



International Carbon Black Association

Unsuitability of the ZEK/AfPS test method for the quantification of PAHs in Carbon Black

Matrix specific test methods like the U.S. FDA method 63 or the ASTM D7771 standard are recommended for the quantification of polycyclic aromatic hydrocarbons (PAHs) in carbon black. These carbon black specific methods prescribe Soxhlet extraction with toluene followed by quantification with gas chromatography coupled with mass spectrometric detection (GC/MS). For precise quantification, deuterated PAH compounds are added to the toluene extracts as internal standards prior to the purification and GC/MS analysis.

In 2008, a test method was established by the German "Zentralstelle der Länder für Sicherheitstechnik (ZLS)" for the determination of a series of PAH compounds in rubber and plastic articles which may come into contact with human skin during intended use. This ZEK test method is intended to be used for GS-Mark certification of toys and articles made out of rubber or plastics. On the 4th of August 2014, the German commission on Product Safety (AfPS) established new GS specifications "AfPS GS 2014:01 PAK"¹ to replace the ZEK specification on the 1st of July 2015. The test method and the individual PAHs considered remain the same but with significant changes for the PAH limits and the categories of finished articles.

The ZEK/AfPS method prescribes a 1 h ultrasonic extraction of the rubber or plastic test specimen with toluene at 60 °C. In contrast to the carbon black specific methods, the deuterated internal PAH standards are added to the solvent prior to the extraction step. The subsequent extract treatment and GC/MS analysis follow the same principles as the FDA and the ASTM methods but with only three deuterated internal standards for the identification and quantification of the 18 PAH compounds of interest.

Although neither intended nor validated for the analysis of PAHs in carbon black, the ZEK method is often applied in the rubber and plastic industry for the quantification of PAHs. Unfortunately, the misuse of the ZEK/AfPS method on carbon black may lead to significantly different PAH results in comparison to the internationally

recognised U.S. FDA and ASTM D7771 methods specific to carbon black. Such discrepancies, inconsistencies, and uncertainties may lead to inadequate product specifications with potential commercial and legal implications.

To clearly assess the suitability or unsuitability of the ZEK/AfPS method for carbon black, the International Carbon Black Association (ICBA) contracted mas | münster analytical solutions gmbh, Münster, Germany.

The study involved replicate extractions and PAH analyses of three different carbon black grades comparing the various methods. The results of this comprehensive investigation are published with "Open Access" in the peer-reviewed journal "Rubber Chemistry & Technology"². The main conclusions can be summarised as follows:

- Since the carbon black is finely dispersed in toluene through the ultrasonic extraction, a specific protocol for the separation of the toluene extract from the carbon black is necessary. Centrifugation of the dispersion proved to be suitable.
- The ZEK/AfPS method does not extract from carbon black all 18 PAHs in a quantitative manner. The extraction efficiencies seem to depend on the volatility and type of the PAH compounds and on the concentration levels in the carbon black.
- When using the two internal standards as stipulated in the ZEK/AfPS method for the quantification of naphthalene and the 7 subsequent PAHs, the results range from 50% to 100% of those obtained with the U.S. FDA method 63.
- For the 10 remaining PAHs, all quantified with a single internal standard as per the ZEK/AfPS method, false positive and false negative results were obtained for carbon black.

These findings unambiguously demonstrate that the ZEK/AfPS test method, as currently established for the determination of 18 PAHs in plastics and rubber, should not be applied to carbon black.

¹ § 21, passage 1, N° 3 of the German product safety law (Produktsicherheitsgesetz, ProdSG). Paragraph § 21 is part of section 5 of the ProdSG dealing with the GS-Mark.

² Stephan Hamm, Kai Hölscher, Thomas M. Gruenberger, Gilles Moninot, Wolfgang Örtel, and Nicole Petiniot (2018) UNSUITABILITY OF THE ZEK/AFPS TEST METHOD FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN CARBON BLACK. Rubber Chemistry and Technology: January-March 2018, Vol. 91, No. 1, pp. 225-250. <http://rubberchemtechnol.org/doi/pdf/10.5254/rct.18.82635>