SUPPLEMENTARY INFORMATION

Organic Impurities, Stable Isotopes, or Both: A Comparison of Instrumental and Pattern Recognition Techniques for the Profiling of 3,4-Methylenedioxymethamphetamine

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In a publication by Van Deursen et al.,[1] 46 target impurities were suggested for the CHAMP profiling method. In a second publication by Weyermann et al.,[2] this list of 46 was modified to 31 (note: the list was published as 32 impurities, but one of the impurities was inadvertently listed twice under two different names[3]). Table 33 details the impurities from both lists, their structures, their published retention times using the CHAMP analysis conditions,[1] and their mass spectral data.[1,3-13] The impurities are named according to the Van Deursen et al.[1] and Weyermann et al.[2] publications.

Table 1. Target impurities as suggested by van Deursen et al.[1] and Weyermann et al.[2] Table continued overleaf.

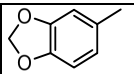
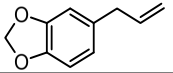
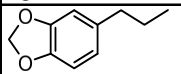
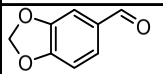
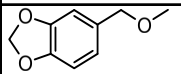
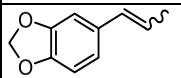
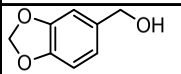
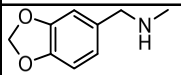
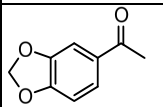
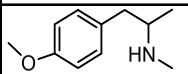
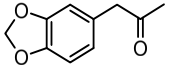
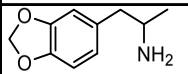
RT	Mass Spectral Data	Weyermann	Van Deursen	Name	Structure
6.48	135/136, 78/77, 51	--	1	1,2-(methylenedioxy)-4-methylbenzene	
9.19	162, 104, 131, 77, 51	--	2	safrole	
9.36	135, 164, 77, 51	1	3	1-(3,4-methylenedioxyphenyl)propane	
9.65	149/150, 121, 63, 91	--	4	piperonal	
9.75	135, 166, 77, 51, 136, 165	--	5	piperonyl methyl ether	
9.95/ 10.54	162, 104, 131, 77, 51	--	6(cis/tr)	isosafrole	
10.46	152, 135, 93, 65, 123	2	7	3,4-(methylenedioxyphenyl)methanol (piperonal alcohol)	
10.84	135/136, 164/165, 44, 77	3	8	*N*-methyl-3,4-(methylenedioxy)benzylamine	
11.22	149, 164, 121, 65, 43, 63	4	9	3,4-methylenedioxyacetophenone	
11.44	58, 121, 78, 91	5	10	*para*-methoxymethamphetamine (pMMA)	
11.71	89, 176, 175, 63, 90	6	--	unknown 176	
11.91	135, 179/178, 77, 51, 43	7	11	3,4-methylenedioxyphenyl-2-propanone (PMK)	
12.06	44, 135/136, 77	--	12	3,4-methylenedioxyamphetamine (MDA)	

Table S-1 (cont'd). Target impurities as suggested by van Deursen et al.[1] and Weyermann et al.[2] Table continued overleaf.

