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Analysing for 4,4'-diaminodiphenylmethane in heritage collections containing solid and medium density flexible linear polyester polyurethanes using liquid chromatography/mass spectrometry

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Abstract

Polyurethane (PUR) shoe soles from collections held by the Alfred Gillett Trust, stored for up to 50 years, were analysed for the presence of 4,4'-diaminodiphenylmethane (4,4'-MDA)—a substance of very high concern in Europe and classified as a carcinogen in USA. A review of the literature revealed no papers on long term room-temperature hydrolysis of urethane or urea linkages leading to the spontaneous formation of 4,4'-MDA in polyester or polyether polyurethanes made from 4,4'-diisocyanatodiphenylmethane (MDI). However, evidence emerged of its potential formation and a possible handling hazard was consequently identified in the heritage collection. By chemical analysis, shortcomings in the current literature could be addressed. Calibration of liquid chromatography–mass spectrometry equipment showed analysis of 4,4'-MDA was possible down to 1 ppm with an error of 2.5 ppm. No 4,4'-MDA was found in the PUR analyte solutions at a concentration > 1 ppm. Under these experimental parameters the samples were shown to comply with the industrially accepted CertiPUR 2017 standard for commercial slab-stock foams. Furthermore, no 4,4'-MDA was found in solution after an 'accelerated anaerobic hydrolysis test' on the sole materials. This test was designed and developed to assess the likelihood of future formation of the aromatic amine via a hydrolysis-only mechanism/s. Finally, 4,4'-MDA itself was heated in air at 70 °C under 'humid' conditions to examine its stability. In this experiment the 4,4'-MDA altered in appearance and was reduced to ca 30% of its original weight. Subject to more work, it is conceivable 4,4'-MDA could be formed by hydrolysis, but degraded over time, and not detected in these tests.

Keywords: 4,4'-Diaminodiphenylmethane, MDI, Polyester, Polyurethane, Hydrolysis, Liquid chromatography/mass spectrometry, CertiPUR 2017

The evidence for potential production of 4,4'-diaminodiphenylmethane

Degradation of PUR artefacts is emerging as a salient theme for collections professionals in heritage

institutions [1]. Problems with degraded PUR soled shoes have been reported [2] and commercially available PUR shoe soles from diverse and largely unknown manufacturers and PUR material suppliers was chosen by the Alfred Gillett Trust (AGT) as a model substance for this investigation. Historically, PUR soles have been manufactured using either polyester (ES) or polyether (ET) polyols with "Pure MDI" [3, 4]. Spontaneous hydrolysis of PUR(ES) by atmospheric moisture and/or microorganisms has been reviewed [5]. Ether groups in PUR(ET) are shown to be stable to hydrolysis [6]. Literature on

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hydrolysis of PUR(ES) concentrates on degradation of the base polyol components and loss of physical performance. Little information exists on the potential production of 4,4'-MDA by scission of the urethane and urea linkages by natural hydrolysis. A priori, the influence of pigment and dye colourants might affect the stability of the urethane or urea linkages.

In the USA 4,4'-MDA appears in the NIOSH Occupational Cancer List [7] (synonyms: 4,4'-methylenedianiline, MDA). It is a substance of very high concern (SVHC) in Europe [9]. In the UK, the HSE [8, 15] imposes limits on employee exposure to 4,4'-MDA in the spraying of rigid PUR foams, because it is a known cause of contact dermatitis [10, 11]. 4,4'-MDA is a product in the recovery processes from scrap PUR [12]. Stability to hydrolysis of the urethane link in polyether polyurethanes at elevated temperature has been reported [13]. Production of small amounts of 4,4'-MDA by the hydrolysis of PUR made from polycarbonate-based polyols was studied for in vivo applications [16]. For furniture applications using MDI in the production of slab stock foam, a voluntary manufacturers specification of ≤ 5 ppm for 4,4'-MDA within the foam structure is given in CertiPUR 2017 [17] and the analytical method published therein was adapted to use samples of 0.5 to 5 g.

Pellizzi et al. [14] reported the formation of TDA (2,4-diaminotoluene) in naturally degraded PUR objects made with TDI formulations, and 4,4'-MDA

formation could be expected in chemically analogous MDI formulations.

