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Identification of Polyamide 6 and Polyamide 66 Oligomers Using Ion Mobility Time-of-flight Mass Spectrometry and Their Migration from Kitchenware to Foodstuff

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INTRODUCTION

Oligomers are non-intentionally added substances formed during the polymer formation or by degradation of the polymer. Since they are unknown components, accurate mass spectrometry techniques are required for its identification. In this work, ion mobility time-of-flight mass spectrometry has been used for the identification of migrants coming from kitchenware. It allowed to identify the PA 6 and PA 66 oligomers through their accurate m/z, the CCS values and the fragmentation pattern. Moreover, an extraction method to extract the oligomers from sunflower oil, cooked beans, soup and whole milk has been developed with recoveries ranging from 87 to 102 % and limits of detection ranging 0.031 to 0.11 mg/kg. Migration studies have been done to simulants and these foods. It has been observed that ethanol 95% used as substitute of sunflower oil overestimated migration since migration of the sum of oligomers was 16 mg/kg in ethanol 95% and 1.4 mg/kg in sunflower oil. Moreover, migration of the sum of oligomers to beans, soup and milk (2.8, 4.3 and 3.3 mg/kg respectively) was lower than the migration to the simulants established for them (7 mg/kg for 10% ethanol, 7.8 mg/kg for acetic acid 3% and 9.8 mg/kg for ethanol 50%). This difference implies that the migration test of the kitchenware to real food was below the specific migration limit of 5 mg/kg while this limit was exceeded for the simulants.

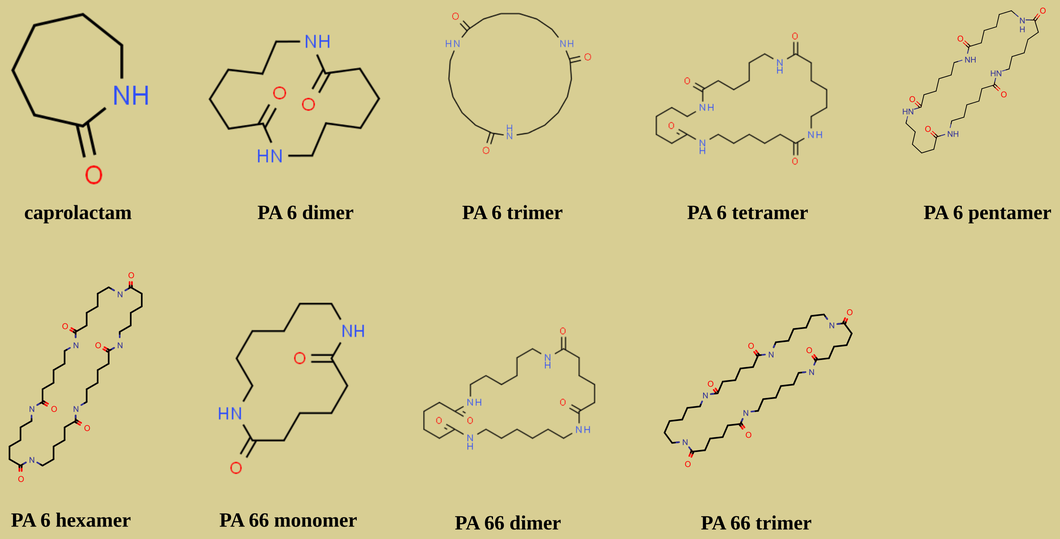
MATERIALS AND METHODS

Polyamide 6 (PA 6) is synthesized by ring-opening polymerization of caprolactam, polyamide 66 (PA 66) is synthesized by polycondensation of hexamethylenediamine and adipic acid. The structure of PA 6 and PA66 are shown in Figure 1. Six PA 6 oligomers and three PA 66 oligomers were studied herein. Their structure are shown below:

PA 6 **PA 66**

Figure 1. PA 6 and PA66 structure

Small amounts of PA cyclic monomers and oligomers are produced as by-products during these processes and remain in the PA-based materials. Typical structures of PA cyclic monomers and oligomers are shown in Figure 2:



caprolactam **PA 6 dimer** **PA 6 trimer** **PA 6 tetramer** **PA 6 pentamer**

PA 6 hexamer **PA 66 monomer** **PA 66 dimer** **PA 66 trimer**

Figure 2. PA oligomers structure

Migration studies into food simulants and to several foods has been studied were done according Regulation 10/2011/EU. In order to identify the compounds migrating from the kitchenware to the food simulants the technique UPLC-IMS/QTOF was selected. This technique provides not only mass accuracy and molecular fragmentation that are parameters needed for molecular elucidation; it also provides ion mobility separation. Each compound analyzed has a collision cross section (CCS) value that will be related to its chemical structure and three-dimensional conformation.

