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Application Data Sheet

No.121

GC-MS
Gas Chromatograph Mass Spectrometer

Test Methods for Certain Aromatic Amines Derived from Azo Colorants

Some azo colorants have been identified as hazardous in that they form carcinogens when degraded. Accordingly, Japan's Ministry of Health, Labour and Welfare will restrict the sale of textiles and leather goods using these azo colorants, starting from April 1, 2016.
Azo colorants have an azo group (A-N=N-B) and account for over 50% of organic pigments. The azo group double bond is degraded on the surface of the skin, by intestinal bacteria, and by the liver, forming amines (A-NH2 and B-NH2). Some of the amines formed (certain aromatic amines) are suspected to be carcinogenic.
Consequently, these azo colorants are already restricted in the EU, China, and South Korea. In Japan, they are currently subject to voluntary restriction, but will be legally restricted starting April 1, 2016.
The analysis methods specified in JIS L 1940 (based on EN 14362-1:2012[1)] and EN 14362-3:2012[2)] test methods) will be applied to test azo colorants.
In South Korea and China, there are a number of manufacturers manufacturing and exporting textiles and leather goods. At testing service laboratories, inspection tests are implemented based on EN 14362-1 and -3 methods.
This data sheet provides an overview of inspection methods for certain aromatic amines derived from azo colorants, as well as a description on separation of certain aromatic amines.

[1)] EN 14362-1:2012 Textiles. Methods for determination of certain aromatic amines derived from azo colorants. Detection of the use of certain azo colorants accessible with and without extracting the fibres
[2)] EN 14362-3:2012 Textiles. Methods for determination of certain aromatic amines derived from azo colorants. Detection of the use of certain azo colorants, which may release 4-aminoazobenzene

Experiment

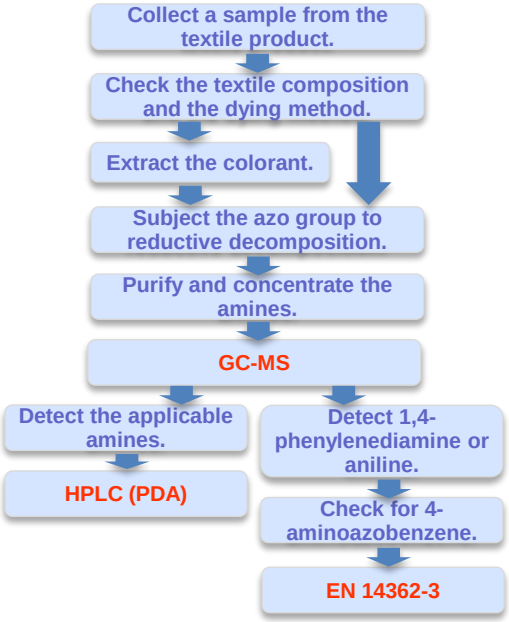

Fig. 1: An Example of Analysis Sequence Based on EN 14362-1

EN14362-1 explains the method for chromatographs, such as GC, GC/MS, HPLC, HPLC/MS and capillary electrophoresis (CE)/MS. Fig. 1 shows the example of analytical sequence when quantifying certain aromatic amines derived from azo colorants in textile products. Firstly, collect a sample from the textile product. Next, subject the azo group to reductive decomposition. Depending on the textile composition and dyeing methods, however, the colorants may need to be extracted in advance. Purify and concentrate the obtained amines, and measure them with GC-MS. If the applicable amines are detected, use another type of chromatography to confirm that the results are not a false positive. In this example, HPLC is used. The detection rate depends on the target substance, sometimes reaches up to several percent.

With the method specified in EN 14362-1, 4-aminoazobenzene is detected as aniline or 1,4-phenylenediamine. These are formed from azo colorants that are not restricted. If aniline or 1,4-phenylenediamine is detected, testing based on EN 14362-3, which can detect 4-aminoazobenzene, is required.

The GC-MS analysis conditions are shown in Table 1. A medium polarity column is utilized for the analysis, as already reported in Application Datasheet No. 29, "The Analysis of Certain Aromatic Amines Formed from Azo Colorants and Pigments".

Table 1: Analysis Conditions

GC-MS:	GCMS-QP2020
Column:	VB-35 (30 m L. × 0.25 mm I.D., df = 0.25 μm; (35%-Phenyl)-methylpolysiloxane; ValcoBond® Capillary Columns)

GC		MS	
Injection Volume:	1 μL	Interface Temp.:	280 °C
Injection Unit Temp.:	240 °C	Ion Source Temp.:	250 °C
Column Temp.:	100 °C (1 min) → (20 °C /min) → 300 °C (3 min)	Measurement Mode:	Scan/SIM
Carrier Gas Control:	Constant linear velocity (37.2 cm/sec)		
Injection Mode:	Split (8:1)		
Carrier Gas:	Helium		

Analysis Results

To show the analysis pattern for the applicable certain aromatic amines, a chromatogram obtained by measuring a standard sample is shown in Fig. 2. Table 2 shows the retention times of these compounds as well as the *m/z* values used for selected ion monitoring (SIM).

