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# The first VOC intercomparison exercise within the Global Atmosphere Watch (GAW)

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**Abstract**

In 2003 the World Calibration Centre for volatile organic compounds (WCC-VOC) which forms part of the Global Atmosphere Watch (GAW) program coordinated the first comprehensive intercomparison exercise among the GAW-VOC community. The intercomparison focused on a synthetic $C_2$–$C_{11}$ VOC standard mixture in nitrogen ($N_2$) and involved nine different stations/laboratories (10 instruments) from seven countries (Brazil, Canada [two labs], Czech Republic, Finland, Germany [two labs; three instruments], Ireland, and Slovakia), representing four measurement programs (GAW, EMEP, CAPMoN, LBA). These sites either run canister or online measurements. WCC-VOC provided each participant of the intercomparison exercise with standard gas canisters which contained 73 VOCs prepared and certified by the National Center for Atmospheric Research (NCAR), Boulder. 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. The primary objective of this first intercomparison was to examine the current performance status of the analytical facilities of each laboratory and to check whether the results meet the Data Quality Objectives (DQO) developed by WCC-VOC. An additional objective was to establish a ranking of properly determined compounds among all laboratories in order to identify compounds which could be most accurately determined by all laboratories.

Due to the variety of sampling and analytical methods among the participants both the number of identified species (16–150 VOCs) and their proper quantification differed largely. Focusing on a subset of 28 VOCs recognized as primary

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GAW target compounds the results show that the DQOs for repeatability are met in most cases. However for the deviation from the WCC-VOC reference values the picture is different. For some VOCs the concentrations differed significantly among the different laboratories. In terms of both uncertainty and repeatability a significant number of atmospherically relevant VOCs (e.g. propane, propylene, isoprene, and benzene) are properly determined by most labs. However, difficulties occur with other important VOCs (e.g. acetylene, i-pentane, toluene). From this subset of VOC results it appears imperative to strengthen harmonization procedures particular with regard to real air samplings. These processes have been initiated and include more frequent intercomparisons also covering ambient air samples, individual performance audits, and a future networkwide calibration standard.


*Keywords:* GAW; VOC; Intercomparison; Canister

## 1. Introduction

Highly volatile organic compounds (VOCs) consist of different classes with specific properties regarding their origins, chemical structure, chemical reaction pathways, reaction kinetics, formation potentials for photooxidants, atmospheric mixing ratios and atmospheric lifetimes. In the presence of nitrogen oxides ($NO_x$) VOCs largely contribute to the formation of photochemical smog in the sunlit atmosphere through their photochemical degradation pathways (Atkinson, 1990, 2000). In these processes formation of various secondary compounds occur, e.g. ozone ($O_3$), peroxycarboxylic nitric anhydrides (PANs) ($RC(O)O_2NO_2$; R: = organic rest), hydrogen peroxide ($H_2O_2$) and in general organic hydrogen peroxides (ROOH), and a broad range of aldehydes RCHO are produced. In addition, short-lived intermediate products occur such as hydroxyl radicals (OH), hydrogen peroxy radicals ($HO_2$) and organic peroxy radicals ($RO_2$). Another characteristic of photochemical processes induced by VOC is the enhanced formation of aerosols (Bowman et al., 1995) that causes increased turbidity of the atmosphere.

Measurements of VOCs have been used in a variety of analyses: inventory evaluation (Goldan et al., 1995; Scheff et al., 1996), monitoring changes of atmospheric levels to infer changes in emissions (Singh et al., 1985), source reconciliation studies (Nelson et al., 1983; Zweidinger et al., 1988; Aronian et al., 1989; McLaren et al., 1996a, b; Doskey et al., 1992), evaluation of photochemical models (Sillman, 1995), investigations of the seasonal cycle of photochemistry (Rudolph et al., 1989; Jobson et al., 1994; Goldstein et al., 1995), and indirect determination of air mass history or radical concentrations (Calvert, 1976; Roberts et al., 1984; McKeen et al., 1990; Parrish et al., 1992; Kramp and Volz-Thomas, 1997; Volz-Thomas and Kolahgar, 2000).

Reliable and representative measurements of VOCs are necessary to describe the anthropogenic and biogenic sources, to follow the photochemical degradation of VOCs in the troposphere, and to assess the effectiveness of control measures. However, due to the complexity of VOC measurements, in particular at low concentration levels, the proper determination of VOCs still remains a challenge. Over the last decade various international VOC intercomparisons were carried out (De Saeger and Tsani-Bazaca, 1992; Hahn, 1994; Romero, 1995; Apel et al., 1994, 1995, 1999, 2003; Bernardo-Bricker et al., 1995; Pérez Ballesta et al., 2001; Slemr et al., 2002; Plass-Dülmer et al., 2006) primarily focusing on canister sampling combined with subsequent laboratory gas chromatographic (GC) analysis. Recently, within the German Tropospheric Research Focus (TFS), online methods have been scrutinized by Volz-Thomas et al. (2002). The TFS program in particular addressed coelution problems in VOC GC instrumentations (Konrad and Volz-Thomas, 2000; Volz-Thomas et al., 2002). All studies have in common that large deviations among the participants were apparent, in particular at low pptv-ranges and when real air samples were analyzed instead of synthetic calibration gas mixtures. The results of these intercomparisons of VOC measurements suggest that co-elution is the most frequent reason for erroneous measurements, and that misidentification of certain compounds is also important regardless which method was used. These errors may be limited by using a mass spectrometer instead of a flame ionization detector (FID). For ambient air canister measurements some specific problems were reported: Contamination artifacts for alkenes (especially ethylene and propylene) may occur, when very clean air masses with alkene

concentrations below 100 pptv are sampled. Losses of higher hydrocarbons, especially of aromatic compounds, are encountered in very dry air samples. In these cases it appears necessary that sufficient water content in the canisters is present to achieve stability of VOC concentrations during storage. Other problems have been identified, e.g. loss of $C_2$ and $C_3$ hydrocarbons due to insufficiently low enrichment temperature (this may also trouble online measurements), and adsorption effects for less volatile VOC compounds ($C_8$–$C_9$ aromatic compounds) during the transfer of the air sample from the canister and during the conditioning of the sample.

Still, the proper determination of VOCs is a difficult task to accomplish. The need for further intercomparisons has been postulated (Parrish and Fehsenfeld, 2000) to ensure high quality data in ambient air studies. Recent studies (Fortin et al., 2005) critically reviewed ambient air VOC results based on canister and online measurements taken in various US sites. The determination of VOCs constitutes an important task within the Global Atmosphere Watch (GAW) program of World Meteorological Organization (WMO). The purpose will be to monitor the atmospheric VOC abundance, to characterize the various compounds with regard to anthropogenic and biogenic sources and to evaluate their role in the tropospheric ozone formation process. An international WMO/GAW panel of experts for VOC measurements (WMO, 1995) developed the rational and objectives for this GAW activity and recommended the configuration and required activities of a GAW World Calibration Center for VOC (WCC-VOC). The German Environmental Agency (UBA) was assigned by WMO to take over responsibilities for the operation of WCC-VOC. Since 2002 WCC-VOC is hosted by the Institute for Meteorology and Climate Research, IMK-IFU, of the Forschungszentrum Karlsruhe (FZK) in Garmisch-Partenkirchen, Germany. Among various activities an important task to be accomplished by WCC-VOC will be to carry out round robin exercises.

This paper reports results from the first comprehensive intercomparison exercise coordinated by WCC-VOC and carried out in 2003. The main objective of the first GAW-VOC intercomparison was to examine the current performance status of the analytical facilities of each laboratory and to check whether the results meet the Data Quality Objectives (DQO) developed by WCC-VOC. These DQOs are listed in Table 1 and are based on experiences from earlier studies (Volz-Thomas et al., 2002; Slemr et al., 2002). An additional objective was to establish a ranking of properly determined compounds among all laboratories based on the DQOs in order to identify the compounds which were most accurately determined by all laboratories.

Table 1
Data Quality Objectives (DQO) for VOC measurements used in the 1st GAW-VOC intercomparison

| Compound[a] | Accuracy (%) | Repeatability (%) |
|---|---|---|
| Alkanes | 10 | 5 |
| Alkenes | 20 | 20 |
| Alkynes | 10 | 5 |
| Aromatics | 15 | 10 |
| Mixing ratio $<0.1$ ppb | 50 | 50 |

[a]Currently, for all compounds a detection limit of 0.1 ppb(C) is assumed.

This first intercomparison included a synthetic VOC standard in $N_2$. Though this standard contained a complex VOC mixture it is still considered an easy task, since its content does not contain compounds which are present in real air matrices, e.g. water, ozone, and oxygenated VOC, which may interfere during the sampling, storage, and analysis process. During the intercomparison of the synthetic standard also some pilot intercomparisons of ambient air samples between individual participants and WCC-VOC canisters at the respective ambient air sampling site were performed. Unfortunately, these studies were not sufficiently representative. Though desirable, it does not appear feasible to bring together all participants worldwide with their offline/online device at one location for concurrent ambient air sampling. It is suggested to include comprehensive ambient air intercomparisons in individual performance audits as they were carried out based on the outcome of this first intercomparison (e.g. Rappenglück, 2005a, b) which may include ambient air intercomparisons covering a diurnal cycle and mutual analysis of canisters.

