MATERIALS ANALYSIS

DETERMINATION OF DIISOCYANATES IN PLASTICS USED IN TEXTILE PRODUCTS USING THE AGILENT 6410B LC/MS/MS

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ABSTRACT

Many textile products have surface coatings of plastic material that are used to give materials a particular aesthetic finish. Among the most widely used polymers are polyurethanes, which are generally obtained from monomers consisting of di-isocyanates (eg. 2,4-TDI). The proposed analytical method enables a range of free diisocyanates to be easily determined using a simple derivatization procedure and analysed by LC/MS/MS

INTRODUCTION

The determination of specific diisocyanates is very important in ensuring the eco-toxicological safety of textile coated products to the final consumer. Regulation 1907/2006/CE sets a limit of 0.1% by weight (i.e. 1000 mg/kg) for MDI, although stricter limits are required by some private regulations, such as the OEKO-TEX® Standard 100.

The proposed analytical method follows the guidelines set out in UNI EN 13130-8:2005, but possesses substantial changes regarding timing and the method of derivatization. However, despite these changes that simplify the method, excellent sensitivity and low detection limits can be achieved.

ANALYTICAL TECHNIQUE

Reagents

Acetonitrile, formic acid, dibutylamine (CAS Number: 111-92-2), N,N′-dimethylformamide (CAS Number: 68-12-2) and diisocyanates from Sigma-Aldrich (Milan, Italy).

Instrumentation

Chromatographic separation was performed on an Agilent 1200 HPLC system using an Agilent Zorbax Eclipse SB-C18 RRHT column and determined on an Agilent 6410B Triple Quadrupole Mass Spectrometer.

Sample Preparation

Samples are prepared using an ultrasonic extraction with dichloromethane and simultaneous derivatization with dibutylamine for 60 minutes. The resulting extract is then concentrated, resumes with 2 ml of N,N′-dimethylformamide and made up to volume with mobile phase; the extracts are analysed by LC/MS/MS.

This extraction procedure is faster and cheaper than UNI 13130-8 procedure.

Operating Conditions

LC Conditions	**Agilent 1200 HPLC System**	
Analytical Column	Agilent Zorbax Eclipse SB-C18 RRHT Column 2.1 x 50 mm, 1.8 µm	
Column Temperature	40°C	
Injection Volume	2 µL	
Mobile Phase	A= acetonitrile with 0.1% formic acid B= 0.05 mM formic acid	
Run Time	13 min, post run 6 min	
Flow Rate	0.25 mL/min	
Gradient	Time (min)	Gradient (% A)
	0	60
	0.5	60
	10	100
	13	100

MS Conditions	**Agilent 6410B Triple Quadrupole**
Acquisition Parameters	ESI Positive Ion Mode
Gas Temperature	320 °C
Gas Flow	10 L/min
Nebulizer Pressure	50 psi
Capillary Voltage	3000V

MRM Transitions

The MRM transitions, fragmentor and collision energies for the compounds are shown below.

Compound	CAS Number	Scan Segment	Prosecursor Ion (m/z)	Product Ion 1 (m/z)	Product Ion 2 (m/z)	Fragmentor Voltage (V)	Collision Energy (V)
2,6-TDI	91-08-9	1	433	303	130	120	12
2-4-TDI	584-84-9	1	433	303	130	120	12
HDI	822-06-0	1	427	298	130	120	12
trans-IPDI	4098-71-9	2	481	352	130	120	12
4,4′-MDI	101-68-8	3	509	380	130	120	12
TMXDI	2778-42-9	3	503	157	130	120	12
cis-IPDI	4098-71-9	3	481	352	130	120	12

RESULTS AND DISCUSSION

Calibration Curves

Calibration was performed using a 7-point calibration. The calibration range and detection limits for each compound are listed in Table 1.

Peak	Compound	Equation	R2	Regression	Range (µg/L)	LOD (µg/mL)
1	2,6-TDI	y=46001942.78x	0.9995	Linear, force by origin	1-1000	0.00049
2	2-4-TDI	y=577870880.63x	0.9983	Linear, force by origin	1-1000	0.00078
3	HDI	y=19309063.78x	0.9996	Linear, force by origin	1-1000	0.00056
4	trans-IPDI	y=17761335.49x	0.9992	Linear, force by origin	0.5-500	0.00021
5	4,4′-MDI	y=8305348.76x	0.9961	Linear, force by origin	1-1000	0.00071
6	TMXDI	y=20555338.51x	0.9998	Linear, force by origin	1-1000	0.00043
7	cis-IPDI	y=36184549.13x	0.9999	Linear, force by origin	0.5-500	0.00023

Table 1. Calibration information and limits of detection.

