Determination of nitrogen-containing organic compounds, found as colorants residues, in commercially available recycled cartons intended for food contact applications.

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Recycling, reuse, and recovery of materials are the most important components when it comes to solid waste management. Without these components, there will be nothing left in the world for people to use in the foreseeable future; a fact that is more realistic than ever as people are already struggling with the insufficiency of available resources (Kopsidas et al. 2021). Nevertheless, more and more countries and major industries are acknowledging the need for a circular economy and have been taking necessary actions in this direction. One such sector is the Food Industry. A variety of recyclable packaging materials such as plastics, paper, metal, and glass are traditionally used in Food Industry as raw materials. Nowadays, recovered paper and plastic materials are also being incorporated in order to address the global waste problem. The challenge, however, is to strike a balance between sustainability and food safety. Recovered materials may be highly risky since any potential migration of chemicals from the packaging material to the food can seriously threaten human health.

In this study, a rapid and simple method was developed to evaluate the concentrations of a mixture of nitrogen-containing compounds in commercially recycled cartons based on ultrasound-assisted extraction (UAE) combined with gas chromatography-mass spectrometry (GC-MS) analysis. Additionally, the recycled carton samples were spiked with the aniline mixture and subjected to migration experiments using Tenax as a food simulant. Migration trials were conducted in both "mild" (10 days at 40ºC) and "extreme" (6h at 70ºC) conditions. The compound mix used for this study consisted of 7 nitrogen-containing organic compounds most commonly encountered in paper packaging usually as pigment residues: 2,4-dichloroaniline, 3,5-dichloroaniline, 2,4-dimethylaniline, 4-chloroaniline, 2-naphthylamine, 5-nitro-2-methylaniline, and 4-aminodiphenyl. The commercially available carton samples in this study comprised four different types of kraft paper; two made of 100% recovered materials (R1, R2), one made of 10-30% recovered materials (R3), and one of 0% recovered materials.

The extraction conditions were optimized for all methods tested by comparing the relative recovery rates resulting by normalizing in percentage the integrations of the contaminants peaks in the respective chromatograms (yields) to the compound exhibiting the highest recovery. The identification of the compounds was achieved using the Wiley 7, NIST 2005 mass spectral library and was further supported by the comparison of their linear retention indices (Kovats indices) to those of the reference standards and/or published data (Van den Dool and Dec. Kratz 1963; NIST 2005). The concentrations of the pollutants were recorded as mg/Kg, following the recommended limits in the industry compliance guide (Document Nº SANTE/12682/2019 2019). For the conversion, the density of the papers used was: R1=667 Kg/m^3, R2=774 Kg/m^3, and R3=706 Kg/m^3.

The rates of migration of the contaminants varied according to the nature of the substance, the nature, and properties of the carton packaging, contact time, and temperature. The estimated concentrations of the studied contaminants are depicted in Table 1. Out of the 3 cartons tested, carton R3 yielded the highest concentrations of pollutants, followed closely by carton R1.

Table 1. Concentrations (mg/Kg) of the substances used in this study in the 3 paperboard samples (R1, R2, R3). Values under the limit of quantification are marked as det (detected)

Contaminant	R1	R2	R3
2,4-dichloroaniline	0.060	0.016	0.060
3,5-dichloroaniline	0.028	0.011	0.091
2,4-dimethylaniline	tr	tr	tr
4-chloroaniline	tr	tr	tr
2-naphthylamine	0.015	tr	0.015
5-nitro-2-methylaniline	tr	tr	tr
4-aminodiphenyl	0.023	tr	0.083

In the case of commercial packaging materials, none of the contaminants was detected in the food simulant regardless of the method used. However, in the case of the contaminated cartons, both under "mild" and "extreme conditions, two of the substances studied (2,4-dichloroaniline and 3,5-dichloroaniline) migrated into Tenax, and their concentrations (Table 2), and migration rates (Table 3) ranged from moderate to very high. Again, out of the 3 cartons tested, carton R3 yielded the highest concentrations of pollutants, followed closely by carton R1.

Table 2. Concentrations (mg/Kg) of the substances that migrated from the 3 paperboard samples (R1, R2, R3) into Tenax under mild and extreme conditions (n.d. stands for not detected).

Contaminant	Mild conditions			Extreme conditions		
	R1	R2	R3	R1	R2	R3
2,4-dichloroaniline	0.010	0.011	0.055	0.033	0.010	0.050
3,5-dichloroaniline	0.016	0.005	0.051	0.027	0.005	0.041
2,4-dimethylaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-chloroaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-naphthylamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5-nitro-2-methylaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-aminodiphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 3. Concentrations (mg/Kg) of the substances that migrated from the 3 paperboard samples (R1, R2, R3) into Tenax under mild and extreme conditions (n.d. stands for not detected).

Contaminant	Mild conditions			Extreme conditions		
	R1	R2	R3	R1	R2	R3
2,4-dichloroaniline	16.66%	68.75%	91.66%	55.00%	62.50%	75.00%
3,5-dichloroaniline	53.33%	45.45%	56.66%	90.00%	45.45%	45.55%
2,4-dimethylaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-chloroaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-naphthylamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5-nitro-2-methylaniline	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-aminodiphenyl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The contaminant 2,4-dichloroaniline was found to migrate to a greater extent in comparison to 3,5-dichloroaniline, both in mild and extreme conditions. Furthermore, the highest migration rate of 2,4-dichloroaniline was recorded in carton R3 and of 3,5-dichloroaniline in paperboard R1. Overall, however, it was found that there is a greater migration tendency of the compounds into Tenax in carton R3, followed by cartons R1 and R2. Finally, it should be noted that in two (R2, R3) out of the three cartons tested a greater migration tendency of the contaminants was recorded under mild conditions, while only in carton R1 migration rates were greater under extreme conditions.

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References

Document Nº SANTE/12682/2019. 2019. *Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed*. https://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727 (August 19, 2021).

Van den Dool, H., and P. Dec. Kratz. 1963. "A Generalization of the Retention Index System Including Linear Temperature Programmed Gas—Liquid Partition Chromatography." *Journal of Chromatography. a* 11(C): 463–71. https://www.scienceopen.com/document?vid=867e41fb-5455-4875-9f85-955347ae7210 (October 1, 2021).

Kopsidas, Odysseas N., Stephanos D. V. Giakoumatos, Odysseas N. Kopsidas, and Stephanos D. V. Giakoumatos. 2021. "Economics of Recycling and Recovery." *Natural Resources* 12(4): 73–90. http://www.scirp.org/journal/PaperInformation.aspx?PaperID=108484 (January 21, 2023).

NIST. 2005. *National Institute of Standards and Technology*. ed. J. Wiley & Sons Ltd. West Sussex.