## 2. Intercomparison approach

### 2.1. Facilities at WCC-VOC

VOCs were analyzed according to a GC method by Habram et al. (1998). The procedure is briefly summarized as follows: Up to eight canisters were

mounted to a 16 port Valco valve. This valve is controlled by the GC software to take sequential samples (400 ml) from all canisters and inject them into the analytical cycle. The set of canisters included six target canister samples, one calibration canister containing benzene and *n*-butane in $N_2$ (filled from a corresponding gas cylinder provided by Messer Griesheim, Krefeld, Germany), and one canister containing 73 VOCs in $N_2$ (filled from a corresponding gas cylinders provided by the National Center for Atmospheric Research (NCAR), Boulder, CO, USA) for identification purposes. VOCs in both canisters were in the ppbv-range. The quantification of individual VOC species was based on the *n*-butane response factor. The two species benzene and *n*-butane were used to check the consistency and stability of the calibration gas itself. In order to remove water the sample passed an empty PFA tube ($300 \times 0.25$ mm ID) at $-30\,^{\circ}C$. Subsequent preconcentration of the sample was accomplished with a commercial sample preconcentration trap (SPT) made by Varian ($800 \times 2.1$ mm ID) and filled with Carbopack® BHT. The SPT was kept at $-120\,^{\circ}C$ using liquid nitrogen ($LN_2$). The sample was desorbed at 200 °C and injected into the GC (Varian 3600CX) with He (purity 99.999%) as the carrier gas. For the separation two columns run in parallel were used: $C_2$–$C_4$ VOCs were separated by a PLOT column GasPro GSC ($17\,m \times 0.32$ mm ID; Astec, Whippany, NJ, USA); for the separation of $C_4$–$C_9$ hydrocarbons a CP-SIL 5 CB column ($50\,m \times 0.25$ mm ID, 1 μm df; 100% Dimethylpolysiloxane, Chrompack, Middelburg, The Netherlands) was used. Both columns were placed in one oven. A multiramp temperature program was used: $-30\,^{\circ}C$ (2.5 min hold, 3.5 °C/min to $-13\,^{\circ}C$, 20 °C/min to 8 °C, 5 °C/min to 70 °C, 10 °C/min to 240 °C (10 min hold). The entire temperature program has a length of 50 min. The hydrocarbons of the sample were detected by FID that was kept at 250 °C. For the FID high purity $H_2$ (99.999%) and synthetic air was used. Repeatability of this system is better than 0.9% for compounds in the range between 5 and 50 ppbv. For aromatic compounds the repeatability for the same concentration range is 1% for benzene and toluene, 2% for ethylbenzene and 3% for the xylenes. The detection limit is between 10 and 15 pptv for most compounds for sample volume of 400 ml. This GC system participated successfully in the European Accurate Measurements of Hydrocarbons in the Atmosphere (AMOHA) intercomparison tasks (Slemr et al., 2002) which focused on canister measurements. Again, this GC system passed comprehensive independent quality assurance procedures within TFS and agreed with the instruments of the experienced participants to within ±20% for most compounds (Volz-Thomas et al., 2002).

### 2.2. The GAW standard

For the first GAW VOC intercomparison a 73 VOC standard in $N_2$ was prepared and certified by NCAR in the mixing ratio range from 170 to 11.30 ppbv. The uncertainty for compounds up to toluene is stated to be about ±3%, for compounds higher than toluene it stated to be about ±4%. The complete list of all VOCs can be found in Table 2. Chromatograms as obtained by WCC-VOC from this standard are shown in Fig. 1. Since this range is typical for ambient air measurements no further dilution is necessary and participants of the intercomparison were able to apply this standard to their measurement devices exactly the way they analyze routine ambient air samples. Among the 73 VOCs in the GAW standard 21 VOCs are traceable to the National Institute of Standards and Technology (NIST) (Table 2). With the exception of propyne and 1,3-butadiene the GAW standard contained almost all 30 VOCs recognized as primary GAW target compounds (WMO, 1995). Among the 73 VOCs some species already represent compounds of the future WCC-VOC implementation stage that is expected to cover $C_{10}$–$C_{14}$ VOCs including biogenic hydrocarbons (e.g. isoprene, α-pinene, decane, undecane and $C_{10}$ aromatic compounds).

### 2.3. The participants

The intercomparison exercise involved nine different stations/laboratories (10 instruments) from seven countries (Brazil, Canada [two labs], Czech Republic, Finland, Germany [two labs; three instruments], Ireland, and Slovakia), representing four measurement programs (GAW, EMEP [Co-Operative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe], The Canadian Air and Precipitation Monitoring Network [CAPMoN], The Large-Scale Biosphere–Atmosphere Experiment in Amazonia [LBA]). These sites either run canister or online measurements, i.e. it is the first worldwide experiment considering both systems. Tables 3 and 4 report analysis methods of each participant. They

Table 2
VOCs in the GAW standard as determined by WCC-VOC prior shipping to the participants and after return to WCC-VOC (Data base: eight canisters prior shipping, six canisters after return)

| Compound[a] | # | Prior shipping | After return | Compound | # | Prior shipping | After return |
|---|---|---|---|---|---|---|---|
| *Ethane* | 1 | 10.85 (1.8) | 11.04 (3.3) | Cyclohexane | 36 | 0.45 (12.6) | 0.54 (13.3) |
| *Ethylene* | 2 | 5.59 (2.0) | 6.11 (5.3) | 2-me-Hexane | 37 | 0.81 (4.8) | 0.87 (3.9) |
| *Acetylene* | 3 | 8.35 (1.8) | 8.37 (2.8) | 2,3 dime-Pentane | 38 | 0.40 (3.5) | 0.43 (5.2) |
| *Propane* | 4 | 9.64 (3.7) | 9.82 (3.1) | 3-me-Hexane | 39 | 0.82 (4.4) | 0.88 (5.6) |
| *Propylene* | 5 | 2.17 (2.4) | 2.34 (7.5) | 2,2,4 trime-Pentane | 40 | 1.68 (1.4) | 1.73 (4.1) |
| i-*Butane* | 6 | 4.08 (2.5) | 4.30 (7.2) | *n-Heptane* | 41 | 4.04 (1.5) | 4.15 (4.1) |
| *n-Butane* | 7 | 8.56 (3.2) | 8.81 (5.9) | 2,3 dime-2-Pentene | 42 | 0.76 (7.3) | 0.48 (67.1) |
| 1-Butene | 8 | 2.13 (3.6) | 2.13 (8.4) | me-Cyclohexane | 43 | 0.83 (4.1) | 0.75 (20.2) |
| *t*-2-Butene | 9 | 0.87 (1.9) | 0.94 (4.8) | 2,3,4 trime-Pentane | 44 | 0.41 (3.6) | 0.44 (11.5) |
| i-Butene | 10 | 3.17 (3.3) | 3.08 (7.1) | *Toluene* | 45 | 2.48 (3.8) | 2.51 (5.8) |
| *c*-2-butene | 11 | 2.05 (1.5) | 2.06 (5.5) | 2-me-Heptane | 46 | 0.39 (1.7) | 0.40 (8.1) |
| 3-me-1-Butene | 12 | 0.80 (1.5) | 0.83 (4.1) | 4-me-Heptane | 47 | 1.06 (1.4) | 1.07 (6.5) |
| i-*Pentane* | 13 | 6.48 (5.0) | 7.09 (9.8) | 3-me-Heptane | 48 | 0.81 (1.1) | 0.83 (7.9) |
| 1-Pentene | 14 | 1.13 (3.8) | 1.19 (8.0) | *n-Octane* | 49 | 0.39 (1.9) | 0.40 (7.5) |
| 2-me-1-Butene | 15 | 1.03 (1.6) | 1.05 (10.0) | et-Benzene | 50 | 0.72 (4.0) | 0.65 (20.3) |
| *n-Pentane* | 16 | 7.20 (1.6) | 7.48 (5.0) | *m,p*-Xylene | 51 | 1.37 (4.6) | 1.14 (31.0) |
| *Isoprene* | 17 | 4.10 (3.4) | 3.79 (11.4) | Styrene | 52 | 0.31 (15.3) | 0.16 (69.6) |
| *t*-2-Pentene | 18 | 0.83 (2.8) | 0.88 (15.6) | *o-Xylene* | 53 | 0.34 (6.6) | 0.30 (28.3) |
| c-2-Pentene | 19 | 2.01 (1.4) | 1.95 (11.3) | *n*-Nonane | 54 | 0.61 (3.7) | 0.58 (26.1) |
| 2-me-2-Butene | 20 | 0.81 (1.8) | 0.76 (11.7) | i-prop-Benzene | 55 | 0.14 (2.2) | 0.12 (40.8) |
| 2,2 dime-Butane | 21 | 2.08 (1.3) | 2.20 (3.4) | *a-Pinene* | 56 | 0.25 (1.2) | 0.16 (55.4) |
| Cyclopentene | 22 | 0.76 (1.4) | 0.74 (11.2) | *n*-prop-Benzene | 57 | 0.13 (5.9) | 0.10 (55.7) |
| 3-me-1-Pentene[b] | 23 | 1.95 (1.6) | 1.98 (4.9) | 3-et-Toluene | 58 | 0.15 (3.1) | 0.12 (77.2) |
| 4-me-1-Pentene[b] | | | | 4-et-Toluene | 59 | 0.25 (8.5) | 0.21 (46.6) |
| 2,3 dime-Butane | 24 | 0.70 (1.4) | 0.73 (4.5) | 1,3,5 trime-Benzene | 60 | 0.47 (5.3) | 0.30 (54.9) |
| Cyclopentane | 25 | 1.48 (1.5) | 1.51 (4.4) | 2-et-Toluene | 61 | 0.31 (6.1) | 0.23 (59.4) |
| 2-me Pentane | 26 | 0.83 (2.9) | 0.94 (6.8) | *1,2,4 trime-Benzene*[c] | 62 | 0.68 (7.1) | 0.60 (62.4) |
| 3-me-Pentane | 27 | 1.04 (2.8) | 1.09 (8.0) | *Decane*[c] | | | |
| 2-me-1-Pentene | 28 | 0.80 (3.9) | 0.73 (25.5) | *t*-Butyl benz | 63 | 0.28 (5.5) | 0.20 (48.4) |
| *n-Hexane* | 29 | 2.60 (1.6) | 2.71 (4.4) | 1,3 diet-Benz | 64 | 0.34 (6.5) | 0.05 (53.5) |
| c-3-Hexene | 30 | 0.44 (3.5) | 0.39 (24.6) | *n*-but-Benzene[d] | 65 | 0.43 (7.4) | 0.19 (80.1) |
| *t*-2-Hexene | 31 | 0.41 (2.7) | 0.37 (24.2) | 1,4 diet-Benzene[d] | 66 | | |
| c-2-Hexene | 32 | 0.75 (3.6) | 0.66 (26.9) | 1,2 diet-Benzene | 67 | 0.22 (6.2) | 0.18 (53.2) |
| Me-Cyclopentane | 33 | 0.80 (2.0) | 0.83 (5.6) | sec-butyl Benzene | 68 | 0.22 (8.1) | 0.15 (73.9) |
| 2,4 dime-Pentane | 34 | 0.79 (2.5) | 0.82 (4.6) | 1,2,3 trime-Benzene[e] | 69 | 0.30 | n/a |
| *Benzene* | 35 | 1.73 (2.4) | 1.81 (4.3) | undecane[e] | | undecane0.34 | n/a |

Values are given in (ppbv). In brackets standard deviation in (%). Numbers (#) refer to the VOC numbers shown in the chromatograms in Fig. 1.

[a]Italics: NIST traceable VOCs.