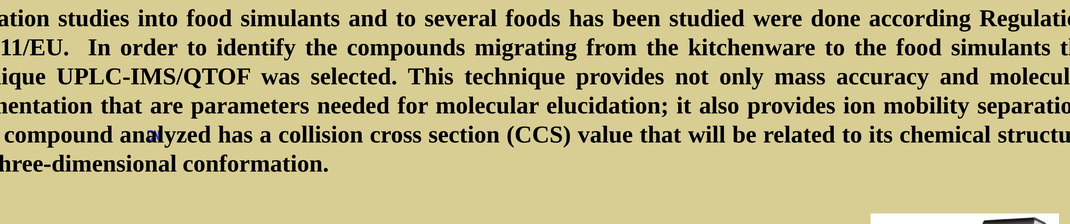


Figure 3. Experimental procedures

RESULTS AND DISCUSSION

Table 1. The retention time, monoisotopic m/z, elemental composition and CCS value obtained for each oligomers

Compounds	RT (min)	m/z	Fomula	CCS (Å²)
PA 6 monomer	2.50	113.0841	C6H12NO	127.88
PA 6 dimer	2.29	227.1753	C12H23N2O2	155.44
PA 6 trimer	3.10	340.2593	C18H34N3O3	182.05
PA 6 tetramer	3.66	453.3436	C24H45N4O4	209.73
PA 6 pentamer	4.03	566.4269	C30H56N5O5	237.61
PA 6 hexamer	4.33	701.4928	C36H66N6O6Na	265.41
PA 66 monomer	2.61	227.1753	C12H23N2O2	153.61
PA 66 dimer	3.88	453.3437	C24H45N4O4	214.07
PA 66 trimer	4.55	701.4935	C36H66N6O6Na	270.69

Three pairs of m/z obtained experimentally had the same elemental composition, the structure can be elucidated by fragment assignment, For example for ion 453.3436, with an elemental composition of C24H45N4O4, the fragments 79.0543, 114.0915, 226.1915 fit with the theoretical fragments of PA 6 tetramer and the fragments 100.1124, 182.1541 and 209.1648 fit with the theoretical fragments of the PA 66 dimer. The mass spectra for PA 6 tetramer are shown in Figure 4. Moreover, for PA 6 tetramer and PA66 dimer, PA 6 hexamer and PA66 trimer, CCS is another parameter to identify the molecule.

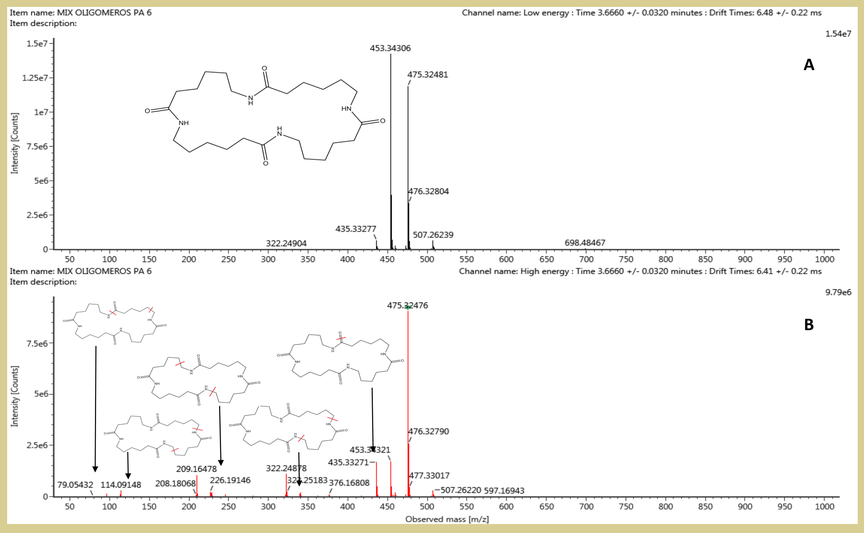


Figure 4. A) Low energy and B) high energy spectrum of the PA 6 tetramer obtained by UPLC-IMS-Q-TOF

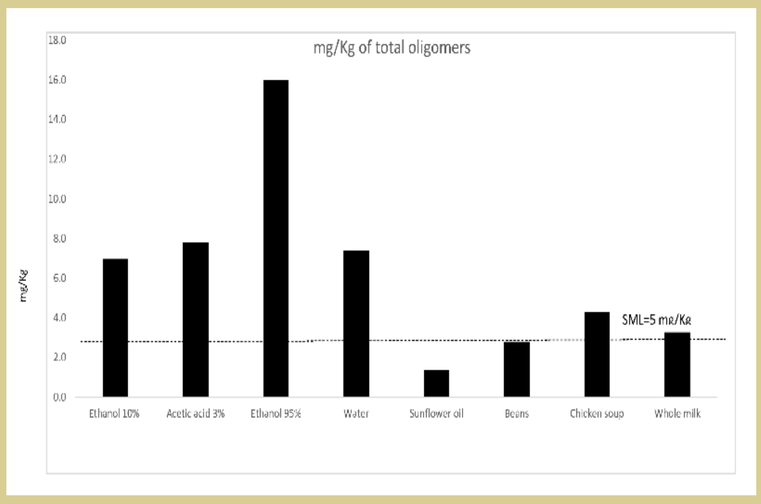


Figure 5. Migration (mg/kg) of the sum of oligomers for each simulant or food studied

The higher values were obtained for ethanol 95%, the sum of oligomers (without caprolactam) was close to 16 mg/kg, which was over the established limit (5 mg/kg). The migration into sunflower was just 1.4 mg/kg.
The simulant overestimated the migration compared with the real food.

CONCLUSIONS

UPLC-IMS-Q-TOF has been the required analytical technique for the identification of oligomers in migration extracts since it allowed to identify oligomers with the same elemental composition, the same CCS value but different fragmentation pattern. Migration of the identified compounds was done and it was observed that migration of PA6 and PA 66 oligomers to ethanol 95%, that is commonly used as substitute of sunflower oil overestimated the migration when compared with migration to sunflower. Moreover, an extraction method of oligomers from cooked beans, soup and whole milk was developed and migration to simulants and real foods was studied. Differences in the oligomer migration values obtained for the simulants established for the foods and oligomer migration values for the real foods were observed.

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