Electronic Supplementary Material (ESI) for Analytical Methods.

Determination of Certain VOC's in Paints and Architectural Coatings by Dynamic Headspace GC-MS - Supplementary Information

Nicholas P. Alderman*, Matthew Courville and Ryszard Tokarczyk*

Environment and Climate Change Canada, Analysis and Air Quality Section, 335 River Road, Ottawa, ON, Canada, K1V 1H2

Description of Calibration

As the samples are concentrated by the adsorbent, traditional calibration of concentration vs response is difficult to conduct. This is due to being unable to take exactly the same small volume of thick paint/sample each time. Therefore we conducted the calibration by weight of analyte in each sample.

A calibration sample of analytes was produced by weighing each analyte into a 10 mL vial. For our calibrations, the analyte concentration (% by mass) was:

Acetone (9.1%), Methyl Acetate (10.7%), DCM (11.9%), 2CBTF (12.4%), 3CBTF (12.2%), 4 CBTF (12.1%), Dimethyl Carbonate (11.3%), t-butyl acetate (9.8%) and Propylene Carbonate (10.7%). 2- and 3-CBTF were added for interest only, are not excluded VOCs and were not part of this study.

Different masses of this sample were then taken for calibration, as shown below in Table S1.

Table S1 – Mass of analytes in each calibration sample

Sample mass (mg)	Acetone (mg)	Methyl acetate (mg)	DCM (mg)	2CBTF (mg)	3CBTF (mg)	4CBTF (mg)	Dimethyl carbonate (mg)	t-butyl acetate (mg)	propylene carbonate (mg)
0.65	0.059	0.069	0.077	0.080	0.079	0.079	0.074	0.063	0.069
1.14	0.103	0.122	0.135	0.141	0.139	0.138	0.129	0.111	0.122
1.73	0.157	0.185	0.205	0.214	0.211	0.209	0.196	0.169	0.185
2.35	0.213	0.251	0.278	0.291	0.287	0.284	0.266	0.229	0.251
5.57	0.504	0.595	0.660	0.690	0.680	0.673	0.630	0.544	0.595
10.4	0.941	1.112	1.232	1.288	1.269	1.257	1.176	1.015	1.111

Table S2 – Calibration of selected excluded VOCs desorbed from a carbon absorbent

Compound	Slope	R^2 Value
Acetone	1697	0.981
Methyl Acetate	4007	0.992
Dichloromethane (DCM)	2667	0.993
Dimethyl Carbonate	1590	0.989
t-butyl Acetate	1402	0.997

4-Chlorobenzotrifluoride (PCBTF)	2537	0.996
Propylene Carbonate	1121	0.993

Table S3 – The retention time and SIM ions of the excluded VOCs

Compound	Retention Time (mins)	Quantification ion	Qualifier ion
Acetone	7.803	43.1	58.1
Acetone-d_6		46.1	64.1
Methyl Acetate	8.318	43.1	74.1
Methyl Acetate-d_6		46.1	80.1
Dichloromethane (DCM)	8.593	48.0	82.9
Dichloromethane (DCM)-d_2		53.0	90.0
Dimethyl Carbonate	11.207	45.1	59.1
Dimethyl Carbonate-d_6		50.0	68.1
t-butyl Acetate	14.04	59.0	101.1
t-butyl Acetate-d_{12}		46.1	66.1
4-Chlorobenzotrifluoride (PCBTF)	20.994	180.0	161.0
4-Chlorobenzotrifluoride (PCBTF)-d_4		184.0	165.0
Propylene Carbonate	28.381	57.0	101.9
(±)-1,2-Propylene-d_6 Carbonate		62.0	89.9

Table S4 – Comparison of accuracy results between laboratory accredited Direct Injection method and the developed DHS method (the DHS method results are shown in brackets)

	Acetone	Methyl Acetate	Dichloro-methane	Dimethyl Carbonate	t-Butyl Acetate	4-CBTF	Propylene Carbonate
Accuracy (%)	1.6 (1.4)	-2.3 (-4.6)	4.8 (-13.9)	0.6 (-1.0)	-9.7 (-6.3)	2.1 (2.9)	2.5 (17.2)
Precision (RSD) (%)	2.3 (11.0)	2.3 (8.6)	2.5 (13.0)	2.0 (7.5)	5.0 (8.9)	1.2 (5.4)	1.7 (10.8)
U (%) (Expanded Uncertainty)	5.6 (23.6)	5.6 (18.5)	6.1 (27.8)	4.9 (16.1)	12.2 (19.2)	2.9 (11.7)	4.2 (23.2)
Expanded uncertainty using Student's distribution coefficient for 2-tailed test at 95% CI							

Table S5 – Literature results from CARB 'Development of an Improved VOC Analysis method for Architectural Coatings' [1] compared to the developed DHS method (the DHS method results are shown in brackets)

	Acetone	Methyl Acetate	Dichloromethane	t-Butyl Acetate	4-CBTF
Repeatability r (%)	1.2-5.0 (1.4)	0.5-4.6 (-4.6)	3.0 (-13.9)	3.8 (-6.3)	1.0-2.7 (2.9)
Reproducibility R (%)	1.9-24.5 (11.0)	0.7-29.3 (8.6)	17.9 (13.0)	15.6 (8.9)	1.5-12.4 (5.4)

Table S6 – Literature results from a static headspace method[2] compared to the developed DHS method (the DHS method results are shown in brackets)

	Acetone	Dichloromethane
Accuracy (%)	-1.6 (1.4)	-4.8 (-13.9)
Precision (RSD) (%)	2.2 (11.0)	3.6 (13.0)
U (%) (Expanded Uncertainty)	4.6 (23.6)	6.0 (27.8)

References

[1] Jones, D.R., Wills, M.T., Development of an Improved VOC Analysis Method for Architectural Coatings, 2008 Report, California Air Resources Board. Available from: https://ww2.arb.ca.gov/sites/default/files/classic//research/apr/past/04-329.pdf

[2] Deconincka, E., Canfyna M., Sacréa, P.-Y., Baudewyns, S., Coursellea P. and De Beer, J.O., A validated GC–MS method for the determination and quantification of residual solvents in counterfeit tablets and capsules, Journal of Pharmaceutical and Biomedical Analysis, 2021, **70**, 64–70.