DETERMINATION OF "LIGHT" ISOCYANATES PRODUCED BY THERMAL DEGRADATION OF POLYURETHANES USING LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY

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INTRODUCTION

Isocyanates (NCO) are highly reactive molecules widely used in industry [1]. They are known respiratory sensitizers and the UK Health and Safety Executive (HSE) requires that worker exposure to NCO is minimised or, ideally, eliminated [2,3]. The method most commonly used for the determination of NCO in air is the HSL method, MDHS 25/3 [4,5].

A recent occupational health concern is the generation of " light" NCO e.g. methyl NCO, isocyanic acid (ICA) and mono-NCO during the thermal degradation of cured NCO [6,7] e.g. during welding/cutting of painted car parts. When carrying out these processes the worker does not wear the protective equipment required when working with uncured NCO and so could be exposed to hazardous levels of NCO.

EXPERIMENTAL

LC/MS

API 2000 triple quadrupole MS (Applied Biosystems, UK) in positive electrospray mode (ES+)

HP1100 LC system (Agilent, UK).

LC columns used were:

C18 - 250 x 2.1 mm 4m Genesis (Jones Chromatography, UK)

Hypercarb - 100 x 2.1 mm 5m (Thermo Hypersil-Keystone, UK)

Results for methods based on selected ion monitoring (+Q1 SIM), multiple reaction monitoring (MRM), scan (+Q1 SCAN), precursor ion scan and combinations of these MS modes are given.

SCREENING METHOD (MRM/SIM) - TABLE 1

Filters treated as described in MDHS 25/3

C18 LC column, acetonitrile/ammonium acetate gradient

MS

PERIOD 1 - SIM monitoring (6 ions)

m/z+

239 d3 isocyanic acid - MP (ISTD) 253 d3 methyl NCO - MP (ISTD)

236 isocyanic acid - MP 250 methyl NCO - MP

264 ethyl NCO - MP 278 propyl NCO - MP

PERIOD 2: EXPERIMENT 1 - SIM monitoring (5 ions)

m/z+

306 t - butyl NCO - EP (ISTD) 292 butyl NCO - MP (n and t isomers)

312 phenyl NCO - MP 320 hexyl NCO - MP

396 diisopropylphenyl NCO - MP

PERIOD 2: EXPERIMENT 2 - MRM monitoring (5 pairs)

m/z+

553 › 193 HDI - MP 559 › 193 TDI - MP (2,4 and 2,6 isomers)

607 › 193 IPDI - MP (E and Z isomers)

635 › 193 MDI - MP (4,4' isomer) 648 › 193 HMDI - MP

(193 is the protonated MP fragment [MP+H]+, common to all NCO - MP)

Isocyanate MP derivative spiked	Spike µg NCO	% Recovery	% RSD	Est LOD (solution) S/N = 3 ng NCO/ml
isocyanic acid	0.030	78	54	2
methyl NCO	0.090	84	21	0.04
ethyl NCO	0.062	89	14	2
propyl NCO	0.110	104	13	46
DIPP NCO	0.145	119	11	2
n and t –butyl NCO	0.32	92	11	2
hexyl NCO	0.069	101	3	0.4
phenyl NCO	0.064	102	5	1
HDI	0.033	114	12	1
MDI	0.088	114	7	2
T-2,4-DI	0.031	96	14	2
T-2,6-DI	0.031	92	21	2
IPDI mix of isomers	0.231	119	10	1
HMDI	0.278	116	7	13

SPECIFIC METHOD (MRM) - TABLE 2

Filters treated with hexanoic anhydride

Hypercarb LC column, acetonitrile/ammonium acetate gradient

MS

PERIOD 1 - MRM monitoring (4 pairs)

m/z+

253 › 196 d3 methyl NCO - MP (ISTD) 236 › 193 isocyanic acid - MP

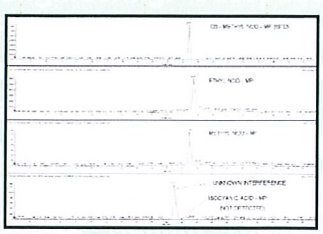
250 › 193 methyl NCO - MP 264 › 193 ethyl NCO - MP

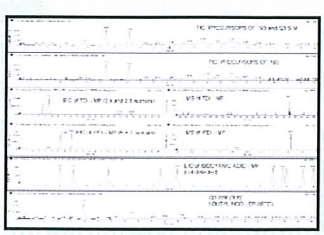
Result ng NCO/ml	NCO – MP derivative		
	Isocyanic acid	Methyl	Ethyl
HIGH			
mean (sd)	580(80)	240(20)	282(25)
%RSD	15	8	9
spike (ng)	537	253	302
% Rec	108	95	94
LOW			
mean (sd)	98(18)	24(3)	29(4)
%RSD	18	11	15
spike (ng)	106	25	30
% Rec	93	93	95
Estimated Limit of Detection (S/N = 3)			
ng NCO/ml	3	4	3

WELDING SAMPLES

Samples were taken of welding fume generated during automated spot welding of a car body part painted with a polyurethane based primer. Figures 1 and 2 give the chromatograms obtained using MRM and precursor ion scan methods.

ICA - MP was not detected by either method. The MRM method detected small amounts of ethyl NCO (~ 30 ng NCO/sample) and very small amounts of methyl NCO (not quantified). The precursor ion scan method detected two large IPDI - MP peaks (total ~ 19,700 ng NCO/sample, which corresponds to ~ 167µg NCO/m3) (UK STEL 70µg NCO/m3). Small amounts of TDI - MP were also detected using this method.





REFERENCES

1. G. Woods (editor), The ICI Polyurethanes Book, 2nd Ed, Pub ICI Polyurethanes and John Wiley and Sons, Chichester, UK, (1990).
2. Health and Safety Executive (HSE), Health and Safety Statistics 2000/2001, (2001).
3. Health and Safety Executive, EH40/2005, Occupational Exposure Limits, (2005).
4. Health and Safety Executive, Methods for the Determination of Hazardous Substances # 25/3, Organic Isocyanates in Air, (MDHS 25/3), (1999).
5. J. White, MDHS 25 Revisited; Development of MDHS 25/3, the Determination of Organic Isocyanate in Air, Ann. Occup. Hyg. Vol 50, No. 1, pp 15-27, (2006).
6. Health and Safety Laboratory, Report # 2003/10, The Determination of Isocyanates in the Presence of Amines, J. White, (2003).
7. Health and Safety Laboratory, Report in preparation, Sanding of Isocyanate Based Paints: Part 2 - Development of Methods for Low Molecular Weight Isocyanates, J. White (2006).