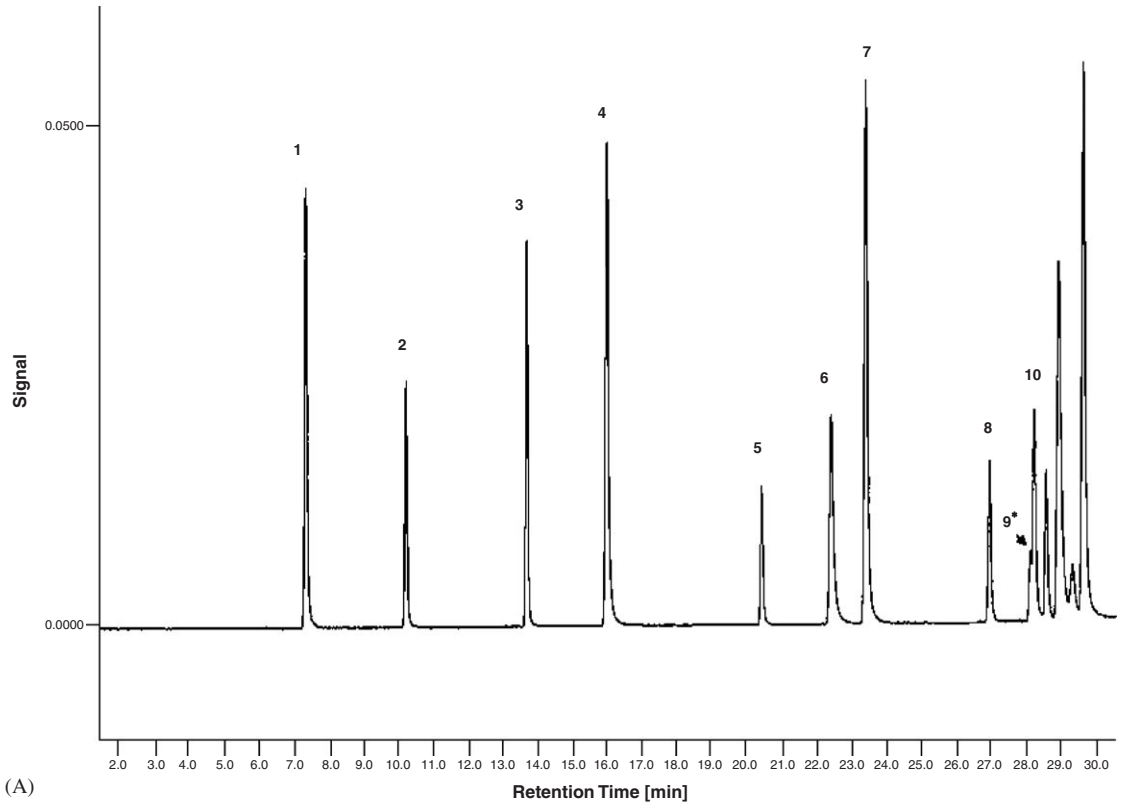
[b]3-me-1-pentene and 4-me-1-pentene cannot be separated by the WCC-VOC GC system and is reported as a sum of both VOCs. NCAR certificate indicates each VOC contribution at 50%. Accordingly this value was used for labs which reported these species.

[c]1,2,4 trime-benzene and decane cannot be separated by the WCC-VOC GC system and is reported as a sum of both VOCs. NCAR certificate indicates each VOC contribution at 50%. Accordingly this value was used for labs which reported these species.

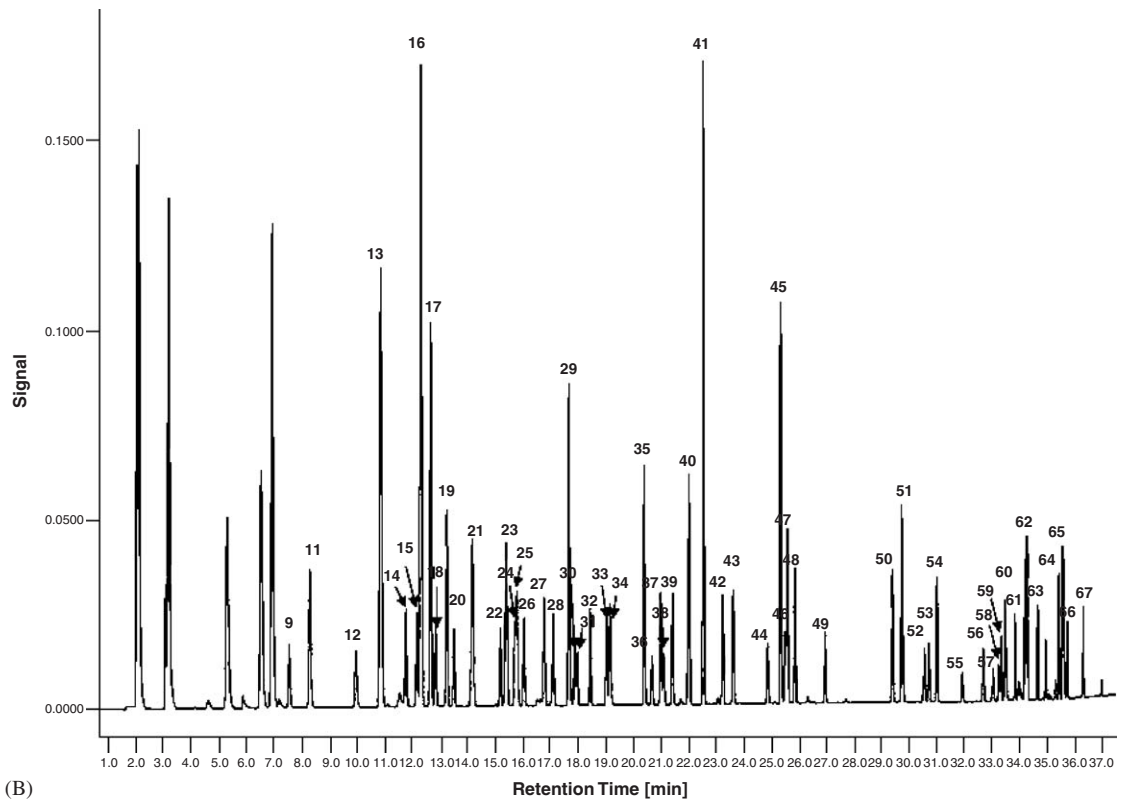
[d]*n*-but-benzene and 1,4 diet-benzene cannot be separated by the WCC-VOC GC system and is reported as a sum of both VOCs. NCAR certificate indicates different contributions of each VOC. Since these contributions could not be verified in the WCC-VOC GC system, both species were excluded from determinations of accuracy in this intercomparison exercise.

[e]1,2,3 trime-benzene and undecane are currently not included in the measurement programme of the WCC-VOC GC system. The values listed in the NCAR certificate are listed. However, both species were excluded from determinations of accuracy in this intercomparison exercise.

show that each participant used quite unique approaches for sample preparation, calibration sources and analysis methods. It also includes (not mentioned in the tables) quite different approaches in quality assurance (QA) and quality control (QC) measures ranging from rather non-existing




(A)




(B)

Fig. 1. Chromatograms of the GAW standard as obtained at WCC-VOC for channel A (PLOT column) and B (CP-SIL 5 CB column). VOC numbers refer to Table 2. VOC numbers (9*) and (9) refer to t-2-butene, however only number (9) was considered.

Table 3
Analysis methods used in the 1st GAW-VOC Intercomparison exercise (I)

| Participant | Number of VOCs determined in the GAW standard[a] | GC | Column | Preconcentration | Refocusing |
|---|---|---|---|---|---|
| *Slovak Republic* EMEP P. Čavolka | 41 | Auto System XL, Perkin-Elmer | N931-6304 PE-ALUMINA, elite series, ID 0.53 mm, $l = 30$ m | None | Tenax TA, 20 mg, 200 nm pore, $l = 132$ mm fused silica tube, −80 °C, $LN_2$ |
| *Finland* GAW/EMEP H. Hakola | 25 | Hewlett-Packard | $Al_2O_3$/KCl, ID 0.32 mm, $l = 50$ m, film thickness = 5 μm | Stainless steel tubing filled with glass beads, $LN_2$ | $LN_2$ |
| *Canada* CAPMoN D. Wang | 150 | Agilent 6890 GC, HP 5973 MSD (Quadrupole) | J&W DB-1 bonded liquid phase, ID 0.32 mm, $l = 60$ m, film thickness = 1 μm | Glass bead, −170 °C, $LN_2$ | −160 °C, $LN_2$ |
| *Canada* GAW/CAPMoN P. Brickell, J. Bottenheim | 33 | HP5890, Series II | Precolumn: Supelco SPB-1 ID 0.53 mm, $l = 45$ m, film thickness = 5 μm column a: J&W GS-Q ID 0.53 mm, $l = 30$ m, film thickness = 2 μm column b: J&W GS-Alumina (KCl) ID 0.53 mm, $l = 30$ m | Silanized glass bead, ca. 2 mL, −180 °C, $LN_2$ | |
| *Czech Republic* GAW/EMEP J. Cech | 66 | Chrompack | $Al_2O_3/Na_2SO_4$, ID 0.32 mm, $l = 50$ m | Glass beads, 200 $cm^3$, LAr, | GLT tubing, $LN_2$ |
| *Ireland* GAW D. Martin, C. Noone | 15 | Hewlett-Packard | $Al_2O_3$/KCL Plot (Chrompack) ID 0.32 mm, $l = 50$ m | Carbosieve S III, Carboxen 1000 and 1003, Carbotrap at −50 °C (Peltier cooling) | |
| *Germany* GAW C. Plass-Dülmer | 57 | Varian 3600 CX | $Al_2O_3$/KCl PLOT (Chrompack) ID 0.53 mm, $l = 50$ m | Glass beads (8 cm × 1/8″ OD), −196 °C, $LN_2$ | |
| *Germany* GAW C. Plass-Dülmer | 66 | Varian 3400 CX, Saturn III Ion Trap | BPX-5 (SGE), ID 0.22 mm, $l = 50$ m, film thickness = 1 μm | Tenax TA + Charcoal (30 cm × 1/8″ OD), 30 °C, compressed air | FS capillara, ∅0.25 mm, l = 20 cm, −196 °C, $LN_2$ |
| *Germany* EMEP R. Junek | 47 | Chrompack-9001 | PLOT FUSED-SILICA—$Al_2O_3$/KCl ID 0.32 mm, $l = 50$ m, film thickness = 5 μm | Carbotrap, Carbotrap C, Carbosieve S III, −25 °C, $LN_2$ | PORA PLOT U/TENAX, −170 °C, $LN_2$ |
| *Brazil* GAW/LBA L. Gatti | 44 | Varian 3800, Saturn 2000 | DB-1 ID 0.32 mm, $l = 60$ m, film thickness = 1 μm | Silanized glass bead, −180 °C, $LN_2$ | |

[a]Includes all VOCs (also oxygenated and chlorinated hydrocarbons) regardless whether they were reported as identified or unknown.

measures to highly advanced algorithms (e.g. Plass-Dülmer et al., 2002).

