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Atmosphärische Umweltforschung

The GAW World Calibration Centre for VOC (WCC-VOC)

GAW 2006 Workshop
Geneva,

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The WCC-VOC - Summary

- The WCC-VOC aims to guarantee a worldwide comparison of reported complex volatile organic compounds (VOC) data sets.
- This is achieved by round-robin exercises, station audits as well as training programs.
- A first round-robin exercise on C2 to C9 hydrocarbons and first audits are promising but also highlight calibration deficits.
- Further harmonising of analytical methods in particular for VOC > C10 and Oxy-VOC as well as intensive training is required for achieving comparable VOC data sets on GAW stations.

The WCC-VOC

- is operating a calibration laboratory for C2-C10 hydrocarbons and formaldehyde
- has elaborated a SOP for 2–valve canister sampling (C2 to C9 non-methane hydrocarbons (NMHC) at sub-ppbv levels,
- has conducted a worldwide round-robin exercise and audits for C2 to C9 hydrocarbons (GAW stations: Arembepe, Brazil, Pallas, Finland; EMEP station: Starina, Solvakia),
- has contributed to training programs (GAWTEC).

The WCC-VOC Round-Robin Exercise

- The intercomparison involved:

  - 9 different stations/laboratories using off-line as well as on-line techniques

  - in 7 countries (Brazil, Canada (2 labs), Czech Republic, Finland, Germany (2 labs; 3 instruments), Ireland, and Slovakia)

  - representing GAW, EMEP, CAPMoN and LBA programs

The Results: Repeatability

green: NIST-traceable VOC

VOC	A	B	C	D	E	F	G	H	I	J
	Participants									
ethane	4.6	1.0	1.2	0.2			0.3	2.8	0.3	
ethylene	4.5	2.7	0.6	0.8			2.5	2.5	0.4	
acetylene	4.7	0.3		**12.7**				2.6	0.6	
propane	3.8	0.2	2.1	0.5	3.9	2.2	0.9	3.0	0.2	
propylene	3.9	0.7	2.2	0.3	6.4	2.0	**23.4**	3.1	1.4	
i-butane	4.0	0.6	3.8	0.8	4.6	2.4	0.3	2.3	0.6	4.4
n-butane	**5.3**	0.3	1.9	0.1	**7.1**	2.5	0.3	2.0	0.6	
1-butene	5.2	**36.9**	2.4	0.2					1.6	
t-2-butene	4.7	2.7	2.6	0.6		2.0			3.0	1.8
i-butene			2.1	5.8				2.9	2.8	
c-2-butene			1.8	1.4		2.6		2.6	4.7	5.2
i-pentane			2.1	0.6	4.0		0.3	2.4		3.2
n-pentane			2.4	0.2		1.8	1.2			
isoprene	1.9	**21.5**	2.4	0.5	4.4	2.8	1.1	1.3	0.8	7.6
t-2-pentene	12.6	3.7	2.7	0.5		11.7	2.2	8.2	3.1	**45.4**
c-2-pentene	2.9	1.3	2.8	0.3		2.6	0.7	3.7	4.0	8.3
2-me pentane			2.9			3.3	2.7			
3-me-pentane			4.4	0.3		3.0	**8.1**			3.0
n-hexane	**9.8**	3.3	4.3	0.3	**6.6**	2.7	1.2	4.6	**5.2**	2.6
benzene	1.4	1.1	1.9	0.9		3.2	2.3	3.8	1.6	
cyclohexane	3.4					3.4		3.3		
n-heptane	3.8		**5.1**	1.2	4.1	2.9	1.0		0.9	3.1
toluene	4.7	7.0	7.7	3.9	7.6	2.9		3.6		3.0
et-benzene			3.8	5.6	5.6	3.0		1.1	3.1	4.6
m,p-xylene			3.3	5.5	5.1	3.2		2.2	3.7	3.7
o-xylene		1.8	3.6		6.8	3.1		7.4		
1,3,5 trime-benzene			4.6			4.9				**10.8**
1,2,4 trime-benzene			2.5			5.3				**14.5**

