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MEGA evaluations for the preparation of REACH exposure scenarios for 4,4'-methylenedianiline (MDA)

1 Introduction

The measured data for workplace exposure evaluated in the following have been gathered and documented in accordance with the principles of the measurement system of the German social accident insurance institutions for exposure assessment (MGU[1], formerly BGMG). The quality of the MGU is upheld by a quality management system that in essence satisfies the requirements of DIN EN ISO 9001. The test laboratories are operated in accordance with DIN EN ISO 17025 "General requirements for the competence of testing and calibration laboratories".

To measure 4,4'-methylenedianiline (MDA) exposure at the workplace, a defined volume of air is sucked by a suitable pump through a XAD-7 tube. After extraction with toluene and derivation with heptafluorobutyric anhydride (HFBA), the substance is qualitatively and quantitatively analysed by gas chromatography with an electron capture detector (ECD). Quantitative analysis is performed using the method of the external standard. The quantification limit is 0.005 mg/m³ for a test air volume of 20 L. Source: 4,4'-Diaminodiphenylmethane (ref. no. 6820). In: IFA-Arbeitsmappe Messung von Gefahrstoffen. 32. Lfg. IV/2004. Ed.: Deutsche Gesetzliche Unfallversicherung (DGUV), Berlin. Erich Schmidt, Berlin 2011 – loose-leaf edition.

All the surveyed data in the MGU are brought together in the MEGA exposure database (measured data on exposure to hazardous substances at the workplace). If individual values fall below the measurement method's analytical quantification limit, half the value is adopted in the evaluation. The MEGA[Pro] software developed by the IFA (formerly BGIA) makes it possible to statistically analyse the data of the MEGA exposure database on the basis of various selection criteria and evaluation strategies.

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[1] Gabriel, S.; Koppisch, D.; Range, D.: The MGU – a monitoring system for the collection and documentation of valid workplace exposure data. Gefahrstoffe – Reinhalt. Luft 70 (2010) No. 1/2, pp. 43-49 http://www.dguv.de/ifa, Webcode m200066

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2 Data situation and evaluation strategy

2.1 Overview of the measured values collected in the MGU, data period 2000 to 2011

There is no workplace limit for 4,4'-methylenedianiline (MDA).
Information on the sampling systems can be found in the IFA work folder (IFA-Arbeitsmappe, in German).

General description	Number of measured values (%)
Total	109
Type of sampling: Stationary	76 (69.7%)
Type of sampling: Personal	33 (30.3%)
Sampling time ≥ 1 h and exposure time ≥ 6 h (comparable to shift measurements)	86 (78.9%)
Sampling time < 1 h or exposure time < 6 h	23 (21.1%)
Number of data < quantification limit (Values < quantification limit were adopted in statistics with half their values)	99 (90.8%)
Number of data > limit value	Not specified
Number of data ≥ quantification limit and ≤ limit value	Not specified
Examples: Exposure conditions	
Without mechanical ventilation With mechanical ventilation No details	40 59 9
Without local exhaust ventilation With local exhaust ventilation No details	8 64 37
General description of 4,4'-methylenedianiline (MDA) measurements in 23 branches of industry and 40 work areas	

2.2 Criteria for inclusion of measured data in the evaluation

- Measured data relating to exposure

- Sampling time ≥ 1 hour

- Exposure time ≥ 6 hours

- Data sets comprising fewer than ten measured data were disregarded.

2.3 Evaluation strategy

The evaluation was performed on the basis of industry groups (Appendix 1) and work area groups (Appendix 2) and broken down further according to type of sampling (stationary or personal).

3 Abbreviations and indices

The following abbreviations and indices are used in the evaluation tables:

+ The distribution value is below the largest analytical quantification limit in the data set.

$ With reference to the given limit value, the percentage of values below the limit value is given.

! The number of measured values below the analytical quantification limit (a. q.) is greater than the number of measured values represented by this cumulative frequency value. No concentration is therefore given for this cumulative frequency value.