Most participants apply preconcentration at temperatures below −170 °C using $LN_2$. Peltier cooling at −50 °C is used by one participant. One method did not include a preconcentration step at all. In most cases glass beads were used as a preconcentration material. In a few cases preconcentration units were filled with two or three adsorbens including either Carbosieve, Carbotrap, Carboxen, or Tenax.

Table 4
Analysis methods used in the 1st GAW VOC Intercomparison Exercise (II)

| Participant | Sampling conditioning: $H_2O$ | Sampling conditioning: $CO_2$ | Sampling conditioning: $O_3$ | Detector | Carrier gas | Standard |
|---|---|---|---|---|---|---|
| *Slovak Republic*<br>EMEP<br>P. Čavolka | Hollow fibre, NAFION type, PERMA PURE, continuous mode | | | FID | $N_2$ | 15 NMHC, 5 ppbv, NIST |
| *Finland*<br>GAW/EMEP<br>H. Hakola | $K_2CO_3$ + NaOH | | | FID | He | 30 NMHC, <10.5 ppbv, NPL |
| *Canada*<br>CAPMoN<br>D. Wang | | | | HP 5973 MSD | He | 150 VOC, <6 ppbv, Scott, In-house |
| *Canada*<br>GAW/CAPMoN<br>P. Brickell, J. Bottenheim | (1) Cold sample line section (2C) with phase separation.<br>(2) Column switching arrangement. | Column switching arrangement | Heated (80 °C) internal unlined stainless steel tubing | 2 FID | He | 34 NMHC, <30.6 ppmv, Scott, In-house |
| *Czech Republic*<br>GAW/EMEP<br>J. Cech | $K_2CO_3$ + NaOH 10 cm × (1/4″) | | | FID | He | 29 NMHC, <11 ppbv NMI |
| *Ireland*<br>GAW<br>D. Martin, C. Noone | Nafion drier, PERMA PURE, continuous mode | | | FID | He | 30 NMHC, <10 ppbv, NPL |
| *Germany*<br>GAW<br>C. Plass-Dülmer | Cold trap at −45 °C (1/8″ silcosteel) | | Heated stainless steel tubings at 150 °C | FID | He | 30 NMHC, <11 ppbv, NPL |
| *Germany*<br>GAW<br>C. Plass-Dülmer | | | $Na_2O_3S_2$ impregnated filter | FID + MS | He | 30 NMHC, <11 ppbv, NPL |
| *Germany*<br>EMEP<br>R. Junek | | | | FID | He | 30 NMHC, <10 ppbv, NPL |
| *Brazil*<br>GAW/LBA<br>L. Gatti | | | | FID + MS | He | 6 VOC, <2 ppbv, Scott |

A refocusing step was employed in six out of 10 instrumentations, often using unfilled tubings or capillara kept at $LN_2$ temperatures. Sampling conditioning was usually employed in online devices. Instrumentation used for offline analysis did not use sample conditioning for $O_3$ and $CO_2$. In some case they also did not include removal of $H_2O$. Most applications used FID as a detector and He as a carrier gas. For calibration, National Physical Laboratory (NPL, UK) standards in the range about 10 ppbv were used for five instrumentations, whereas others used standards from Scott Specialty (USA), Nederlands Meetinstitut (NMI, Netherlands) or National Institute of Standards and Technology (NIST, USA), mostly in the low ppbv range. Only one participant used ppmv ranges.

### 2.4. Logistics

For each participant WCC-VOC filled one 1 L stainless steel two-valve canister (Kinetics, Eschau-Hobbach, Germany) with the GAW standard. In their history these canisters have been exclusively used for VOC standards in the mixing ratio range

similar to this GAW standard. According to Habram (1998), conditioning was performed by flushing continuously humidified $N_2$ gas (dew point 15 °C) through the canisters which led to an initial water coating of the walls. WCC-VOC analyzed these canisters prior to shipping and after return to WCC-VOC (Table 2). Since some canisters returned empty the data set for return analysis is based on fewer canisters. Before shipping the standard deviation among the canisters is in most cases below 5%. In several cases the deviation is higher: cyclohexane (12.6%), 2,3-dime-2-pentene (7.3%), styrene (15.3%), *o*-xylene (6.6%). For higher aromatic compounds the standard deviation is usually between 5% and 10%. WCC-VOC took special care that the participants received the standards within short time of shipping (usually within 1 week) and ran the analysis promptly after receipt of the GAW standard canister. The return of the canisters occurred on very different time schedules and thus reflects very different storage times. The average values as obtained in the return analyses were in most cases in good agreement with the average values obtained prior shipping. However, often higher deviations among the canisters themselves were observed. They were notably high for some alkenes, e.g. 2,3 dime-2-pentene or hexenes (due to their high reactivity), and for VOCs above $C_8$ (due to their low volatility which will enhance wall adsorption losses).

Reference values for the interpretation of the intercomparison were obtained as follows: average mixing ratios of each individual VOC were calculated from each data set, i.e. from the analysis of all canisters prior to shipping and the re-analysis of the canisters after return to WCC-VOC (Table 2). From these two data sets an average value was calculated for each VOC. This value was supposed to reflect best the canister content during the participant's analysis. If either the VOC mixing ratio prior shipping or after return to WCC-VOC was not within the DQO-range of this mean value, this VOC was flagged (*) and not included in performance evaluation of the participants' lab. Flagged compounds included 2,3-dime-2-pentene, styrene, α-pinene, 1,3,5 trime-benzene, t-butyl benzene, 1,3 diet-benzene, sec-butyl benzene. In addition we flagged *n*-butyl benzene, 1,4 diet-benzene, 1,2,3 trime-benzene and undecane for technical reasons (further explanation see Table 2).

### 2.5. Tasks for the participants

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. All participants of the intercomparison exercise received an Excel worksheet prepared by WCC-VOC serving as a protocol. The participants were asked to follow these procedures. For logistic and technical reasons the intercomparison exercise was split into two participating groups. After having arranged a time schedule each group the first GAW VOC intercomparison was initiated in February 2003 and was conducted throughout the year 2003. The latest data set was submitted to WCC-VOC in February 2004. Data evaluation was performed after the last data submission and started in 2004. Data evaluation and intercomparison considered both a subset of 28 primary GAW VOC target compounds (WMO, 1995) and the entire suite of 73 VOCs of the GAW standard.

## 3. Results and discussion

### 3.1. Results of the first GAW VOC intercomparison exercise, Part I: 28 GAW target VOCs

Tables 5–7 and Fig. 2(I) present a subset of 28 VOCs recognized as primary GAW target compounds. For this intercomparison we only considered baseline resolved compounds for which no interferences with other known or unknown compounds were reported or if reported coelution contributions less than 5% were considered as negligible. The results show that the DQOs for repeatability are met in most cases (Table 5). The determination of repeatability was based on the number of measurements of the WCC-VOC standard. Since sample volumes varied among the VOC systems, also the number of measurements varied. Compared with the repeatability, the deviation from the reference values showed quite a different picture. For some VOCs the concentrations differed significantly among the different laboratories (Table 6).

Considering VOCs that meet the DQOs for both, uncertainty and repeatability (Tables 5 and 6) leads to the ranking of properly identified and quantified VOCs among the target VOCs (Table 7). Due to the different VOC ranges reported by the participants this ranking took into account: (*X*) the number of

Table 5
Repeatability (%) for each VOC determination of the GAW standard

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A (4) | B (2) | C (3) | D (3) | E (5) | F (4) | G (2) | H (3) | I (3) | J (3) |
| *Ethane* | 4.6 | 1.0 | 1.2 | 0.2 | | | 0.3 | 2.8 | 2.2 | |
| *Ethylene* | 4.5 | 2.7 | 0.6 | 0.8 | | | 2.5 | 2.5 | 2.3 | |
| *Acetylene* | 4.7 | 0.3 | | 12.7 | | | | 2.6 | 5.7 | |
| *Propane* | 3.8 | 0.2 | 2.1 | 0.5 | 3.9 | 2.2 | 0.9 | 3.0 | 2.2 | |
| *Propylene* | 3.9 | 0.7 | 2.2 | 0.3 | 6.4 | 2.0 | 23.4 | 3.1 | 2.3 | |
| i-*Butane* | 4.0 | 0.6 | 3.8 | 0.8 | 4.6 | 2.4 | 0.3 | 2.3 | 2.2 | 4.3 |
| *n-Butane* | 5.3 | 0.3 | 1.9 | 0.1 | 7.1 | 2.5 | 0.3 | 2.0 | 5.3 | |
| 1-Butene | 5.2 | 36.9 | 2.4 | 0.2 | | | | | 2.7 | |
| *t*-2-Butene | 4.7 | 2.7 | 2.6 | 0.6 | | 2.0 | | | 3.1 | 1.7 |
| i-Butene | 4.7 | | 2.1 | 5.8 | | | | 2.9 | 2.5 | |
| c-2-Butene | 3.1 | | 1.8 | 1.4 | | 2.6 | | 2.6 | 3.8 | 5.1 |
| i-*Pentane* | 9.3 | | 2.1 | 0.6 | 4.0 | | 0.3 | 2.4 | | 3.1 |
| *n-Pentane* | 9.4 | | 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 | 5.8 | 7.5 |
| *t*-2-Pentene | 12.6 | 3.7 | 2.7 | 0.5 | | 11.7 | 2.2 | 8.2 | 2.3 | 7.7 |
| c-2-Pentene | 2.9 | 1.3 | 2.8 | 0.3 | | 2.6 | 0.7 | 3.7 | 2.3 | 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 | 5.7 | 2.6 |
| *Benzene* | 1.4 | 1.1 | 1.9 | 0.9 | | 3.2 | 2.3 | 3.8 | 2.7 | |
| Cyclohexane | 3.4 | | | | | 3.4 | | 3.3 | | |
| *n-Heptane* | 3.8 | | 5.1 | 1.2 | 4.1 | 2.9 | 1.0 | | 2.8 | 3.0 |
| *Toluene* | 4.7 | 7.0 | 7.7 | 3.9 | 7.6 | 2.9 | | 3.6 | | 2.9 |
| Et-Benzene | | | 3.8 | 5.6 | 5.6 | 3.0 | | 1.1 | 10.3 | 4.5 |
| *m,p*-Xylene | | | 3.3 | 5.5 | 5.1 | 3.2 | | 2.2 | 13.9 | 3.6 |
| *o-Xylene* | | 1.8 | 3.6 | | 6.8 | 3.1 | | 7.4 | | |
| 1,3,5 trime-Benzene[b] | | | 4.6 | | | 4.9 | | | | 10.7 |
| *1,2,4 trime-Benzene* | | | 2.5 | | | 5.3 | | | | 14.5 |

Results that did not meet the DQOs are shown in shaded boxes; in brackets number of measurements.
[a]Italics: NIST traceable VOCs.
[b]Flagged compounds.

laboratories who properly identified and quantified a specific VOC related to the number of all participants, and (*Y*) only related to those participants who identified this specific compound. As can be seen, quite a few NIST traceable VOCs are properly determined by most labs, among them compounds such as propane, propylene, isoprene, and benzene representing alkanes, alkenes, and aromatics. These compounds were accurately determined by at least 2/3 of the laboratories and at least 4/5 of the laboratories which identified these species also correctly quantified them. However, difficulties occur with other important NIST traceable VOCs (e.g. acetylene, i-pentane, toluene).