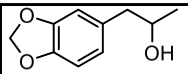
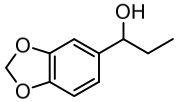
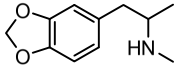
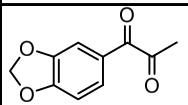
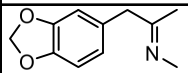
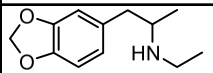
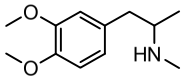
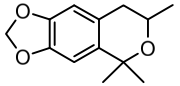
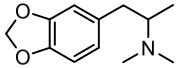
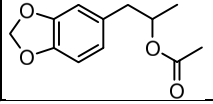
RT	Mass Spectral Data	Weyermann	Van Deursen	Name	Structure
12.21	135/136, 180, 77, 106, 51, 45	8	13	3,4-methylenedioxyphenyl-2-propanol (PMK-OH)	
12.47	93, 151, 77, 180	9	14	3,4-methylenedioxyphenyl-1-propanol	
13.16	58, 77, 135	--	15	3,4-methylenedioxymethamphetamine (MDMA)	
13.16	149, 121, 65, 63, 91, 192	--	16	1-(3,4-methylenedioxyphenyl)propane-1,2-dione	
13.33	147, 190, 89, 117, 63, 43, 135	--	44	unknown 147	
13.51	56, 135, 77, 191, 136	--	17	*N*-[2-(3,4-methylenedioxyphenyl)-1-methylethylidene]-*N*-methylamine	
13.6	72, 77, 73, 42, 135, 51, 44, 70	--	45	3,4-methylenedioxyethylamphetamine (MDEA)	
unknown	151, 194, 107, 135	10	--	3,4-dimethoxy-benzylmethylketone	
--	--	11	--		*mistake in Weyermann et al paper: this compound is the same as no. 18 (or van Deursen no. 28)*
13.87	205, 43, 220, 190, 157	12	18	trimethyl-3,4-methylenedioxychromane	
13.93	72, 56, 44, 73, 58, 70	--	19	3,4-methylenedioxydimethylamphetamine	
13.93	222, 162, 147, 135, 121, 104, 91, 77, 69, 63	13	20	2-(3,4-methylenedioxyphenyl)-1-methylethyl acetate	

Table S-1 (cont'd). Target impurities as suggested by van Deursen et al.[1] and Weyermann et al.[2] Table continued overleaf.

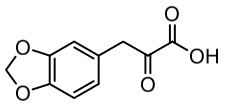
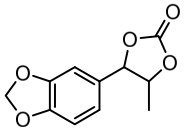
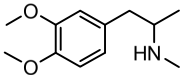
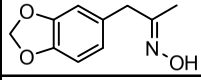
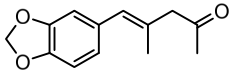
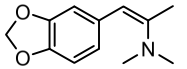
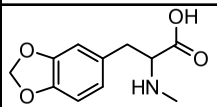
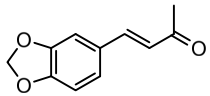
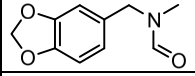
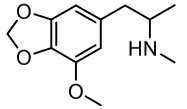
RT	Mass Spectral Data	Weyermann	Van Deursen	Name	Structure
13.96	164, 135, 134, 163, 208, 58, 76, 149	14	21	3-(3,4-methylenedioxyphenyl)-2-oxopropanoic acid	
14.1	178, 134, 43, 222, ?148?, 163, 72	15	22	4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxolan-2-one	
14.11	58, 152, 56	16	23	3,4-dimethoxymethamphetamine	
14.78	135, 193, 146, 77, 51, 105, 118	--	24	3,4-(methylenedioxy)benzylmethylketoxime	
14.86	175, 218, 117, 145, 115, 160	17	25	5-(3,4-methylenedioxyphenyl)-4-methylpent-4-en-2-one	
15.32	148, 190, 147, 205, 89	--	26	*N*-[2-(3,4-methylenedioxyphenyl)-1-methylvinyl]-*N*,*N*-dimethylamine	
15.42	88, 56, 178, 135, 58, 77	--	27	*N*-methyl-3,4-methylenedioxyphenylalanine	
15.64	190, 175, 145, 89, 117, 63	18	28	4-(3,4-methylenedioxyphenyl)but-3-en-2-one (MD-P3B)	
15.8	135, 193, 77, 42, 51, 136, 93, 150	20	29	*N*-methyl-*N*-formyl-3,4-methylenedioxybenzylamine	
15.94	58, 166, 77, 43	21	30	*N*-[2-(7-methoxy-3,4-methylenedioxyphenyl)-1-methylethyl]-*N*-methylamine	

Table S-1 (cont'd). Target impurities as suggested by van Deursen et al.[1] and Weyermann et al.[2] Table continued overleaf.