An example of a typical chromatogram is show in Figure 1. Calibration curves for cis-IPDI, 2,6-TDI and 2,4-TDI are shown in Figures 2, 3 and 4.

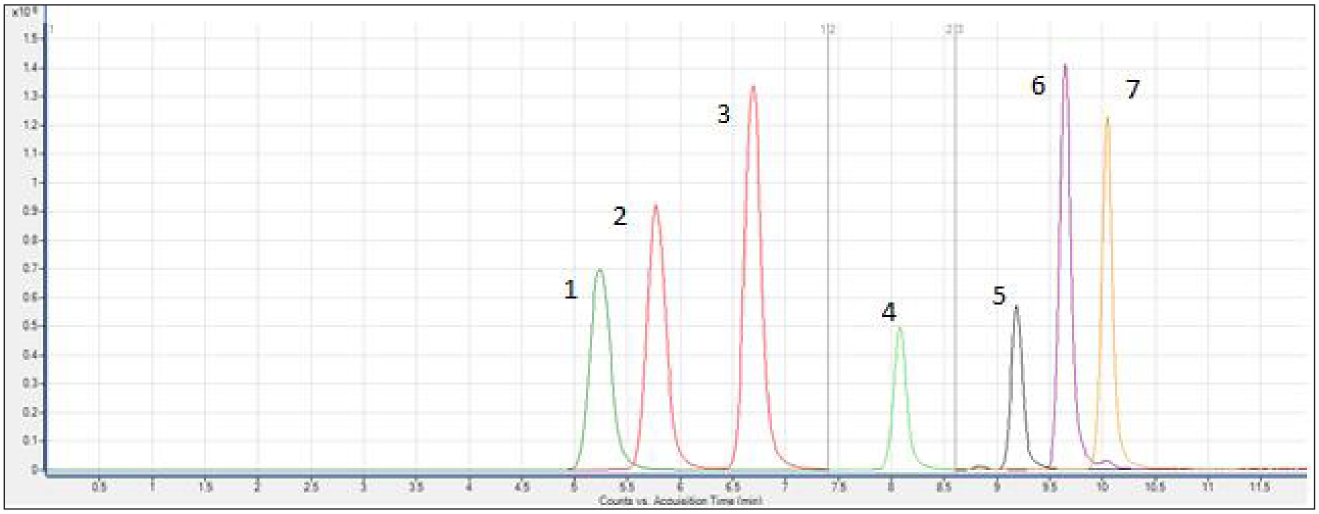

Figure 1. Standard at 0.05 µg/mL showing elution sequence: (1) 2,6-TDI (2) 2,4-TDI (3) HDI (4) trans-IPDI (5) 4,4′-MDI (6) TMXDI (7) cis-IPDI

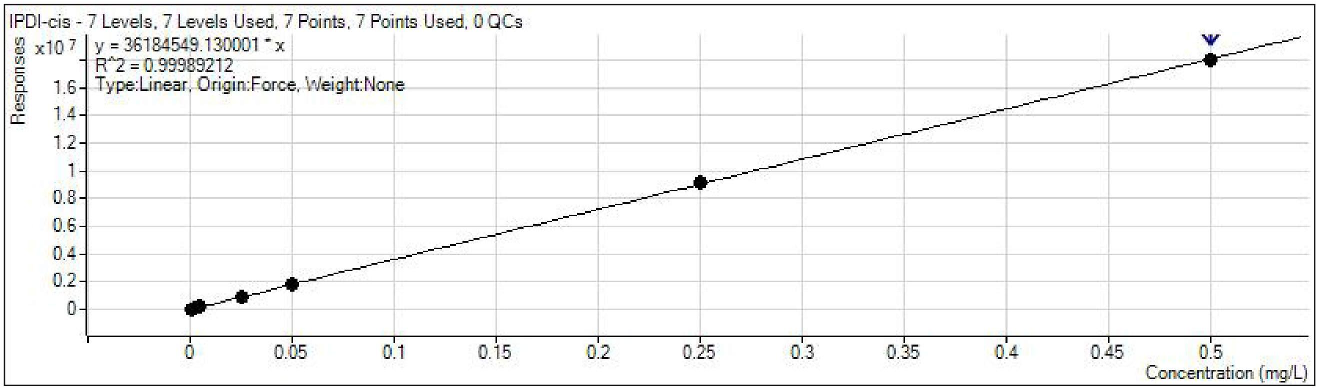

Figure 2. Calibration curve for cis-IPDI.