Taking into account the percentage of identified VOCs in the standard and the total number of VOCs meeting the DQOs a ranking of the performance of the participating labs can be obtained. In order to take into account the different VOC ranges which were reported by the intercomparison participants our approach in Fig. 2(I) considers: (*X*) the number of VOCs reported by each participant which were found within the DQOs related to the number of VOCs under consideration, and (*Y*) the number of VOCs reported by each participant which were found within the DQOs related to the number of VOCs identified by this participant. The overall ranking of the laboratory performance was based on the ''total score'' being the sum of (*X*) and (*Y*). The top four participants include three labs which are well established labs with a strong background in intercomparisons (e.g. in the AMOHA program; see Slemr et al., 2002; Plass-Dülmer, 2006) and strong commitment to QA/QC procedures. Interestingly enough among the top four labs is one lab (lab D) that participated for the very first time in an intercomparison. It has to be noted though that we only considered baseline

Table 6
Deviation (%) from the WCC-VOC reference values for each VOC

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | H | I | J |
| *Ethane* | 2.9 | −64.5 | −4.2 | −2.0 | | | −2.9 | −5.2 | −1.9 | |
| *Ethylene* | 0.6 | −74.7 | 0.6 | 2.6 | | | −20.2 | −11.5 | −6.6 | |
| *Acetylene* | −13.9 | −54.8 | | 3.9 | | | | −22.5 | −25.2 | |
| *Propane* | 8.6 | 0.0 | −1.1 | 1.2 | −28.3 | −3.9 | −3.6 | −10.0 | −1.9 | |
| *Propylene* | 4.1 | −5.5 | 1.6 | 7.5 | −67.2 | −1.4 | −18.8 | −5.8 | −2.6 | |
| i-*Butane* | 6.5 | 76.8 | 5.5 | 8.1 | −35.4 | −12.4 | −0.9 | −6.8 | −0.2 | 5.3 |
| *n-Butane* | 5.2 | 76.1 | −1.7 | 4.1 | −31.6 | −10.3 | −4.1 | −4.9 | −2.1 | 9.6 |
| 1-Butene | 4.2 | 137.3 | 6.4 | 11.2 | | | | | 3.2 | |
| *t*-2-Butene | −0.6 | 41.3 | 3.3 | 5.0 | | −21.3 | | | −6.6 | 8.4 |
| i-Butene | 8.2 | | 3.9 | 11.5 | | | | 3.5 | −2.7 | |
| c-2-Butene | −2.8 | | 1.4 | 3.8 | | −8.0 | | −13.1 | −7.8 | 2.8 |
| i-*Pentane* | −18.1 | | −6.7 | 0.5 | −45.4 | | −10.1 | −16.0 | | −6.9 |
| *n-Pentane* | −27.8 | | −3.4 | 1.7 | | −2.1 | −2.5 | | | |
| *Isoprene* | 9.6 | −98.0 | −2.6 | −13.8 | −78.0 | −13.5 | 1.3 | 9.3 | 5.3 | 2.6 |
| *t*-2-Pentene | −53.6 | −25.2 | 86.5 | 3.4 | | −9.6 | −6.9 | −31.4 | −14.2 | 20.0 |
| c-2-Pentene | −19.5 | 21.7 | 5.3 | 1.0 | | −4.9 | −0.1 | −10.9 | −3.9 | 2.6 |
| 2-me Pentane | | | −0.5 | | | −22.2 | −4.9 | | | |
| 3-me-Pentane | | | −1.8 | 10.4 | | −10.2 | −7.0 | | | −0.3 |
| *n-hexane* | −27.3 | 236.6 | −3.0 | 4.3 | −40.8 | −11.5 | 0.2 | −30.7 | −12.8 | −0.6 |
| *Benzene* | 3.9 | 201.1 | −7.6 | 0.6 | | −1.8 | −2.7 | −16.7 | −7.4 | |
| Cyclohexane | 38.6 | | | | | −29.2 | | | | |
| *n-heptane* | 3.8 | | −7.7 | 3.0 | −45.7 | 5.4 | 2.2 | | −2.6 | −1.8 |
| *Toluene* | 26.2 | −80.0 | −5.9 | 9.3 | −22.8 | 15.6 | | −7.3 | | 9.2 |
| Et-Benzene | | | 6.6 | 2.3 | 85.1 | 6.7 | | −16.8 | 8.7 | 11.0 |
| *m,p*-Xylene | | | 13.7 | 6.6 | 46.3 | −6.5 | | −8.6 | 17.3 | 9.6 |
| *o-Xylene* | | 1604.0 | 9.9 | | 243.2 | −19.4 | | −25.2 | | |
| 1,3,5 trime-Benzene[b] | | | −13.4 | | | −88.7 | | | | 1.7 |
| *1,2,4 trime-Benzene* | | | 38.8 | | | −81.2 | | | | 7.6 |

Results that did not meet the DQOs are shown in shaded boxes.
[a]Italics: NIST traceable VOCs.
[b]Flagged compounds.

Table 7
Ranking of properly identified and quantified VOCs

| VOC[a] | *X* (%) | *Y* (%) | VOC | *X* (%) | *Y* (%) |
|---|---|---|---|---|---|
| *Propane* | 80.0 | 88.9 | *n*-Butane | 50.0 | 55.6 |
| *Propylene* | 80.0 | 88.9 | 1-Butene | 40.0 | 80.0 |
| *c*-2-Pentene | 80.0 | 88.9 | *n*-Pentane | 40.0 | 80.0 |
| *Isoprene* | 80.0 | 80.0 | Toluene | 40.0 | 50.0 |
| *c*-2-Butene | 70.0 | 100.0 | *t*-2-Pentene | 40.0 | 44.4 |
| *Benzene* | 70.0 | 87.5 | *n*-Hexane | 40.0 | 40.0 |
| *n*-Heptane | 70.0 | 87.5 | 3-me-Pentane | 30.0 | 60.0 |
| *i-Butane* | 70.0 | 70.0 | *i*-Pentane | 30.0 | 42.9 |
| *Ethane* | 60.0 | 85.7 | 2-me Pentane | 20.0 | 66.7 |
| i-Butene | 50.0 | 100.0 | 1,2,4 trime-Benzene | 10.0 | 33.3 |
| *Ethylene* | 50.0 | 71.4 | Acetylene | 10.0 | 20.0 |
| *t*-2-Butene | 50.0 | 71.4 | *o*-Xylene | 10.0 | 20.0 |
| Et-Benzene | 50.0 | 71.4 | Cyclohexane | 0.0 | 0.0 |
| *M,p*-Xylene | 50.0 | 71.4 | | | |

*X*: related to all participants; *Y*: related to all participants who identified this specific VOC.
[a]Italics: NIST traceable VOCs.

resolved VOCs resulting in a slightly worse picture for the online techniques as applied by I, J, and H since some coelutions occur among the 28 target compounds (see Table 10a) that have been excluded for this task and is the reason for the relatively low *X* values shown in Fig. 2(I). Also G applied an online GC technique, however the number of reported VOCs is limited and in most cases do not include VOCs associated with the coelution observed with I, J, and H. Some labs (B, E) show poor results. Though both labs show good results as far as repeatability is concerned, their results for the deviation from the reference values are poor leading to an overall poor performance. Apart from Lab C, all other top four participants used the same standard, i.e. gas cylinder from NPL containing the suite of GAW target VOCs. Labs B and E, however, used different standards. Also, those standards did not cover all target VOCs and were