LCMS analysis

A commercial sample of 4,4'-MDA (Sigma Aldrich, >97%, GC) was obtained to construct a calibration curve in the range 0–100 ppm using LCMS methods. A 4,4'-MDA solution in 1% aqueous acetic acid was used in this process, made by serial dilution of a 1000 ppm stock solution using volumetric methods. The extracted ion chromatogram (EIC) obtained by mass spectrometry was then used to construct new calibration graphs in the range 0 ppm to 10 ppm. The limit of detection of this method was determined to be <1 ppm. To account for variances in the LCMS system over time, this calibration process was repeated for each of 4 batches of PUR samples supplied over several months (Fig. 1).

Thirty PUR soles were selected from a range of manufacturers spanning 1970 to 1999. The analysis samples were sourced from the interior of the sole portion to avoid contamination by surface impurities which could distort the analysis results. The analysis liquors were prepared by mixing each cut sample independently with aqueous 1% acetic acid at a 1:5 weight/weight ratio in an ultrasonic bath for 2 h. To eliminate possible error at this very low-level detection (<1 ppm), after each sample LCMS run a supplementary LCMS quality control run was performed. The original

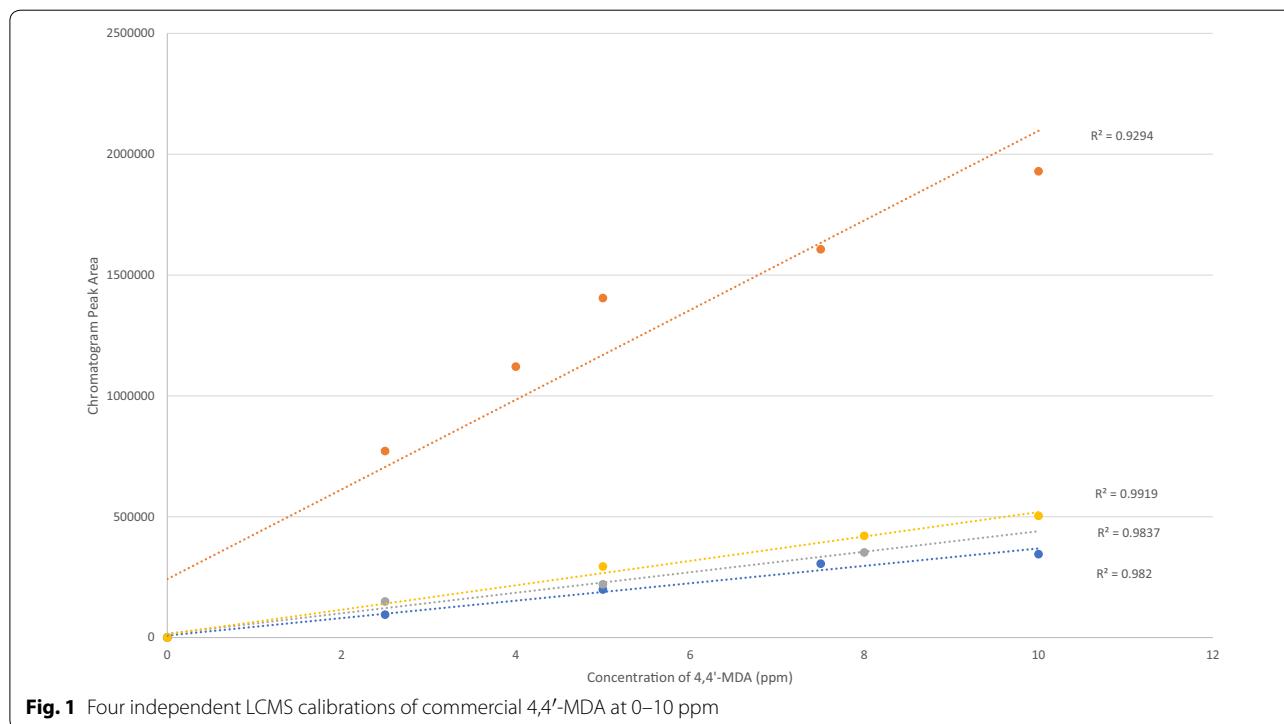


Fig. 1 Four independent LCMS calibrations of commercial 4,4'-MDA at 0–10 ppm

Table 1 Normal and spiked LCMS results obtained from naturally hydrolysed polyurethane shoe soles stored for up to 50 years