Results that did not meet the DQOs are shown in red

The Results: Deviation [%] from the WCC-VOC reference values

green: NIST-traceable VOC

VOC	Participants A	B	C	D	E	F	G	H	I	J
ethane	3.8	-64.2	-3.4	-1.2			-2.1	-4.4	-1.1	
ethylene	5.2	-73.5	5.2	7.3			-16.5	-7.5	-2.3	
acetylene	-13.8	-54.7		4.0				-22.4	-25.1	
propane	9.6	1.0	-0.1	2.1	-27.6	-3.0	-2.7	-9.1	-1.0	
propylene	8.0	-1.9	5.4	11.5	-66.0	2.3	-15.7	-2.3	1.1	
i-butane	9.4	81.5	8.4	11.0	-33.7	-10.1	1.8	-4.3	2.5	8.1
n-butane	6.7	78.8	-0.2	5.7	-30.6	-9.0	-2.6	-3.5	-0.7	
1-butene	4.2	137.3	6.4	11.2					3.2	
t-2-butene	3.4	47.0	7.5	9.2		-18.1			-2.8	12.7
i-butene	6.9		2.7	10.3				2.3	-3.8	
c-2-butene	-2.4		1.8	4.3		-7.6		-12.7	-7.4	3.2
i-pentane	-14.3		-2.3	5.2	-42.9		-5.8	-12.1		-2.5
n-pentane	-26.3		-1.5	3.7		-0.2	-0.6			
isoprene	5.5	-98.0	-6.2	-17.0	-78.8	-16.7	-2.5	5.2	1.4	-1.2
t-2-pentene	-52.2	-22.9	92.3	6.6		-6.8	-4.0	-29.3	-11.6	23.8
c-2-pentene	-20.8	19.8	3.6	-0.6		-6.4	-1.7	-12.2	-5.4	1.0
2-me pentane			5.9			-17.2	1.2			
3-me-pentane			0.7	13.3		-7.9	-4.6			2.3
n-hexane	-27.3	236.6	-3.0	4.3	-40.8	-11.5	0.2	-30.7	-12.8	-0.6
benzene	6.3	208.2	-5.5	2.9		0.5	-0.4	-14.7	-5.2	
cyclohexane	51.4					-22.7				
n-heptane	5.1		-6.5	4.3	-45.0	6.7	3.5		-1.4	-0.5
toluene	27.2	-79.8	-5.1	10.1	-22.2	16.6		-6.5		10.1
et-benzene			1.1	-3.0	75.5	1.1		-21.1	3.0	5.3
m,p-xylene			4.1	-2.4	34.0	-14.3		-16.3	7.4	0.4
o-xylene		1529.6	5.1		228.2	-22.9		-28.5		
1,3,5 trime-benzene			-29.0			-90.8				-16.6
1,2,4 trime-benzene			30.0			-82.4				0.8

Results that did not meet the DQOs are shown in red

The Conclusion

The results obtained in the C2-C9 hydrocarbon round robin exercise are promising, however, still comparable determination of VOC at low concentration levels remains a challenge,

in particular when real air samples are compared and it appears imperative to strengthen harmonization procedures.

The Future

- Round-Robin exercises with less VOC (5-10) containing hydrocarbons as well as oxyVOC on a more rigorous time schedule basis, possibly including exchange of canisters/sampling tubes for concurrent air sampling.

- SOPs for the stage two/three GAW-VOC measurement program (C10–C14) hydrocarbons including biogenic ones, as well as oxy VOC) need to be worked out on the basis of the recommendations of this VOC-Expert Workshop.

- Training in GAWTEC courses ensures sound data quality and will be continued, particularly focussing on stage two/three VOC compounds.

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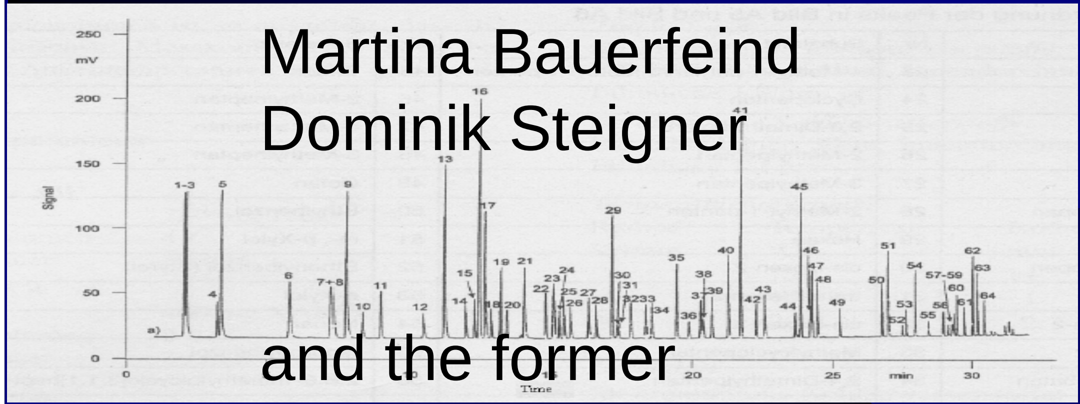

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