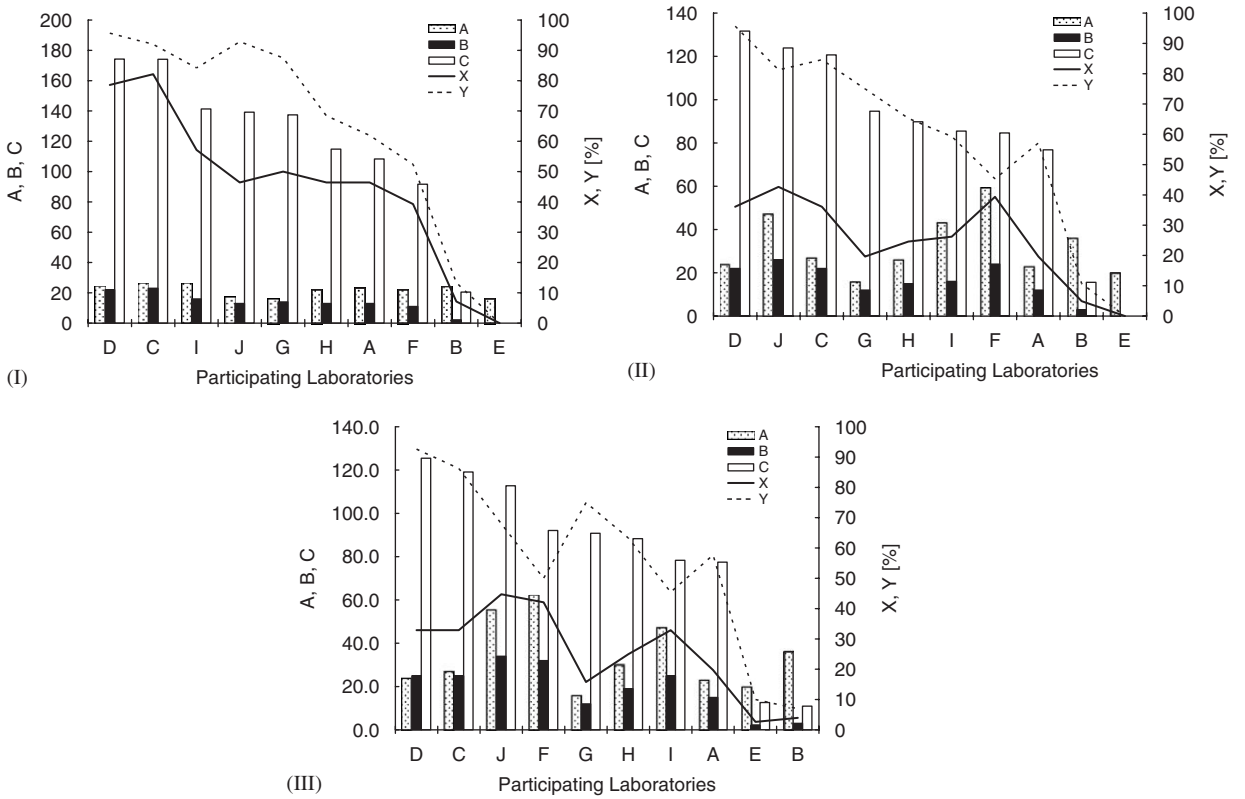



Fig. 2. Ranking of the participating laboratories: (I) based on the 28 GAW-VOC target compounds of the GAW standard. Flagged compounds according to Tables 5 and 6 have been excluded; (II) based on 61 VOC compounds of the GAW standard. Only compounds which have been determined as resolved compounds by the participant are considered (for convenience *m*/*p*-xylene is regarded as a resolved compound). Flagged compounds according to Tables 8–10 have been excluded; (III) based on the resolved and coeluting or combined VOC of the GAW standard (in total 76 compounds). Flagged compounds according to Tables 8–10 have been excluded. Ranking was based on the "total score" (see text) denoted as (C) in the figure. (A) Denotes total number of VOCs and (B) number of VOC within DQOs reported by each lab for the cases I, II, or III.

not available as a mixture standard as it is the case for the NPL standard. From this subset of VOC results it appears imperative to strengthen harmonization procedures. Also, using the same standard mixture appears to help to minimize calibration biases, in particular in cases where laboratories have not yet gained a strong experience.

### *3.3. Results of the first GAW-VOC Intercomparison Exercise, Part II: all 73 VOCs of the GAW standard (only baseline resolved peaks)*

Fig. 2(II) presents 61 of the 73 VOCs of the GAW standard (after removing flagged VOCs). Again, coeluting peaks are not being considered in this presentation (coelution contributions less than 5% were considered as negligible). As far as repeatability is concerned overall good results were obtained (not shown). Notably, lab F did not only report significantly more species than any other lab (61 out of 73 compounds, including flagged compounds), it was the only lab for which all compounds were found to be within the DQO for repeatability. Unfortunately, the results for uncertainty show a quite different picture for all participants (not shown), in particular for lab F: Only 24 out of 52 unflagged species that showed good results for repeatability also showed good results for uncertainty. Though still lab F (together with lab J) determined accurately most species of the GAW standard, Fig. 2(II) shows that based on the total score lab F ranks among the last four labs. This means that though many species are measured the fraction of accurately determined species to the total number of determined compounds is low. The reverse effect can be seen looking at lab G. Lab G reported only a few VOCs of the GAW standard leading to a low rank in the $X$ values shown in

Fig. 2(II). However, most of the species were determined accurately leading to an overall good lab performance (fourth place in Fig. 2(II)). According to Fig. 2(II) again labs D and C are among the top three labs. Lab J did an overall fairly good job with regard to the fraction of accurately determined VOCs ($X$ values in Fig. 2(II)) and reaches the second place based on the total scores. Again, labs B and E show the poorest results. Though lab B shows excellent deviation values for propane, propylene, and 1-pentene, most of the VOCs reported by B have large deviations, sometimes reaching more than 1000%, indicating significant analytical deficiencies.

### 3.4. Results of the first GAW-VOC Intercomparison Exercise, Part III: all 73 VOCs of the GAW standard (all peaks)

Tables 8–11 and Fig. 2(III) present all 73 VOCs of the GAW standard separated between resolved peaks and coeluting species. Peaks are considered as resolved peaks if one major compound's contribution to a specific coelution is greater than 90%. Coelutions are treated as follows: coelutions of at least two compounds with unknown specific contribution (participants H–J and one compound from participant F) are compared to corresponding sums of compounds of resolved peaks from all participants (whenever applicable). Using this approach we make an attempt to consider the various coelutions reported in this intercomparison exercise.

Tables 8 and 9 show the repeatability and the deviations from the reference values for resolved VOC. Contrary to the corresponding Tables 5 and 6 the numbers of reported VOCs for each participant are larger since prerequisites are not as strict and some peaks with minor coelutions were included as mentioned before. Table 10a shows the list of coelutions and their repeatability. In cases where species of different classes coeluted, the compound that exhibited the largest DQO error bars also determined the corresponding DQOs for the sum of coeluting compounds. According to Table 10a only lab I did not meet the DQOs for repeatability. Table 10b shows the results for the deviation from the reference values. However this table includes the pertinent values for the sum of corresponding baseline resolved VOCs for all other labs that did not report coelution problems. Apart from lab B the coelutions 1-butene/i-butene, t-2-butene/1-butene, and 1-butene/2-methylpropene are accurately determined by all the labs who reported this coelution. This is also true for 1-pentene/2-methyl-2-butene, *n*-pentane/cyclopentane, *n*-pentane/2-methyl-1-butene, and benzene/2.3-dimethylpentane for labs F,

Table 8
Repeatability (%) for each VOC determination of the GAW standard

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A (4) | B (2) | C (3) | D (3) | E (5) | F (4) | G (2) | H (3) | I (3) | J (3) |
| *Ethane* | 4.6 | 1.0 | 1.2 | 0.2 | 4.0 | | 0.3 | 2.8 | 2.2 | |
| *Ethylene* | 4.5 | 2.7 | 0.6 | 0.8 | 3.7 | | 2.5 | 2.5 | 2.3 | |
| *Acetylene* | 4.7 | 0.3 | | 12.7 | | | | 2.6 | 5.7 | |
| *Propane* | 3.8 | 0.2 | 2.1 | 0.5 | 3.9 | 2.2 | 0.9 | 3.0 | 2.2 | |
| *Propylene* | 3.9 | 0.7 | 2.2 | 0.3 | 6.4 | 2.0 | 23.4 | 3.1 | 2.3 | |
| i-*Butane* | 4.0 | 0.6 | 3.8 | 0.8 | 4.6 | 2.4 | 0.3 | 2.3 | 2.2 | 4.3 |
| *n-Butane* | 5.3 | 0.3 | 1.9 | 0.1 | 7.1 | 2.5 | 0.3 | 2.0 | 5.3 | 2.6 |
| 1-Butene | 5.2 | 36.9 | 2.4 | 0.2 | | | | | 2.7 | |
| *t*-2-Butene | 4.7 | 2.7 | 2.6 | 0.6 | | 2.0 | | | 3.1 | 1.7 |
| i-Butene | 4.7 | 36.9 | 2.1 | 5.8 | | | | 2.9 | 2.5 | |
| c-2-Butene | 3.1 | 18.7 | 1.8 | 1.4 | | 2.6 | | 2.6 | 3.8 | 5.1 |
| 3-me-1-Butene | | 14.7 | | | | | | 2.1 | 20.4 | 2.7 |
| i-*Pentane* | 9.3 | 8.7 | 2.1 | 0.6 | 4.0 | | 0.3 | 2.4 | 5.9 | 3.1 |
| 1-Pentene | | 3.9 | | | 3.7 | 2.3 | | | 6.5 | 5.3 |
| 2-me-1-Butene | | 10.4 | | | | 2.3 | | 6.3 | 6.5 | |
| *n-Pentane* | 9.4 | 0.3 | 2.4 | 0.2 | 4.4 | 1.8 | 1.2 | | 4.9 | |
| *Isoprene* | 1.9 | 21.5 | 2.4 | 0.5 | 4.4 | 2.8 | 1.1 | 1.3 | 5.8 | 7.5 |
| *t*-2-Pentene | 12.6 | 3.7 | 2.7 | 0.5 | | 11.7 | 2.2 | 8.2 | 2.3 | 7.7 |
| c-2-Pentene | 2.9 | 1.3 | 2.8 | 0.3 | | 2.6 | 0.7 | 3.7 | 2.3 | 8.3 |

Table 8 (*continued*)