Sample number	Approx. date of manufacture	AGT Sample identification code	PUR sample construction	PUR sample colour	Normal LCMS solution results		Spiked LCMS solution results	
					Chromatogram peak area	ppm in PUR sample	Chromatogram peak area	ppm in PUR sample
1	1970	M19+SD118	Single density	Black	0	0	256,000	4.8
2	1974	1234/2926	Single density	Dark brown	0	0	217,000	3.9
3	1972	M19+SD100	Single density	Tan	0	0	200,000	3.6
4	1970	M19+SD122	Single density.	Black	0	0	162,000	2.9
5	1971	1234/1918A	Single density	Black	0	0	201,000	3.7
6	1970	1974/770	Single density	Black	0	0	206,000	3.8
7	1977	1234/3115	Single density solid elastomer	Tan-orange	0	0	211,000	3.9
8	1970	M19+SD123	Single density	Black	0	0	203,000	3.8
9	1975	1234/2934	Single density	Beige-mid-brown	0	0	169,000	3.1
10	1975	1234/2933	Single density	Mid-brown	0	0	183,000	3.4
11	1974	1234/2889	Single density	Black	0	0	194,000	3.5
12	1973	1234/2864	Single density	Tan-orange	0	0	181,000	3.3
13	1975	W19/SD865	Single density	Beige-mid-brown	0	0	197,000	3.6
14	1973	1234/2865B	Single density	Mid-brown	0	0	190,000	3.5
15	1981	M19/SD339	Dual density Outsole	Tan- orange	0	0	105,000	2.6
16	1981	M19/SD339	Dual density. Mid-sole	Black	0	0	119,000	3.1
17	1989	C19+SD614	Dual density. Midsole	Off-white	10,200	0.3	98,700	2.5
18	1985	C19+SD458LA	Single density	Light grey	0	0	119,000	3.0
19	1997	Sundapple	Single density	White	0	0	102,000	2.6
20	1996	0161	Dual density. Outsole	Black	11,800	0.3	189,000	4.5
21	1996	0161	Dual density. Midsole	Grey	0	0	138,000	3.5
22	1982	W19+SD132	Single density	Tan	0	0	135,000	3.4
23	1980–1999	SHO/5/23/3	Single density	Cream	0	0.00	778,000	2.7
24	1980–1999	SHO/5/8/1	Single density	Cream	0	0.00	776,000	2.7
25	1980–1999	CR/361/17	Single density	Brown	24,700	0.02	342,000	1.2
26	1980–1999	SHO/5/37/1	Single density	Cream	27,800	0.02	419,000	1.4
27	1980–1999	SHO/5/5/2	Single density	Cream	0	0.00	768,000	2.7
28	1980–1999	SHO/5/155	Single density	Cream-brown	23,100	0.02	333,000	1.1
29	1982	W19/SD1322	Single density. High blow (hydrolysed 4 weeks)	Tan	0	0.00	149,000	3.0
30	1982	W19/SD1322	Single density. High blow (hydrolysed 8 weeks)	Tan	0	0.00	757,000	2.6

All samples were coloured by pigments or dyestuffs and showed appreciable physical degradation. Results for accelerated hydrolysis tests are shown in Sample numbers 29 and 30

shoe sample liquor was 'spiked' with an additional 5 ppm of 4,4'-MDA by adding a 10 ppm 4,4'-MDA in 1% acetic acid solution in 50/50 ratio to the original shoe sample liquor. The 4,4'-MDA level in the sample can be determined by

subtracting 5 ppm from the measured LCMS value in the spiked sample. This spiking methodology allows the performance of the analytical method to be validated by ensuring that the amount of 4,4'-MDA added is equal to that

Table 2 Normal and spiked LCMS results obtained from accelerated ageing of commercial grade 4,4'-MDA

	Normal LCMS solution results		Spiked LCMS solution results	
	Chromatogram peak area	ppm in PUR sample	Chromatogram peak area	ppm in PUR sample
Aged 4,4'-MDA	469,000	1.6	1,370,000	4.9

analytically observed. Importantly, correlation between the un-spiked and 'corrected value' for the spiked samples validates our data (Table 1).