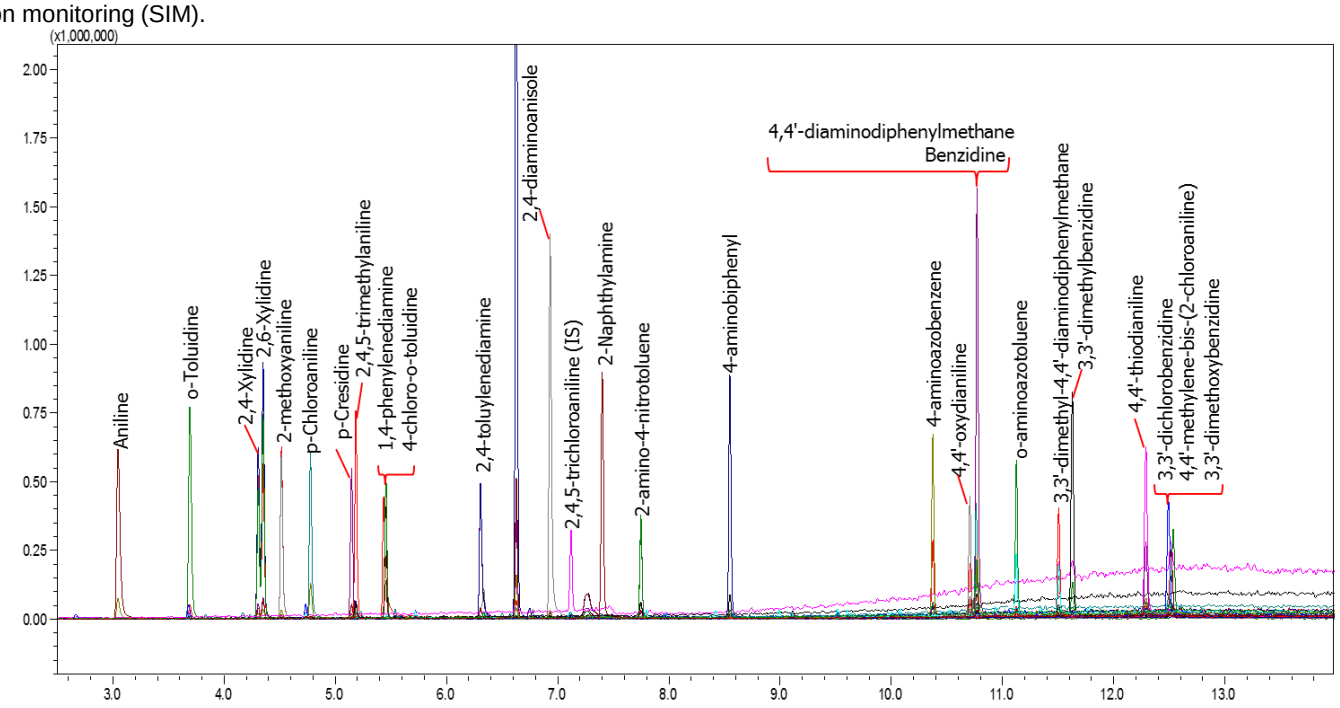

Fig. 2: Chromatogram Obtained by Measuring Certain Aromatic Amines

Table 2: Retention Times and SIM *m/z* Values

No.	Compound	RT (min)	Quantitative Ion (m/z)	No.	Compound	RT (min)	Quantitative Ion (m/z)
1	Aniline	3.04	93	15	2-amino-4-nitrotoluene	7.74	152
2	o-Toluidine	3.68	106	16	4-aminobiphenyl	8.54	169
3	2,4-Xylidine	4.30	121	17	4-aminoazobenzene	10.37	92
4	2,6-Xylidine	4.34	121	18	4,4'-oxydianiline	10.70	200
5	2-methoxyaniline	4.50	123	19	4,4'-diaminodiphenylmethane	10.76	198
6	p-Chloroaniline	4.77	127	20	Benzidine	10.76	184
7	p-Cresidine	5.13	122	21	o-aminoazotoluene	11.12	106
8	2,4,5-trimethylaniline	5.18	120	22	3,3'-dimethyl-4,4'-diaminodiphenylmethane	11.50	226
9	1,4-phenylenediamine	5.42	108				
10	4-chloro-o-toluidine	5.44	141	23	3,3'-dimethylbenzidine	11.62	212
11	2,4-toluylenediamine	6.29	121	24	4,4'-thiodianiline	12.28	216
12	2,4-diaminoanisole	6.92	123	25	3,3'-dichlorobenzidine	12.48	252
13	2,4,5-trichloroaniline (IS)	7.11	195	26	4,4'-methylene-bis-(2-chloroaniline)	12.51	231
14	2-Naphthylamine	7.39	143	27	3,3'-dimethoxybenzidine	12.53	244

Summary

GC-MS was used to quantify certain aromatic amines originating from azo colorants. Test methods such as EN 14362, ISO 24362, and JIS L1940 are used as analysis methods for textile products. ISO 17234-1:2015 and ISO 17234-2:2011 test methods are used for leather goods.

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