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A (4) | B (2) | C (3) | D (3) | E (5) | F (4) | G (2) | H (3) | I (3) | J (3) |
| 2-me-2-Butene | | 0.7 | | | | 3.2 | | | 10.8 | 10.3 |
| 2,2 dime-Butane | | 0.1 | | | | 2.8 | | 2.6 | | 3.1 |
| Cyclopentene | | | | | | 2.9 | | 1.6 | | |
| 3-me-1-Pentene | | | | | | 7.1 | | | | |
| 4-me-1-Pentene | | 3.3 | | | | 3.1 | | | 11.8 | |
| 2,3 dime-Butane | | 0.8 | | | | 2.3 | | | 15.6 | 2.2 |
| Cyclopentane | | | | | | 2.8 | | | 6.1 | |
| 2-me Pentane | 3.7 | 1.7 | 2.9 | 0.2 | | 3.3 | 2.7 | 8.6 | 20.3 | |
| 3-me-Pentane | 8.6 | 2.2 | 4.4 | 0.3 | | 3.0 | 8.1 | 4.5 | 15.2 | 3.0 |
| 2-me-1-Pentene | | | | | | 3.1 | | | | 3.6 |
| *n-Hexane* | 9.8 | 3.3 | 4.3 | 0.3 | 6.6 | 2.7 | 1.2 | 4.6 | 5.7 | 2.6 |
| c-3-Hexene | | | | | | | | | | 0.5 |
| *t*-2-Hexene | | 21.3 | | | | 2.3 | | | 24.5 | |
| c-2-Hexene | | 0.1 | | | | 2.7 | | | 6.2 | 4.8 |
| me-Cyclopentane | | 19.0 | | | | 3.1 | | | | 4.0 |
| 2,4 dime-Pentane | | | | | | 3.0 | | | 40.5 | 2.5 |
| *Benzene* | 1.4 | 1.1 | 1.9 | 0.9 | 2.4 | 3.2 | 2.3 | 3.8 | 2.7 | |
| Cyclohexane | 3.4 | 5.1 | | | | 3.4 | | 3.3 | 10.3 | 6.2 |
| 2-me-Hexane | | | | | | 2.9 | | | | 7.7 |
| 2,3 dime-Pentane | | | | | | 2.7 | | | 16.3 | |
| 3-me-Hexane | | 10.4 | | | | 3.0 | | | | 1.7 |
| 2,2,4 trime-Pentane | | | | | | 2.7 | | | | 6.1 |
| *n-Heptane* | 3.8 | 0.0 | 5.1 | 1.2 | 4.1 | 2.9 | 1.0 | | 2.8 | 3.0 |
| 2,3 dime-2-Pentene[b] | | | | | | | | | | |
| me-Cyclohexane | | | | | | 3.0 | | | 6.2 | 3.4 |
| 2,3,4 trime-Pentane | | 3.0 | | | | 2.8 | | | | 4.6 |
| *Toluene* | 4.7 | 7.0 | 7.7 | 3.9 | 7.6 | 2.9 | | 3.6 | 40.1 | 2.9 |
| 2-me-Heptane | | | | | | 2.7 | | | 16.3 | 12.1 |
| 4-me-Heptane | | | | | | 2.8 | | | 7.9 | 6.4 |
| 3-me-Heptane | | | | | | 2.8 | | | 40.2 | 2.9 |
| *n*-Octane | | | 5.1 | | 5.2 | 2.9 | | | 40.5 | 2.5 |
| Et-Benzene | | | 3.8 | 5.6 | 5.6 | 3.0 | | 1.1 | 10.3 | 4.5 |
| *m,p*-Xylene | | | 3.3 | 5.5 | 5.1 | 3.2 | | 2.2 | 13.9 | 3.6 |
| Styrene[b] | | | | | | | | | | |
| *o-Xylene* | | 1.8 | 3.6 | | 6.8 | 3.1 | | 7.4 | 13.7 | |
| *n-nonane* | | | | | 7.5 | 2.3 | | | 6.1 | 6.0 |
| i-prop-Benzene | | | | | | 2.6 | | | | |
| *a-Pinene*[b] | | | | | | | | | | 1.2 |
| *n*-prop-Benzene | | | | | | 3.8 | | | | 9.2 |
| 3-et-Toluene | | | | | | 4.5 | | | | 9.4 |
| 4-et-Toluene | | | | | | 4.4 | | | | 8.2 |
| 1,3,5 trime-Benzene[b] | | | 4.6 | | | 4.9 | | | | 10.7 |
| 2-et-Toluene | | | | | | 4.1 | | | | |
| *1,2,4 trime-Benzene* | | | 2.5 | | | 5.3 | | | | 14.5 |
| *Decane* | | | | | 5.9 | 1.9 | | | | |
| *t*-butyl Benz[b] | | | | | | 3.6 | | | | 5.9 |
| 1,3 diet-Benz[b] | | | | | | 6.9 | | | | 9.0 |
| *n*-but-Benzene[b] | | | | | | 6.1 | | | | 9.3 |
| 1,4 diet-Benzene[b] | | | | | | 7.1 | | | | |
| 1,2 diet-Benzene[b] | | | | | | 5.4 | | | | 8.8 |
| sec-butyl Benzene[b] | | | | | | 3.8 | | | | 13.2 |
| 1,2,3 trime-Benzene[b] | | | | | | 4.7 | | | | 5.9 |
| *Undecane*[b] | | | | | | 1.5 | | | | 9.8 |

Resolved compounds and in cases of coelution major compounds reported; results that did not meet the DQOs are shown in shaded boxes; in brackets number of measurements.

[a]Italic: NIST-traceable VOC.

[b]Flagged compounds.

Table 9
Deviation (%) from the WCC-VOC reference values for each VOC

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | H | I | J |
| *Ethane* | 2.9 | – 64.5 | – 4.2 | – 2.0 | – 19.5 | | – 2.9 | – 5.2 | – 1.9 | |
| *Ethylene* | 0.6 | – 74.7 | 0.6 | 2.6 | – 10.6 | | – 20.2 | – 11.5 | – 6.6 | |
| *Acetylene* | – 13.9 | – 54.8 | | 3.9 | | | | – 22.5 | – 25.2 | |
| *Propane* | 8.6 | 0.0 | – 1.1 | 1.2 | – 28.3 | – 3.9 | – 3.6 | – 10.0 | – 1.9 | |
| *Propylene* | 4.1 | – 5.5 | 1.6 | 7.5 | – 67.2 | – 1.4 | – 18.8 | – 5.8 | – 2.6 | |
| *i-Butane* | 6.5 | 76.8 | 5.5 | 8.1 | – 35.4 | – 12.4 | – 0.9 | – 6.8 | – 0.2 | 5.3 |
| *n-Butane* | 5.2 | 76.1 | – 1.7 | 4.1 | – 31.6 | – 10.3 | – 4.1 | – 4.9 | – 2.1 | 9.6 |
| 1-Butene | 4.2 | 137.3 | 6.4 | 11.2 | | | | | 3.2 | |
| *t*-2-Butene | – 0.6 | 41.3 | 3.3 | 5.0 | | – 21.3 | | | – 6.6 | 8.4 |
| i-Butene | 8.2 | – 15.4 | 3.9 | 11.5 | | | | 3.5 | – 2.7 | |
| *c*-2-Butene | – 2.8 | 126.8 | 1.4 | 3.8 | | – 8.0 | | – 13.1 | – 7.8 | 2.8 |
| 3-me-1-Butene | | – 97.5 | | | | | | – 7.6 | – 38.5 | 8.6 |
| i-*Pentane* | – 18.1 | 167.0 | – 6.7 | 0.5 | – 45.5 | | – 10.1 | – 16.0 | – 17.3 | – 6.9 |
| *1-Pentene* | | – 4.3 | | | – 37.3 | – 5.0 | | | – 22.3 | – 9.8 |
| 2-me-1-Butene | | – 56.7 | | | | 3.6 | | 18.5 | 0.5 | |
| *n-Pentane* | – 27.8 | 162.8 | – 3.4 | 1.7 | – 28.3 | – 2.1 | – 2.5 | | – 9.3 | |
| *Isoprene* | 9.6 | – 98.0 | – 2.6 | – 13.8 | – 78.0 | – 13.5 | 1.3 | 9.3 | 5.3 | 2.6 |
| *t*-2-Penten e | – 53.6 | – 25.2 | 86.5 | 3.4 | | – 9.6 | – 6.9 | – 31.4 | – 14.2 | 20.0 |
| *c*-2-Pentene | – 19.5 | 21.7 | 5.3 | 1.0 | | – 4.9 | – 0.1 | – 10.9 | – 3.9 | 2.6 |
| 2-me-2-Butene | | 137.9 | | | | – 39.2 | | | –19.5 | 7.0 |
| 2,2 dime-Buta ne | | 251.8 | | | | – 15.5 | | – 19.4 | | – 2.3 |
| *Cyclopent ene* | | | | | | – 28.8 | | 0.8 | | |
| 3-me-1-Pen tene | | | | | | – 3.8 | | | | |
| 4-me-1-Pen tene | | 95.6 | | | | – 7.7 | | | – 29.5 | |
| 2,3 dime-Buta ne | | 178.1 | | | | – 20.9 | | | – 39.8 | – 20.4 |
| *Cyclopent ane* | | | | | | 45.6 | | | – 0.6 | |
| 2-me Pentane | 15.1 | 192.3 | – 0.5 | 206.3 | | – 22.2 | – 4.9 | – 2.2 | – 13.8 | |
| *3-me-Pentane* | 0.1 | 254.6 | – 1.8 | 10.4 | | – 10.2 | – 7.0 | – 6.6 | 20.8 | – 0.3 |
| 2-me-1-Pen tene | | | | | | – 2.7 | | | | 1.2 |
| *n-Hexane* | – 28.8 | 229.9 | – 4.9 | 2.3 | – 41.9 | – 13.3 | – 1.7 | – 32.1 | – 14.5 | – 2.6 |
| *c*-3-Hexene | | | | | | | | | | – 2.8 |
| *t*-2-Hexe ne | | – 74.1 | | | | – 23.0 | | | 25.1 | |
| *c*-2-Hexene | | 511.3 | | | | – 21.3 | | | – 7.7 | 7.7 |
| *Me-Cyclope ntane* | | – 41.2 | | | | – 16.3 | | | | 6.7 |
| 2,4 dime-Pentan e | | | | | | – 4.3 | | | – 8.8 | – 1.7 |
| *Benzene* | 3.9 | 201.1 | – 7.6 | 0.6 | 4.0 | – 1.8 | – 2.7 | – 16.7 | – 7.4 | |
| *Cyclohexan e* | 38.6 | 1275.8 | | | | – 29.2 | | – 21.8 | – 9.7 | 15.3 |
| *2-me-Hexan e* | | | | | | – 2.0 | | | | 1.9 |
| 2,3 dime-Pentan e | | | | | | 1.3 | | | – 17.0 | |
| 3-me-Hexan e | | 170.4 | | | | – 1.0 | | | | 17.1 |
| 2,2,4 trime-Pent ane | | | | | | 1.8 | | | | 5.0 |
| *n-Heptane* | 3.8 | 172.8 | – 7.7 | 3.0 | – 45.7 | 5.4 | 2.2 | | – 2.6 | – 1.8 |
| 2,3 dime-2-Pente ne[b] | | | | | | | | | | |
| *Me-Cyclohe xane* | | | | | | 7.0 | | | – 0.1 | 4.6 |
| 2,3,4 trime-Pent ane | | 1206.8 | | | | – 13.9 | | | | – 8.6 |
| *Toluene* | 26.2 | – 80.0 | – 5.9 | 9.3 | – 22.8 | 15.6 | | – 7.3 | – 2.3 | 9.2 |
| 2-me-Hep tane | | | | | | – 6.7 | | | 97.7 | – 27.0 |
| 4-me-Hep tane | | | | | | 10.6 | | | – 3.1 | 4.2 |
| 3-me-Hep tane | | | | | | 3.6 | | | – 47.3 | 1.9 |
| *n*-Octane | | | – 2.2 | | – 47.6 | – 22.7 | | | – 5.1 | 29.7 |
| *et-Benzen e* | | | 6.6 | 2.3 | 85.1 | 6.7 | | – 16.8 | 8.7 | 11.0 |
| *m,p*-Xylene | | | 13.7 | 6.6 | 46.3 | – 6.5 | | – 8.6 | 17.3 | 9.6 |
| Styrene[b] | | | | | | | | | | |
| *o-Xylene* | | 1604.0 | 9.9 | | 243.2 | – 19.4 | | – 25.2 | 17.3 | |
| *n-Nonane* | | | | | – 50.7 | – 17.4 | | | 15.4 | 12.3 |