The results of the LCMS analysis of the shoe liquors of naturally hydrolysed and spiked samples are shown in Table 1. No. 4,4' MDA was detected above 0.3 ppm (within an error of ca. 2.5 ppm) under these experimental conditions.

Accelerated hydrolysis tests

It is conceivable 4,4'-MDA would be produced by spontaneous hydrolysis in future years [13]. To intentionally accelerate hydrolysis of the urethane and urea links in a PUR foam, ca 0.4 g to 0.5 g of two highly blown PUR samples were suspended over deionised water in sealed pressure tubes and held at 70 °C for 4 weeks and 8 weeks respectively. The highly blown PUR formulations contain larger proportions of MDI and could be more likely to produce 4,4'-MDA. The residues were analysed by LCMS in a similar way to that described in the LCMS analysis section above (Table 1, Sample numbers 29 and 30).

Accelerated atmospheric ageing effects on commercial grade 4,4'-MDA chemical (97% purity)

A vial containing 22.1 mg of commercial 4,4'-MDA was suspended in a flask over a deionised water reservoir. The flask was open to the atmosphere and held at 70°C for 4 weeks with a condenser attached to prevent loss of water. After analysis of the resultant sample by LCMS, only ca. 30% of the original 4,4'-MDA remained in the "aged" acetic acid solution compared to a recently prepared 5 ppm solution (Table 2). The aged 4,4'-MDA left a yellow insoluble deposit indicating decomposition.

Conclusions

In naturally hydrolysed and accelerated hydrolysed PUR(ES) no 4,4'-MDA was detected in the resultant liquor under these experimental conditions, even in physically degraded sole samples. The maximum

4,4'-MDA concentration recorded was 0.3 ppm, indicating the level of 4,4'-MDA in PUR(ES) is ≤ 5 ppm under these experimental conditions and below the CertiPUR 2017 [16] limit for PUR foams. The colour of the PUR had no observable influence on hydrolysis under these conditions. The method used was developed in the absence of a procedure to analyse heritage objects containing polyurethane for the existence of 4,4'-MDA, and confirmed that heritage collection items in this instance are safe to handle for the foreseeable future. In moist aerobic conditions, 4,4'-MDA degrades at 70 °C through an as-yet undetermined mechanism. Conceivably 4,4'-MDA might be formed by hydrolysis of the urethane or urea linkages degrading over time but not able to be detected in this work, using these experimental conditions. Further investigation is required for confirmation, or otherwise, to monitor long-term levels of 4,4'-MDA produced by polyurethane held in heritage collections.

Abbreviations

AGT: Alfred Gillett Trust; EIC: extracted ion chromatogram; ES: ester; ET: ether; GC: gas chromatography; HSE: Health and Safety Executive; LCMS: Liquid chromatography–mass spectrometry; MDI: 4,4'-diisocyanatodiphenylmethane; ppm: parts per million; PUR: polyurethane; TDA: 2,4-diaminotoluene; TDI: 2,4-toluenediisocyanate; UoN: University of Nottingham; SVHC: substance of very high concern; 4,4'-MDA, MDA: 4,4'-diaminodiphenylmethane, 4,4'-methylenedianiline.

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Authors' contributions

RT drafted the manuscript and designed the testing programme. TEC provided samples from the heritage collection at AGT. GM and JD developed the LCMS analytical technique, oversaw sample preparation, analysis work and interpreted the results. GJJ undertook the LCMS analytical work. All authors read and approved the final manuscript.

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Availability of data and materials

The data sets generated and/or analysed during the current study are not publicly available due to ownership by a private collection but are available from the corresponding author on reasonable request.

Competing interests

This research has been carried out without any commercial or financial relationships that might knowingly involve any competing interests.

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