GAW-WCC-VOC/CCQM-GAWG-VOC Workshop

IMK-IFU Garmisch-Partenkirchen, July 03/04, 2006

Contact: Rainer Steinbrecher

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft
Institut für Meteorologie und Klimaforschung
Atmosphärische Umweltforschung

Umwelt Bundes Amt
Für Mensch und Umwelt

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The GAW World Calibration Centre for VOC and Central Calibration Laboratories (CCLs)

with

Rainer Steinbrecher
and
Colleagues

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The Summary

- Hydrocarbons in the atmosphere contribute significantly to regional and global air quality, oxidizing power as well as climate change.
- The GAW-WCC-VOC aims to guarantee a worldwide comparison of reported complex VOC data sets.
- This is achieved by round-robin exercises, station audits as well as training programs.
- A first round-robin exercise and first audits are promising but also highlight problems.
- The future GAW-VOC concept.

The WCC-VOC

- The GAW-WCC-VOC is hosted by the Forschungszentrum Karlsruhe,
IMK-IFU (Garmisch-Partenkirchen, Germany):

- It ensures GAW-Network wide quality assured data sets

by

- conducting worldwide round-robin exercises and audits for GAW stations and

- training of GAW stations staff (GAW-TEC).

The WCC-VOC

- Example of a Round-Robin inter-comparison exercise:

  - 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 Procedure

- Standard gas canisters provided by the WCC-VOC with 73 VOCs in N_2 prepared and certified by NCAR, Boulder, with 16 VOCs NIST-traceable.
- The participating laboratories were expected to identify and quantify as many compounds of the WCC-VOC standard canister as possible based on their routine identification and calibration methods.
- A standard questionnaire for air sampling, Analytical system and method, reporting results was circulated for completing

Current Data Quality Objectives

- alkanes and alkynes:
  uncertainty: 10% (accuracy) repeatability: 5% (precision)

- alkenes:
  uncertainty: 20% repeatability: 20%

- aromatics:
  uncertainty: 15% repeatability: 10%

The Results: Repeatability (Precision)

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

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Results of the first GAW-VOC Round-Robin exercise:

Deviation [%] from the WCC-VOC reference values (Accuracy)

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

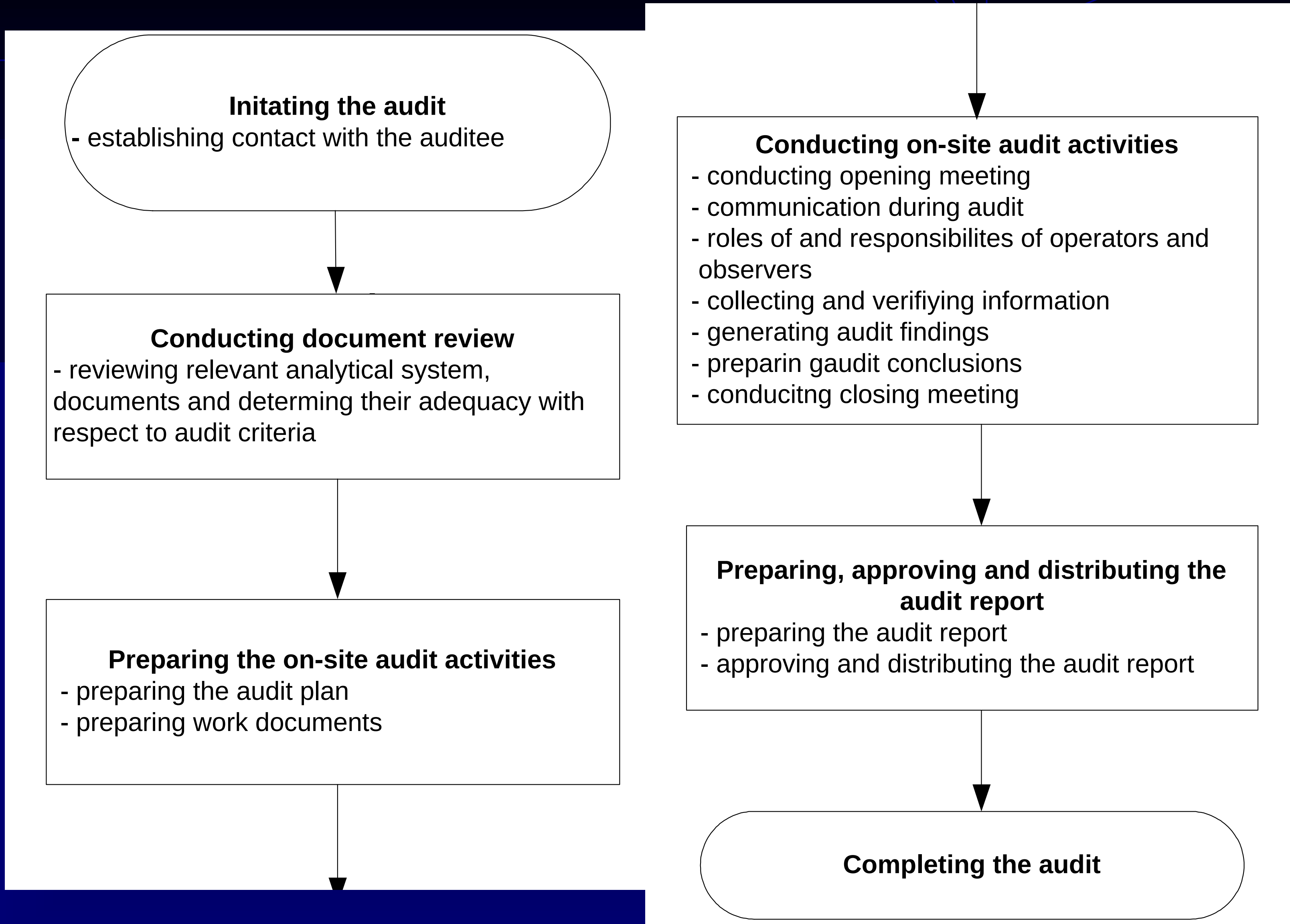
Results of the first GAW-VOC Round-Robin exercise:

Compound r*anking according precision and accuracy*

VOC	X [%]	Y [%]	VOC	X [%]	Y [%]	VOC	X [%]	Y [%]
propane	80.0	88.9	i-butane	60.0	60.0	t-2-pentene	40.0	44.4
c-2-pentene	80.0	88.9	n-butane	60.0	66.7	n-hexane	40.0	40.0
isoprene	80.0	80.0	i-butene	50.0	100.0	2-me pentane	20.0	66.7
c-2-butene	70.0	100.0	et-benzene	50.0	71.4	o-xylene	10.0	20.0
benzene	70.0	87.5	m,p-xylene	50.0	71.4	acetylene	0.0	0.0
propylene	70.0	77.8	n-pentane	40.0	80.0	cyclohexane	0.0	0.0
ethylene	60.0	85.7	3-me-pentane	40.0	80.0	1,3,5 trime-benzene	0.0	0.0
t-2-butene	60.0	85.7	1-butene	40.0	80.0	1,2,4 trime-benzene	0.0	0.0
ethane	60.0	85.7	i-pentane	40.0	57.1			
n-heptane	60.0	75.0	toluene	40.0	50.0			

X: related to all participants; Y: related to all participants who identified this specific VOC
NIST traceable compounds are listed in green

Audits



Adopted from ISO19004

Audits

- Pallas ↑
- Arambepe →
- Starina →

Starina, Slovakia

GAW-TEC VOC

- Atmospheric Chemistry and VOC

- VOC and Gas-Chromatography

- QA/QC and GAW-VOC

- Data reporting and GAW

Conclusions

- The results obtained in the audits and inter-comparisons are promising, however, still accurate determination of VOC at low concentration levels remains a challenge .

- It appears imperative to strengthen harmonization procedures.

The Future GAW-VOC Concept

- QA/QC procedures with less VOC on a more rigorous time schedule basis, possibly including exchange of canisters for concurrent air sampling.
- Update SOPs for sampling procedures according new requirements.
- Update training in GAWTEC courses focussing on new compounds ensuring a continuously sound data quality

The Future GAW-VOC Reference Standard

Compound	
Ethane	Acetone
Propane	DMS
Acetylene	Benzene
Isoprene	Toluene
Formaldehyde	Iso-Butane
Monoterpenes	n-Butane
Acetonitrile	Iso-Pentane
Methanol	n-Pentane
Ethanol	

Compound	*Accuracy*	*Precision*
Ethane	10%	5%
Propane	10%	5%
Acetylene	10%	5%
Isoprene	15%	15%
Formaldehyde	15%	15%
Monoterpenes	15%	15%
Acetonitrile	15%	15%
Methanol	15%	15%
Ethanol	15%	15%
Acetone	15%	15%
Dimethylsulfide (DMS)	15%	15%
Benzene	15%	10%
Toluene	15%	10%
Iso-/n-Butane	10%	5%
Iso-/n-Pentane	10%	5%
mixing ratio < 0.1 ppb	± 10 ppt	± 10 ppt

The Future GAW-VOC Central Calibration Laboratory CCL

The basic concept for the traceability of standards is the relation to a CCL-calibrated gas mixtures (Scale) to which all laboratory and transfer standards of the WCC will be related.

The GAW-SAG „Reactive Gases“ and the Subgroup VOC would appreciate if the CCQM Gas Analysis Working Group will host the GAW-VOC Scale

WMO & GAW-VOC say

Thanks for your attention