textile industry, 8% in the pharmaceutical industry and minor percentages in the petroleum, cosmetic and paper industries or in construction.

As an example of the growth in PAA production there is the case of ANL. This compound is not only an important organic chemical raw material, but also an important product. There are more than 300 kinds of chemical products and intermediates derived from it. Only in the year 2001, in USA, the production of ANL was of 8.67×10^8 kg [2]. World consumption of ANL grew at an average annual rate of 3% during 2006–10, and by nearly 7% per year from 2009 to 2014. This increase was driven by the strong recovery in most regions and countries since 2010, and growth in methylene diphenyl diisocyanate (MDI) production, which is used to make polyurethane foam, both rigid and flexible. The global

production of aniline was about 2.97×10^9 kg in 2000 and now has exceeded 3.00×10^9 kg (3000 kt/y). It is predicted that the demand for ANL will have a larger increase with the expansion of demand for MDI.

Many of the commercial products, PAA based, can be used in the production of food contact materials (FCMs). Additionally, PAAs may also arise from isocyanates that can be used in the manufacture of FCMs, such as polyurethanes, which are frequently used as adhesives in multilayer films. If the production conditions are not carefully monitored, excess residual PAAs can remain in the final product and potentially migrate into food during use of FCM.

PAAs are potentially harmful and suspected to cause cancer and have other adverse effects. Several PAAs have been classified as "possibly carcinogenic to humans" by the World Health Organization and International Agency for Research on Cancer (WHO/IARC) [3]. For example, 2,4-TDA and 4,4′-MDA are listed in group 2B (possibly carcinogenic to humans) while ANL has been classified in group 3 (not classifiable as to its carcinogenicity to humans). Hence, their presence in foodstuffs should be generally avoided. According to present legislation, the European Union has set a legal limit on the permitted level of PAA migration from materials intended to come in contact with food. As laid down by Regulation 10/2011 [4] these articles should not release PAAs above a detection level of 10 µg kg^{-1} in food or food simulant.

One common food contact source of PAAs, polyamide cooking utensils, was identified for several years [5]. These utensils, such as turners, whisks and spoons, are popularly used due to their low cost, high temperature resistance and non-scratch properties. The migration of PAAs from polyamide utensils into foodstuffs can occur [6–9] however, due to remaining residues present from the coloring process (using azo-dyes) and co-monomer addition [9–12].

Many techniques have been described in the literature for the determination of PAAs in extracts of FCMs. These included liquid chromatography-tandem mass spectrometry (LC-MS/MS) in migrates from several samples of FCMs finding that unacceptably high amounts of PAAs are released by black nylon kitchen utensils to the food simulant (the'non-detectable' limit was exceeded by up to 2100 times) [13]. Aznar et al. [14] described a method for the determination of PAAs based on a solid-phase extraction step using cation-exchange cartridges and the subsequent analysis of the extracts by ultra-high-performance liquid chromatography with mass spectrometry. Brauer et al. [15] proposed a screening method using high pressure liquid chromatography (HPLC) to determine specifically the migration of primary aromatic amines from food contact articles. Lambertini et al. [16] developed a reliable liquid chromatography–mass spectrometry method for investigation of PAA migration from food packaging and during industrial curing of multilayer plastic laminates. Recently [17] by means of a liquid chromatography–orbitrap-high resolution mass spectrometry (LC–HRMS) operating in full scan mode a procedure is developed to determine migrating substances in kitchen utensils including also PAAs. In Ref. [17] a comprehensive analytical method based on ultra-performance liquid chromatography coupled with triple quadrupole mass spectrometry (UPLC-MS/MS) has been applied to determine PAAs in polystyrene and polyethylene master batches for foods.

Rubio et al. [18] presents a headspace solid-phase microextraction and gas chromatography coupled with mass spectrometry (HS-SPME-GC/MS) method for trace determination of PAAs in water. Prior to extraction the analytes were derivatized in the aqueous solution by diazotation and subsequent iodination. A PARAFAC or PARAFAC2-based calibration model was carried out for each analyte.

In [19] a rapid screening method to determine primary aromatic amines in kitchen utensils using direct analysis in real time mass spectrometry (DART-MS) is developed and it could be used to identify potentially volatile samples, thus limiting the number of samples that would require very time consuming migration testing by means of a chromatographic method.

All these methodologies are often laboratory-based and time-consuming and may lead to large capital costs for multisample analysis. However continued vigilance is needed of the migration of PAAs as a result of the frequent violation of the limits stated. For example, notifications on PAAs given by the Rapid Alert System for Food and Feed, RASFF, relating to the migration from kitchen utensils made of nylon mainly imported from China, report an annual number of notifications that range from 18 to 35 since 2010. Specifically, between 17% and 34% of all the alerts correspond to migrants from FCMs. In most cases, ANL and 4–4′ MDA were identified [20].

In this context, molecular fluorescence spectroscopy is of interest due to its high sensitivity, ease of use and especially because cost reduction of every analysis is possible. These advantages, allow one to increase the sample size in routine control without increasing the expense and without to block the official laboratories with a lot of analysis. Nevertheless, the recorded signals proceeding from the compounds of interest can be overlapped by the presence the signals of other molecules or ions; for this reason, the excitation-emission matrices (EEM) need to be analyzed by means of three ways techniques in order to obtain the separation of the signals of the different fluorophores. This separation is possible even in presence of the quenching effect [21]. When PARAFAC is used, with trilinear data, the mathematical decomposition is unique, so that the factors obtained mathematically correspond with the fluorophores present in the sample. Once the trilinearity of the data tensor has been checked, the unequivocal identification of each analyte is possible by means of two independent ways: both the excitation and emission spectra. In addition, it is possible to quantify in presence of other absent compounds in the calibration standards (the 'second order' property).

In this work the generalized standard addition method was used, adding to the extract obtained in the migration test, ternary mixtures of three PAAs and using as analytical signal the sample loading related to each amine. As a consequence, other fluorophores which have migrated from the analyzed sample, but different from the amines analyzed, are kept almost constant in the successive additions (also their loading sample), and consequently the data tensor loses the trilinearity. To solve this, a procedure consisting of subtracting the factors related to fluorophores of the matrix from the original tensor was proposed, recovering the trilinearity and so one can identify unequivocally and quantify the PAAs in the samples from the test of migration. This procedure has already been used in our laboratory [22] in the determination of pesticides in a complex matrix.

Therefore, in this work, a strategy that couples standard addition and the three-way EEM data with "mathematical separation" based on PARAFAC was developed for the unequivocal identification and quantification of the three PAAs, despite the fact that the signals of the three amines were highly overlapped with each other and with the fluorescent matrix constituents. Finally, the recovery and the capability of detection of the method were also studied. Thanks to the selectivity of PARAFAC calibration, which greatly simplifies sample treatment avoiding the use of toxic solvents, the developed method follows most green analytical chemistry principles.

2. Theory

2.1. PARAFAC

According to Leurgans and Ross [23], signals coming from