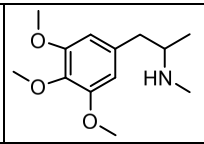
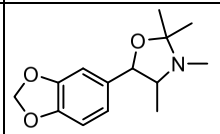
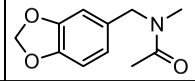
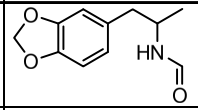
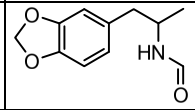
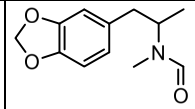
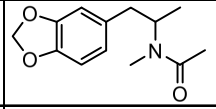
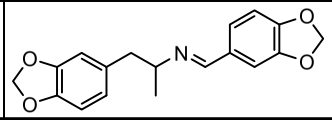
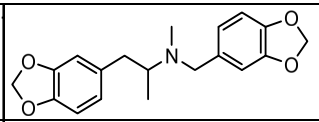
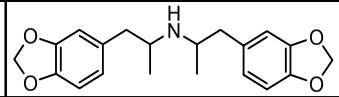
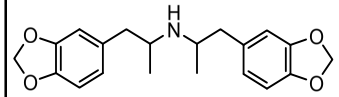
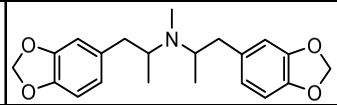
RT	Mass Spectral Data	Weyermann	Van Deursen	Name	Structure
15.99	58, 182	--	31	trimethoxymethamphetamine	
16.68	99, 192, 134, 71, 56, 84	19	32	5-(3,4-methylenedioxyphenyl)-2,2,3,4-tetramethyl-1,3-oxazolidine	
16.76	135, 150, 207, 77, 43, 164	22	33	*N*-methyl-*N*-acetyl-3,4-methylenedioxybenzylamine	
17.16	135, 162, 72, 44, 77, 51	23	34	*N*-formyl-methylenedioxyamphetamine (*N*-formyl-MDA)	
17.29	44, 162, 135, 77, 86	24	35	*N*-acetyl-methylenedioxyamphetamine (*N*-acetyl-MDA)	
18.02	86, 162, 58, 135, 77, 51, 30, 56	25	36	*N*-formyl-methylenedioxymethamphetamine (*N*-formyl-MDMA)	
18.40	58, 162, 100, 43, 77, 135	26	37	*N*-acetyl-methylenedioxymethamphetamine (*N*-acetyl-MDMA)	
24.68	176, 149, 77, 91, 135, 118	--	38	*N*-[β-3,4-(methylenedioxy)-phenylisopropyl]-3,4-(methylenedioxy)benazldimine	

Table S-1 (cont'd). Target impurities as suggested by van Deursen et al.[1] and Weyermann et al.[2] Table continued overleaf.

RT	mass spec	Weyermann	Van Deursen	ID	Structure
25.38	135, 192, 77, 105, 51	27	41	*N*-(3,4-methylenedioxyphenylmethyl)-*N*-[2-(3,4 methylenedioxyphenyl)-1-methylethyl]-*N*-methylamine (MD-benzyl-MDMA)	
25.56	163, 135, 206, 105, 133, 77	28	39	di-[1-(3,4-methylenedioxyphenyl)-2-propyl]amine (MD-DPIA 1)	
25.81	163, 135, 206, 105, 133, 77	29	39	di-[1-(3,4-methylenedioxyphenyl)-2-propyl]amine (MD-DPIA 2)	
26.29	135, 192, 77, 136, 105, 51	30	46	unknown 192	
27.07/ 27.15	163, 220, 135, 105, 58, 77	31	40	di-[1-(3,4-methylenedioxyphenyl)-2-propyl]methylamine (MD-DPIMA 1 + 2)	
27.21	218, 135, 157, 187, 77	32	42	unknown 218	
28.63	178, 218, 179, 42, 120, 135, 81	--	43	unknown 178	

Abbreviations

CHAMP	Collaborative Harmonisation of Methods for the Profiling of Amphetamine Type Stimulants
DA	Discriminant analysis
GCMS	Gas Chromatography Mass Spectroscopy
HCA	Hierarchical Cluster Analysis
IRMS	Isotope Ratio Mass Spectrometry
MDMA	3,4-Methylenedioxymethamphetamine (see Glossary definition)
PCA	Prinicpal Component Analysis
PMK	Piperonylmethylketone *or* MDP-2-P

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