

**Release of aromatic amines from structural waterproofing –  
Development of a method for analytical quantification as a basis for the  
assessment within the framework of the German national technical approval  
(abZ)**

PUR and epoxy injection resins can emit carcinogenic amines. Therefore the relevant expert committee has recommended investigating 19 amines classified as carcinogenic, 18 of which are aromatic amines (hereinafter named DIBt amines).

In the context of approval tests, the release of the aromatic amines from PUR injection resins is assessed by inverse column elution (ICE) and subsequent determination of the amines in selected ICE eluate fractions. The report presents a validated UPLC-MS/MS analysis method (ultra-high performance liquid chromatography coupled with tandem mass spectrometry) for 17 carcinogenic aromatic DIBt amines.

In samples, determination limits between 0.008 and 0.048 µg/L are achieved for 15 stable DIBt amines. Determination limits of approx. 2 µg/L are obtained in samples for two unstable amines. A substance-specific comparison with the GC-MS method (gas chromatography coupled with mass spectrometry) used until now for analysis of amines based on ultrapure water and ICE eluate samples with added aromatic amines (18 DIBt amines plus isomers) shows an exemplary and reproducible (2 of 2) recovery of the added concentrations using the UPLC-MS/MS method.

In the established GC-MS method analysis, only 4-chloro-2-methylaniline was found in both ultrapure water samples at concentrations between 0.1 and 0.3 µg/L. In the concentration range between 0.4 and 1.2 µg/L, 5 of 15 stable DIBt amines were not detected in either of the two samples. In the prepared ICE eluate samples, inferior results are obtained due to matrix effects with both analytical methods, so the routine use of the standard addition method is recommended.

Comparing the timeline for the amine release with the TOC curve using an injection resin ICE eluate shows that the amine release can occur with a time relative to the TOC curve. Therefore, the selection of the ICE eluate fractions for amine analysis based on the TOC maxima can lead to inferior results. For example, in the ICE eluate fractions, up to 15 µg/L 4,4'-methylenedianiline (4,4'-MDA), up to 4.8 µg/L 4,4'-methylene-bis-(2-chloroaniline) and up to 1.0 µg/L 4-chloroaniline were detected by UPLC-MS/MS analysis. In contrast, none of the 18 aromatic amines were detected by GC-MS analysis.

To assess which amines in injection resin ICE eluates are relevant for national technical approval, up to 15 injection resins should be tested for the release of aromatic amines. Since the eluate fractions of only one injection resin were available during the project, we recommend that routine analyses of further injection resins be carried out by means of UPLC-MS/MS in the future. A description of the UPLC-MS/MS method is contained in the report.