* Measured values below the analytical quantification limit of the measuring method concerned are adopted in the evaluation with half the analytical quantification limit value.

Appendix 1

Statistic evaluations for industry groups

4,4'-Methylenedianiline (MDA), sampling time ≥ 1 h and exposure time ≥ 6 h
Industry groups, general

D.No. = Data set number/ Designation Branch of industry	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 2 4,4'-Methylenedianiline Total	86	36	78 90.7	8	0.006	! a. q.	! a. q.	! a. q.	+ 0.0035
D.No. 4 4,4'-Methylenedianiline Plastics and plastic foam, processing; Manufacture of plastic sheets, tubes and profiles	13	6	12 92.3	4	0.002	! a. q.	! a. q.	! a. q.	+ 0.001
D.No. 5 4,4'-Methylenedianiline Iron and steel foundry, mixed; Iron foundry; Light metal foundry	47	18	43 91.5	2	0.006	! a. q.	! a. q.	! a. q.	0.0073

* AII = social accident insurance institution

Industry groups: Stationary measurements

D.No. = Data set number/ Designation Branch of industry	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 10 4,4'-Methylenedianiline Total	58	28	54 93.1	8	0.005	! a. q.	! a. q.	! a. q.	+ 0.0025
D.No. 12 4,4'-Methylenedianiline Plastics and plastic foam, processing; Manufacture of plastic sheets, tubes and profiles	11	5	10 90.9	4	0.002	! a. q.	! a. q.	! a. q.	+ 0.001
D.No. 13 4,4'-Methylenedianiline Iron and steel foundry, mixed; Iron foundry; Light metal foundry	31	14	30 96.8	2	0.005	! a. q.	! a. q.	! a. q.	! a. q.

* AII = social accident insurance institution

Industry groups: Personal measurements

D.No. = Data set number/ Designation Branch of industry	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 11 4,4'-Methylenedianiline Total	28	16	24 85.7	5	0.006	! a. q.	! a. q.	+ 0.0036	0.0072
D.No. 15 4,4'-Methylenedianiline Plastics and plastic foam, processing; Manufacture of plastic sheets, tubes and profiles	2	1	2 100	1	0.002				
D.No. 16 4,4'-Methylenedianiline Iron and steel foundry, mixed; Iron foundry; Light metal foundry	16	8	139 81.3	2	0.006	! a. q.	! a. q.	0.0068	0.0524

* AII = social accident insurance institution

Industry groups: Measurements with local exhaust ventilation

D.No. = Data set number/ Designation Branch of industry	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 37 4,4'-Methylenedianiline Total	52	21	46 88.5	7	0.006	! a. q.	! a. q.	+ 0.0025	+ 0.0054
D.No. 21 4,4'-Methylenedianiline Plastics and plastic foam, processing; Manufacture of plastic sheets, tubes and profiles	8	2	8 100	2	0.002				
D.No. 22 4,4'-Methylenedianiline Iron and steel foundry, mixed; Iron foundry; Light metal foundry	21	9	18 85.7	2	0.006	! a. q.	! a. q.	0.0075	0.0413

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Industry groups: Measurements without local exhaust ventilation

D.No. = Data set number/ Designation Branch of industry	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 36 4,4'-Methylenedianiline Total	26	14	24 92.3	4	0.005	! a. q.	! a. q.	! a. q.	+ 0.0025
D.No. 18 4,4'-Methylenedianiline Plastics and plastic foam, processing; Manufacture of plastic sheets, tubes and profiles	4	3	3 75	3	0.001				
D.No. 19 4,4'-Methylenedianiline Iron and steel foundry, mixed; Iron foundry; Light metal foundry	21	10	20 95.2	1	0.005	! a. q.	! a. q.	! a. q.	! a. q.