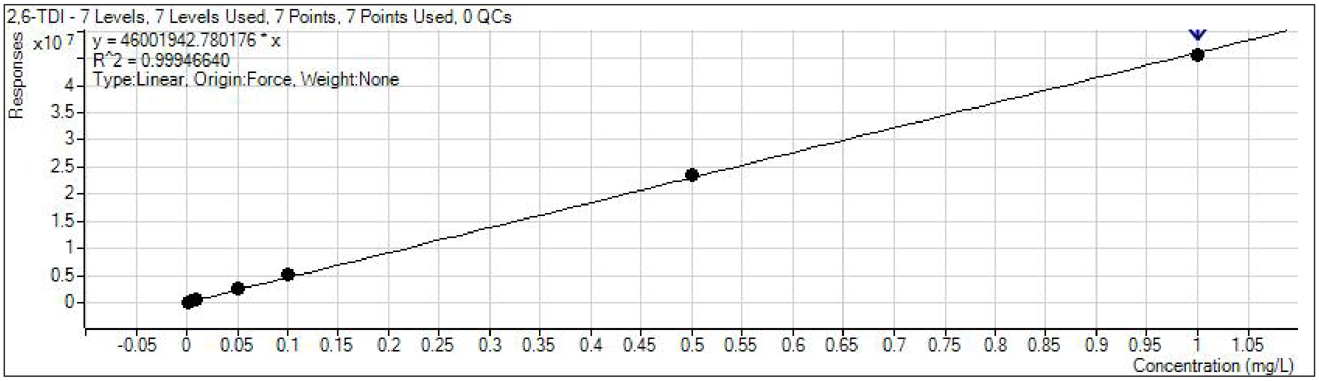

Figure 3. Calibration curve for 2,6-TDI.

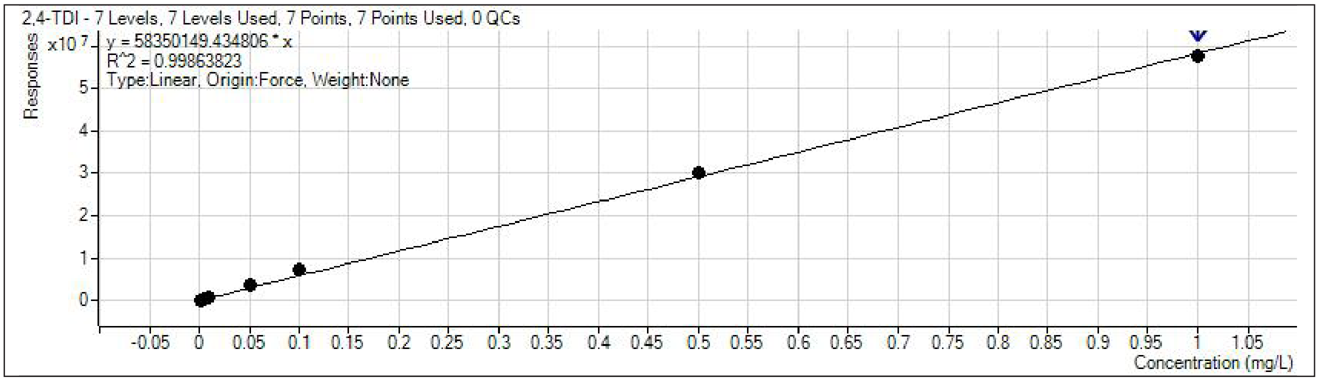

Figure 4. Calibration curve for 2,4-TDI.

CONCLUSIONS

The proposed analytical method enables a range of diisocyanates to be determined. It is easily expandable to specific isocyanates which may be required in future and private regulations. The simplicity of the derivatization allows samples to be prepared safely, rapidly and economically whilst maintaining analytical sensitivity.

REFERENCES

[1] UNI EN 13130-8:2005: Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics.

[2] Daniel Karlsson, Jakob Dahlin, Åsa Marand, Gunnar Skarping, Marianne Dalene, “Determination of airborne isocyanates as di-n-butylamine derivatives using liquid chromatography and tandem mass spectrometry”, Analytica Chimica Acta, 534, 2005, 263–269.

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