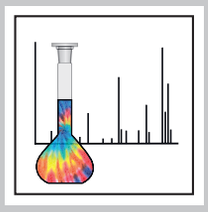
doi:10.2533/chimia.2020.419 Chimia 74 (2020) 419



Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

A Division of the Swiss Chemical Society

Simultaneous Quantification of 58 Hazardous Aromatic Amines and Positional Isomers in Textiles by LC-MS/MS

Patrick Kämpfer*[a], Stéphanie Crettaz[a], Susanne Nussbaumer[a], Michael Scherer[b], Scott Krepich[b], and Otmar Deflorin[a]

*Correspondence: P. Kämpfer[a], E-mail: patrick.kaempfer@be.ch. [a]Official Food Control Authority of the Canton of Berne, Muesmattstrasse 19, CH-3012 Berne; [b]Sciex, Stadtturmstrasse 19, CH-5401 Baden

Keywords: Aromatic amines · Azo dyes · Clothing textiles · Isomeric amines · LC-MS/MS

Azo dyes are best suited for coloring textiles, however, they have the disadvantage of the potential occurrence of aromatic amines (AAs) used in the manufacturing process of these colors. AAs can be released upon physical skin contact through skin bacteria by wearing textiles. Due to their carcinogenic and mutagenic characteristics, 22 of these AAs are regulated by the European Union (REACH regulation). The regulated amines may be emitted by reductive cleavage of the textiles with a maximum of 30 mg kg^{-1}. A normalized test method used in laboratories worldwide to determine these amines is the DIN EN 14362-1.

The most powerful method to determine the AAs is HPLC-MS/MS. Unfortunately, some of these amines (*e.g.* toluidine) have different isomers that can lead to false-positive findings. These isomers cannot be separated by mass spectrometry, however, so the chromatography parameters had to be optimized. Choosing a modern stationary phase with a biphenyl modification, the interaction with the aromatic functional group of the amines works best. By finding the optimal pH conditions at 3.5, the isomers can be baseline separated. To enhance the sensitivity of some amines, *e.g. o*-toluidine, a post-column addition with formic acid is used. In addition, more amines suspected as carcinogenic or mutagenic were implemented in the analytical method. For better identification and differentiation of all 58 amines, a combination of retention times, MRM-transitions, ion ratios and enhanced product ion scans (EPI) showed excellent information. The linearity of the system was tested with eight points. The very good regression coefficient (>0.99) allowed calibration of the system with only one point. The method was completely validated and presented excellent quantitative performance.

Finally, the described method was applied on 150 different textile samples from local stores. The results show that about 50% of the samples contain one or even more AAs, but only in three samples regulated amines were found. The study shows that even more amines than the 22 regulated are present in textiles. **The developed method is a powerful tool to differentiate important positional isomers from regulated AAs and to analyze additional, non-regulated AAs of interest.**

Textiles with different colors and fibers were analyzed.

Acknowledgement

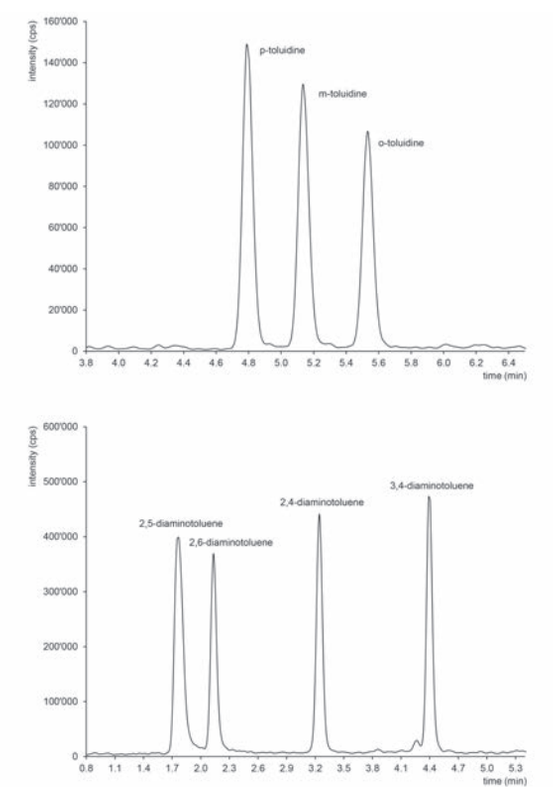
The Swiss Federal Food Safety and Veterinary Office (FSVO) is acknowledged for financing and supporting this study.

Received: March 6, 2020

References

P. Kämpfer, S. Crettaz, S. Nussbaumer, M. Scherer, S. Krepich, O. Deflorin, *J. Chromatogr. A* **2019**, *1592*, 71, doi: 10.1016/j.chroma.2019.01.039.

S. Crettaz, P. Kämpfer, B. J. Brüschweiler, S. Nussbaumer, O. Deflorin, *J. Consum. Prot. Food Saf.* **2019**, doi: 10.1007/s00003-019-01245-1.



Positional isomers of toluidine and diaminotoluene are separated by chromatography at pH 3.5.

Can you show us your analytical highlight?
Please contact: Dr. Veronika R. Meyer, Unterstrasse 58, CH-9000 St. Gallen
Tel.: +41 71 222 16 81, E-mail: VRMeyer@bluewin.ch