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Appendix 2

Statistical evaluations for work area groups

4,4'-Methylenedianiline (MDA), sampling time ≥ 1 h and exposure time ≥ 6 h
Work area groups: General

D.No. = Data set number/ Designation Work area	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 7 4,4'-Methylenedianiline Moulding in foundries	14	3	13 92.9	1	0.006	! a. q.	! a. q.	! a. q.	0.015
D.No. 8 4,4'-Methylenedianiline Casting	23	11	20 87	1	0.005	! a. q.	! a. q.	+ 0.005	0.0077
D.No. 9 4,4'-Methylenedianiline Manufacture of plastic sheets, tubes and profiles, Extruder, Casting processes, miscellaneous	15	9	15 100	7	0.002	! a. q.	! a. q.	! a. q.	! a. q.
D.No. 39 4,4'-Methylenedianiline Mixing	11	3	8 72.7	3	0.002	! a. B	+ 0.001	+ 0.002	0.003

* AII = social accident insurance institution

Work area groups: Stationary measurements

D.No. = Data set number/ Designation Work area	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 24 4,4'-Methylenedianiline Moulding in foundries	11	3	10 90.9	1	0.005	! a. q.	! a. q.	! a. q.	0.0207
D.No. 25 4,4'-Methylenedianiline Casting	14	9	14 100	1	0.005	! a. q.	! a. q.	! a. q.	! a. q.
D.No. 26 4,4'-Methylenedianiline Manufacture of plastic sheets, tubes and profiles, Extruder, Casting processes, miscellaneous	10	7	10 100	5	0.002	! a. q.	! a. q.	! a. q.	! a. q.
D.No. 40 4,4'-Methylenedianiline Mixing	10	2	8 80	2	0.002	! a. B	! a. B	+ 0.002	0.003

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Work area groups: Personal measurements

D.No. = Data set number/ Designation Work area	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 27 4,4'-Methylenedianiline Moulding in foundries	3	1	3 100	1	0.006				
D.No. 28 4,4'-Methylenedianiline Casting	9	5	6 66.7	1	0.005				
D.No. 29 4,4'-Methylenedianiline Manufacture of plastic sheets, tubes and profiles; Extruder, Casting processes, miscellaneous	5	3	5 100	3	0.002				
D.No. 41 4,4'-Methylenedianiline Mixing	1	1	0	1					

* AII = social accident insurance institution

Work area groups: Measurements without local exhaust ventilation

D.No. = Data set number/Designation Work area	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 30 4,4'-Methylenedianiline Moulding in foundries	3	2	3 100	1	0.005				
D.No. 31 4,4'-Methylenedianiline Casting	16	9	15 93.8	1	0.005	! a. q.	! a. q.	! a. q.	+ 0.005
D.No. 32 4,4'-Methylenedianiline Manufacture of plastic sheets, tubes and profiles, Extruder, Casting processes, miscellaneous	3	2	3 100	2	0.001				
D.No. 42 4,4'-Methylenedianiline Mixing	0	0	0	0					

* AII = social accident insurance institution

Work area groups: Measurements with local exhaust ventilation

D.No. = Data set number/Designation Work area	Number of measured data	Number of firms	Frequency < number of values %	Number of AIIs*	Largest quantification limit in mg/m³	Concentrations in mg/m³			
						50 percentile *	75 percentile *	90 percentile *	95 percentile *
D.No. 33 4,4'-Methylenedianiline Moulding in foundries	11	1	10 90.9	1	0.006	! a. q.	! a. q.	! a. q.	0.021
D.No. 34 4,4'-Methylenedianiline Casting	5	4	3 60	1	0.005				
D.No. 35 4,4'-Methylenedianiline Manufacture of plastic sheets, tubes and profiles; Extruder, Casting processes, miscellaneous	11	6	11 100	6	0.002	! a. q.	! a. q.	! a. q.	! a. q.
D.No. 43 4,4'-Methylenedianiline Mixing	11	3	8 72.7	3	0.002	! a. B	+ 0.001	+ 0.002	0.003

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