

Determination of certain aromatic amines derived from azo colorants in dyed leathers (ISO 17234-1:2015)

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Abstract

This application describes the determination of certain aromatic amines derived from azo colorants, prior to HPLC-UV analysis.

Introduction

An aromatic amine is an organic compound consisting of an aromatic ring attached to an amine. The simplest aromatic amine is aniline. Primary aromatic amines (PAAs) are known as contaminants from azo dyes and colour pigments in commercial textile products and some of them are considered to be carcinogenic [1]. For human health protection, specific regulations have been introduced in order to minimize their presence in textiles and leathers by the most important international authorities [2, 3]. In our days, the textile and leather producing industry can promote their products by using special labels that indicate consumers the absence of azo dyes authorities [4]. For monitoring their occurrence, there is a demand for efficient liquid-liquid extraction procedures of primary amines and for sensitive chromatographic methodologies.

The liquid-liquid extraction procedure of primary aromatic amines can be performed on Kieselguhr, for instance CHROMABOND® XTR. The sample extract can be applied and immobilized on a Kieselguhr cartridge and allows efficient liquid-liquid extraction of the amines. By using alkaline activated XTR material an alkalization step after applying sample extract on Kieselguhr cartridge is not necessary anymore to achieve good recovery rates for volatile amines.

This application note deals with a sample preparation procedure of critical PAAs using alkaline activated Kieselguhr and its chromatographic determination on NUCLEODUR® Sphinx RP with UV detection.

Compounds of interest

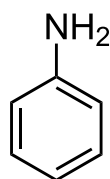


Figure 1: Simplest example for primary aromatic amines.

Sample preparation

For leather samples according to DIN 17234-1:2015:

- Degrease sample with hexane
- Extract sample with preheated citrate buffer for 25 minutes in a water bath at 70 °C
- Stop reaction by cooling with cold water
- Perform liquid-liquid extraction of the sample extract is performed on Kieselguhr phase with MTBE

For this application note we started with the control of the analytic system as described in point 9.4 within DIN 17234-1:2015:

- Weigh in 600 mg sodium dithionite in a flask and solve in 3 mL of dest. water
- Add 1 mL off standard solution ($\beta = 30 \mu\text{g/mL}$ in methanol for each compound)
- Add 16 mL of citrate buffer solution, 0.06 mol/L, pH=6.0, preheated up to $70 \pm 5 \text{ }^\circ\text{C}$
- Apply mixture on Kieselguhr phase, alkaline activated
- Extract four times with 20 mL of methyl *tert*-butyl ether (MTBE)
- Collect MTBE extract in a 100 mL flask and reduce volume down to 1 mL with a rotary evaporator in a water bath ($T \leq 50 \text{ }^\circ\text{C}$)
- Transfer the residue into a 10 mL test tube with standard taper (NS)
- Reduce volume down to 0.5 mL with a rotary evaporator in a water bath ($T \leq 50 \text{ }^\circ\text{C}$) and fill up to 1 mL with eluent A

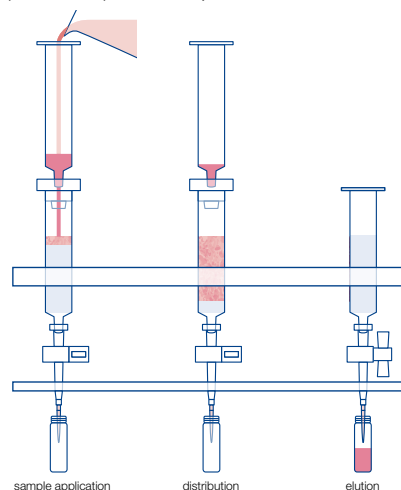


Figure 2: Liquid-liquid extraction procedure on CHROMABOND® XTR-NB.

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Subsequent analysis: HPLC-UV

Chromatographic conditions

Column dimension:

EC 250/4 NUCLEODUR® Sphinx RP, 5 µm (REF 760803.40)

Eluent A:

0.575 g ammonium dihydrogen phosphate and 0.7 g disodium hydrogen phosphate are solved in water, filled up to volume of 1 L with water and adjusted at pH 6.9 + 100 mL methanol

Eluent B:

methanol

Gradient:

from 10 % B to 50 % B in 40.0 min, from 50 % B to 80 % B in 20 min, back to 10 % B in 5.0 min, hold for 5.0 min

Flow rate:

0.8 mL/min

Temperature:

30 °C

Injection volume:

30 µL

Detection:

240 nm

Analyte	CAS Number	RT [min]
2,4-Diaminoanisole	615-05-4	8.38
2,4-Diaminotoluene	95-80-7	8.89
o-Anisidine	90-04-0	21.0
Benzidine	92-87-5	24.2
4,4'-Oxydianiline	101-80-4	25.6
4-Chloroaniline	106-47-8	27.8
4,4'-Diaminodiphenylmethane	101-77-9	32.9
4-Chloro-2-methylaniline	95-69-2	37.4
4,4'-Methylene-bis(2-methylaniline)	838-88-0	44.4
4-Aminobiphenyl	92-67-1	46.0

Table 1: Retention times of certain amines.

