Application Note #025

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Fast Analysis of Controlled Dyes in Textiles by Positive/Negative ESI LC/MS/MS

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Introduction

Currently "ecologic textiles" are popular in the world, especially in developed countries. Many dyes are used in textile manufacture and research has indicated that some dyes are harmful to human health. For example twenty three aromatic amines used as dyes are known to be carcinogenic and are routinely analyzed by GC/MS. Many other dyes (disperse dyes, direct dyes etc) are also allergenic and carcinogenic. Many countries now require that these compounds be monitored in imported textiles. Due to the complexity and multiplicity of these dyes¹, LC/MS/MS combined with electrospray ionization (ESI) source has proven useful as a fast screening technique using MRM for positive identification and quantitation.

Instrument

- Varian 1200L LC/MS/MS triple quadrupole equipped with ESI source
- ProStar[™] 410 autosampler
- ProStar 210 Solvent Delivery System

Material and Reagent

- 100 mg/ml Stock solution for twenty-seven dyes (allergenic and carcinogenic)
- All other reagents are HPLC grade

Sample preparation

The textile is sheared into pieces, 1.0 g piece samples weighed and transferred into a capped tube, 10 mL methanol is added and the capped sample extracted for 10 min in an ultrasonic bath at 70°C. The extracted solution is filtered through 0.45 Mm 13 mm syringe filter into the 2 mL standard vial ready for LC/MS analysis.

HPLC conditions

- Column 150 mm x 3 mm RP-C18 5 μm
- Solvent A: 10 mmol Ammonium Acetate in water
- Solvent B: Acetonitrile
- A%/B % = 25/75
- Flow rate: 0.3 mL/min
- Column temperature: 40 °C
- Injection volume: 10 μL

MS Parameters

API Drying Gas 20 psi at 320 °C API Nebulizing Gas 50 psi Shield 600V Scan time 0.4 sec Collision gas 2.1 mTorr (Ar) Needle 5000 V (positive ion), -4500 V (negative ion) Detector 1350 V



Figure 1. MS/MS Breakdown of Disperse Yellow 9 demonstrating response of two intense product ions (258, 228).



Figure 2. LC/MS/MS Chromatogram of Dye mixture



Figure 3. Multiple co-elutions resolved using multi-channel selective reaction monitoring

MS/MS Conditions for Analytes

No.	Compound name	MWt	ESI	Precursor ion	Product ion (quant)	Collision Energy	Coef.R ²
1	C.I. Disperse Blue 1	268.26	+	268	252	-17	0.9942
2	C.I. Disperse Blue 3	296.33	+	297	252	-19	0.9993
3	C.I. Disperse Blue 7	358.35	+	359	314	-18	0.9882
4	C.I. Disperse Blue 26	298.30	+	299	284	-26	0.9816
5	C.I. Disperse Blue 35	284.27	+	285	270	-24	0.9997
6	C.I. Disperse Blue 102	344.40	+	366	147	-23	0.9836
7	C.I. Disperse Blue 106	335.39	+	336	178	-17	0.9922
8	C.I. Disperse Blue 124	377.42	+	378	220	-16	0.9912
9	C.I. Disperse Orange 1	318.34	+	319	122	-18	0.9985
10	C.I. Disperse Orange 3	242.24	+	243	122	-16	0.9994
11	C.I. Disperse Orange 37	392.25	+	392	350	-25	0.9890
12	C.I. Disperse Red 1	314.35	+	315	134	-23	0.9995
13	C.I. Disperse Red 11	268.27	+	269	253	-23	0.9999
14	C.I. Disperse Red 17	344.37	+	345	164	-24	0.9833
15	C.I. Disperse Yellow 1	275.22	-	274	166	10	0.9969
16	C.I. Disperse Yellow 9	274.24	+	275	258	-16	0.9898
17	C.I. Disperse Yellow 39	264.33	+	291	245	-27	0.9816
18	C.I. Disperse Yellow 49	388.47	+	375	238	-14	0.9993
19*	C.I. Disperse Yellow 3	269.31	+	270	150	-17	0.9997
20*	C.I. Disperse Brown 1	432.02	-	431	371	15	0.9904
21	C.I. Disperse Orange 11	237.26	+	238	223	-23	0.9994
22	C.I. Basic Red 9	287.37	+	288	195	-31	0.9927
23	C.I. Basic Violet 14	300.41	+	301	195	-36	0.9940
24	C.I. Direct Blue 6	932.76	-	421	185	32	0.9975
25	C.I. Acid Red 26	480.43	-	435	302	30	0.9987
26	C.I. Direct Red 28	696.70	-	651	152	35	0.9984
27	C.I. Direct Black 38	781.76	-	736	278	36	0.9999

Table 1. MS/MS Condition for quantitative ions and results. Note: * marked dyes (No.19 and No.20) have both allergenic and carcinogenic character. No.1 to No.20 are allergenic dyes. No.19 to No.27 are carcinogenic dyes

Result and discussion

MS conditions shown in Table 1 were developed by continuous infusion of each dye into the MS. After selecting positive or negative ionization and optimizing capillary voltage, MS/MS breakdown curves were automatically generated (Figure 1). The optimum collision energy (CE) for each product ion, corresponds to the maximum intensity of the corresponding breakdown curve.

Example of multiple co-elutions resolved using multi-channel selective reaction monitoring – 1000 ppb Matrix Matched Standard (Figure 3).

Excellent linearity (Figure 4) was obtained for all the dyes.

Conclusion

The Varian 1200L LC/MS/MS system demonstrates excellent performance for the analysis of allergic and carcinogenic dyes in textiles. The 1200L can do fast screens and quantitatively analyze these compounds in the desired range from 500 to 1500 ppb and selectively confirm the presence of these dyes in real textile samples even after a very simple clean-up process. MRM operation allows screening for multiple dyes with only one injection.

System robustness and method reliability have been demonstrated through 6 months of daily operation during



Figure 4. Examples of calibration curves (500 to 1500 ppb)

which more than 5000 textile extracts have been analyzed in the Shanghai SGS. The only maintenance has been daily rinsing of the API capillary with methanol. This simple procedure takes two or three minutes and is performed while under full vacuum.

References:

[1] Min Huang, Jehuda Yinon, and Michael E.Sigman, J.Forensic Sci, Mar.2004, Vol. 49, No.2

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