Chromatograms:

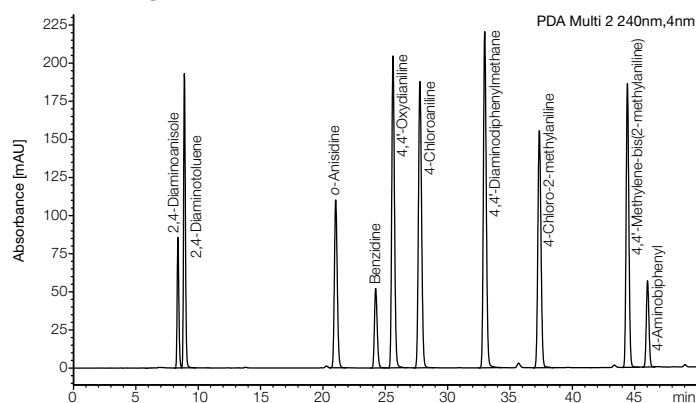


Figure 3: Separation of primary aromatic amines on NUCLEODUR® Sphinx RP ($\beta = 30 \mu\text{g/mL}$ in Eluent A).

Recovery rates

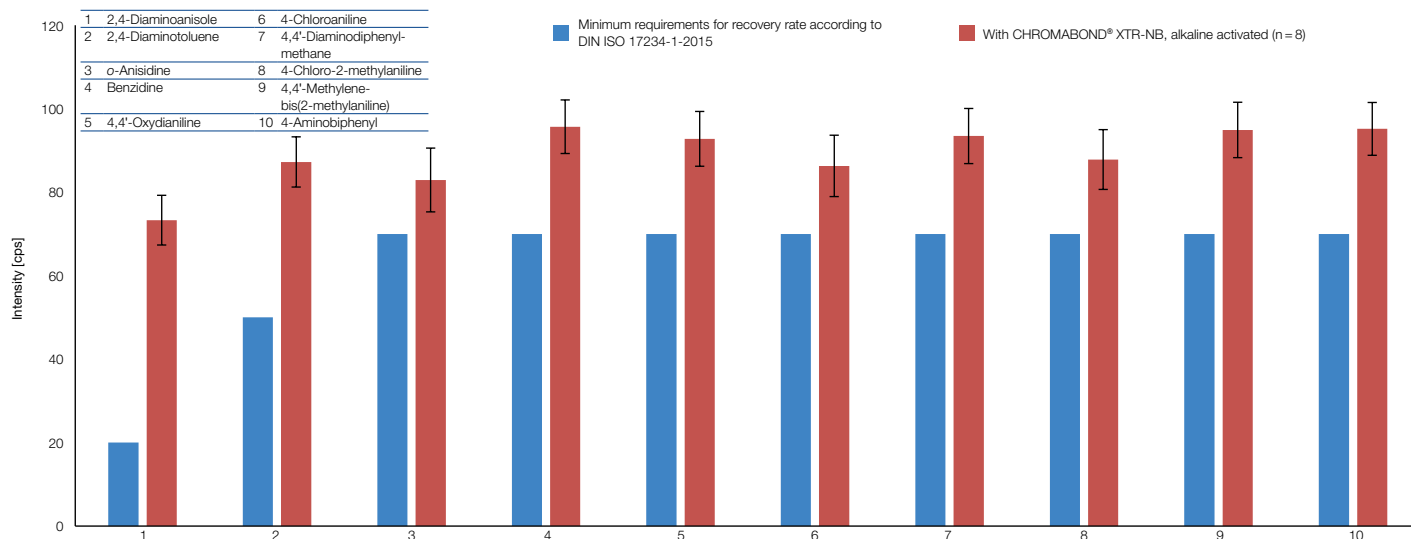


Figure 4: Recovery rates of certain amines.

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Conclusion

The results show that the determination of certain primary aromatic amines could be carried out successfully with alkaline activated CHROMABOND® XTR-NB. Figure 4 shows that the recovery rates of amines are much better than required by DIN. By using alkaline activated CHROMABOND® XTR-NB it is not necessary to alkalize Kieselguhr anymore. The determination of critical volatile analytes like 2,4-Diaminoanisole can be performed with recovery rates of more than 70 %. That leads to very sensitive determination of PAAs in low concentration levels.

The chromatographic method in this application note was adapted to analyte mixture. For faster chromatographic separation with LC-MS/MS detection we recommend a NUCLEODUR® π² column (MN Appl. No. 128580).

References

- [1] Romualdo Benigni (2002), Carcinogenicity of the aromatic amines: from structure–activity relationships to mechanisms of action and risk assessment. *Mutation Research* 511 (2002) 191–206.
- [2] Updated BfR Opinion No. 041/2012, 6 July 2012.
- [3] Leather – Chemical tests for the determination of certain azo colorants in dyed leathers – Part 1: Determination of certain aromatic amines derived from azo colorants (ISO 17234-1:2015); German version EN ISO 17234-1:2015.
- [4] For instance: STANDARD 100 by OEKO-TEX®, EU Ecolabel Textile Products.

Additional information

The following applications regarding “Determination of certain aromatic amines derived from azo colorants in dyed leathers (ISO 17234-1:2015)” and further applications can be found on our online application database at www.mn-net.com/apps

SPE: MN Appl. No. 306640

HPLC: MN Appl. No. 128720

Product information

The following MACHEREY-NAGEL products have been used in this application note:

REF 730507.100NB, CHROMABOND® XTR-NB, 70 mL, 14.5 g

REF 760803.40, EC 250/4 NUCLEODUR® Sphinx RP, 5 µm

REF 702293, Screw neck vials N 9, 1.5 mL

REF 702107, N 9 PP Screw cap, yellow, center hole,
silicone white / PTFE red

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