Table 9 (*continued*)

| VOC[a] | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | H | I | J |
| *i-prop-Benzene* | | | | | | – 32.7 | | | | |
| *a-Pinene*[b] | | | | | | | | | | 39.5 |
| *n*-prop-Benzene | | | | | | – 30.5 | | | | 62.6 |
| 3-et-Toluene | | | | | | – 63.2 | | | | 3.8 |
| 4-et-Toluene | | | | | | – 62.7 | | | | 10.3 |
| 1,3,5 trime-Benzene[b] | | | – 13.4 | | | – 88.7 | | | | 1.7 |
| 2-et-Toluene | | | | | | – 52.4 | | | | |
| *1,2,4 trime-Benzene* | | | 38.8 | | | – 81.2 | | | | 7.6 |
| *Decane* | | | | | – 78.0 | – 56.7 | | | | |
| *t*-butyl Benz[b] | | | | | | – 22.2 | | | | 59.2 |
| 1,3 diet-Benz[b] | | | | | | – 85.9 | | | | 120.9 |
| *n*-but-Benzene[b] | | | | | | n.d. | | | | |
| 1,4 diet-Benzene[b] | | | | | | n.d. | | | | |
| 1,2 diet-Benzene[b] | | | | | | – 80.2 | | | | 44.5 |
| sec-butyl Benzene[b] | | | | | | – 29.9 | | | | 79.7 |
| 1,2,3 trime-Benzene[b] | | | | | | – 88.2 | | | | – 35.5 |
| *Undecane*[b] | | | | | | – 82.2 | | | | – 13.6 |

Resolved compounds and in cases of coelution major compounds reported; results that did not meet the DQOs are shown in shaded boxes.
n.d.: not determined prior to shipping.
[a]Italic: NIST-traceable VOC.
[b]Flagged compounds.

Table 10

| VOC | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A (4) | B (2) | C (3) | D (3) | E (5) | F (4) | G (2) | H (3) | I (3) | J (3) |
| (a) Repeatability (%) for each VOC determination of the GAW standard (coeluting compounds) | | | | | | | | | | |
| 1 | | | | | | | | | | 6.2 |
| 2 | | | | | | | | 2.6 | | |
| 3 | | | | | | 2.1 | | | | |
| 4 | | | | | | | | 2.0 | | |
| 5 | | | | | | | | 2.1 | | |
| 6 | | | | | | | | | | 5.8 |
| 7 | | | | | | | | | 6.5 | |
| 8 | | | | | | | | | | 3.3 |
| 9 | | | | | | | | 4.6 | | |
| 10 | | | | | | | | | | 2.6 |
| 11 | | | | | | | | | 40.5 | |
| 12 | | | | | | | | | | 3.4 |
| 13 | | | | | | | | | 7.9 | |
| 14 | | | | | | | | | 6.2 | |
| 15 | | | | | | | | | | 11.8 |
| 16[a] | | | | | | | | | | 5.7 |
| 17[a] | | | | | | | | | | |
| 18[a] | | | | | | | | | | |
| (b) Deviation (%) from the WCC-VOC reference values for each VOC (Either coeluting compounds or combined compounds for intercomparison) | | | | | | | | | | |
| 1 | 3.5 | 42.3 | 1.9 | 8.2 | | | | | – 3.2 | 0.7 |
| 2 | – 2.4 | 98.1 | 0.2 | 3.8 | | | | – 11.6 | – 4.8 | |
| 3 | 3.5 | 42.3 | 1.9 | 8.2 | | 2.3 | | | – 3.2 | |
| 4 | | 53.1 | | | | – 18.7 | | – 11.4 | – 21.2 | – 3.0 |
| 5 | | | | | | 2.0 | | 2.2 | – 8.6 | |

Table 10 (*continued*)

| VOC | Participants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A (4) | B (2) | C (3) | D (3) | E (5) | F (4) | G (2) | H (3) | I (3) | J (3) |
| 6 | | 135.6 | | | | −0.4 | | | −8.1 | 1.3 |
| 7 | | 170.7 | | | | −15.8 | | | −17.1 | 0.1 |
| 8 | | | | | | −3.6 | | | | 30.8 |
| 9 | | 100.0 | | | | −19.5 | | −35.0 | | −11.1 |
| 10 | | | | | | 7.5 | | | −8.4 | −0.2 |
| 11 | | | | | | | | | −9.4 | |
| 12 | | | | | | −1.5 | | | −9.5 | 2.3 |
| 13 | | | | | | −1.6 | | | −3.4 | 9.4 |
| 14 | | | | | | | | | −0.2 | |
| 15 | | | | | | −53.8 | | | | 41.2 |
| 16[a] | | | | | | −55.5 | | | | −0.4 |
| 17[a] | | | | | | −69.0 | | | | |
| 18[a] | | | | | | −69.1 | | | | |

Results that did not meet the DQOs are shown in shaded boxes.
1: 1-butene+i-butene; 2: *t*-2-butene+1-butene; 3: 1-butene+ 2-me-propene; 4: 1-pentene +2-me-2-butene; 5: *n*-pentane+ cyclopentane ; 6: *n*-pentane+2-me-1-butene; 7: me-cyclopentane+2,2 -dime-butane ; 8: 4-me+3-me-pentene; 9: 2,3-dime-butane+me-cyclopentane; 10: 2- me-pentane +cyclopentane; 11: 2,2-+2,4-dime-pentane; 12: benzene+2,3-dime-pentane; 13: 3-me-hexane +2-me-hexane; 14: me-cyclohexane+2,2,3-trime-butane; 15: *o*-xylene+styrene; 16: 1-et-2-me-benzene+*n*-decane+i-butyl-cyclohexane; 17: 1,2,4-trime-benzene+ *n*-decane; and 18: *n*-but-benzene+1,4-diet-benzene.
[a]Flagged compounds.

Table 11
Ranking of properly identified and quantified VOCs

| VOC[a] | *X* (%) | *Y* (%) | VOC | *X* (%) | *Y* (%) | VOC | *X* (%) | *Y* (%) |
|---|---|---|---|---|---|---|---|---|
| *Propane* | 80 | 88.9 | 4 | 30 | 60 | Cyclopentane | 0 | 0 |
| *Isoprene* | 80 | 80 | *i-Pentane* | 30 | 33.3 | t-2-Hexene | 0 | 0 |
| c-2-Pentene | 70 | 87.5 | 2-me-1-Pentene | 20 | 100 | Cyclohexane | 0 | 0 |
| *Benzene* | 70 | 77.8 | 2,4 dime-Pentane | 20 | 66.7 | 4-me-Heptane | 0 | 0 |
| *Ethylene* | 70 | 77.8 | 3-me-Heptane | 20 | 66.7 | n-Octane | 0 | 0 |
| *Propylene* | 70 | 77.8 | 13 | 20 | 66.7 | *n-Nonane* | 0 | 0 |
| c-2-Butene | 70 | 70 | 3-me-1-Butene | 20 | 50 | i-prop-Benzene | 0 | 0 |
| *Ethane* | 60 | 75 | 2-me-2-Butene | 20 | 50 | 1,3,5 trime-Benzene | 0 | 0 |
| i-*butane* | 60 | 75 | c-2-Hexene | 20 | 50 | 2-et-Toluene | 0 | 0 |
| *t*-2-butene | 60 | 66.7 | 2-me Pentane | 20 | 25 | *1,2,4 trime-Benzene* | 0 | 0 |
| *n-Heptane* | 50 | 83.3 | 3-me-1-Pentene | 10 | 100 | *Decane* | 0 | 0 |
| *n-Butane* | 50 | 83.3 | c-3-Hexene | 10 | 100 | 1,2 diet-Benzene | 0 | 0 |
| i-butene | 50 | 83.3 | Cyclopentene | 10 | 50 | 9 | 0 | 0 |
| *n-Pentane* | 50 | 83.3 | 2-me-Hexane | 10 | 50 | 11 | 0 | 0 |
| 3-me-Pentane | 50 | 71.4 | 2,3 dime-Pentane | 10 | 50 | 14 | 0 | 0 |
| 1 | 50 | 71.4 | 2,2,4 trime-Pentane | 10 | 50 | 15 | 0 | 0 |
| 2 | 50 | 62.5 | 3-et-Toluene | 10 | 50 | | | |
| 3 | 50 | 50 | 4-et-Toluene | 10 | 50 | | | |
| 1-Butene | 40 | 80 | 8 | 10 | 50 | | | |
| i-*Pentane* | 40 | 57.1 | 4-me-1-Pentene | 10 | 33.3 | | | |
| *t*-2-Pentene | 40 | 44.4 | me-Cyclopentane | 10 | 33.3 | | | |
| *n-Hexane* | 40 | 44.4 | 3-me-Hexane | 10 | 33.3 | | | |
| *Toluene* | 40 | 44.4 | me-Cyclohexane | 10 | 33.3 | | | |
| et-Benzene | 40 | 40 | 2,3,4 trime-Pentane | 10 | 33.3 | | | |
| *m,p*-Xylene | 30 | 100 | 2-me-Heptane | 10 | 33.3 | | | |
| 1-Pentene | 30 | 100 | 2,2 dime-Butane | 10 | 25 | | | |
| 2-me-1-Butene | 30 | 100 | 7 | 10 | 25 | | | |

Table 11 (*continued*)

| VOC[a] | *X* (%) | *Y* (%) | VOC | *X* (%) | *Y* (%) | VOC | *X* (%) | *Y* (%) |
|---|---|---|---|---|---|---|---|---|
| 4 | 30 | 75 | *Acetylene* | 10 | 20 | | | |
| 5 | 30 | 75 | *o-Xylene* | 10 | 16.7 | | | |
| 6 | 30 | 60 | 2,3 dime-butane | 0 | 0 | | | |

*X*: related to all participants; *Y*: related to all participants who identified this specific VOC.
1: 1-butene + *i*-butene; 2: *t*-2-butene + 1-butene; 3: 1-butene + 2-me-propene; 4: 1-pentene + 2-me-2-butene; 5: *n*-pentane + cyclopentane; 6: *n*-pentane + 2-me-1-butene; 7: me-cyclopentane + 2,2-dime-butane; 8: 4-me + 3-me-pentene; 9: 2,3-dime-butane + me-cyclopentane; 10: 2-me-pentane + cyclopentane; 11: 2,2- + 2,4-dime-pentane; 12: benzene + 2,3-dime-pentane; 13: 3-me-hexane + 2-me-hexane; 14: me-cyclohexane + 2,2,3-trime-butane; 15: *o*-xylene + styrene; 16: 1-et-2-me-benzene + *n*-decane + i-butyl-cyclohexane; 17: 1,2,4-trime-benzene + *n*-decane; and 18: *n*-but-benzene + 1,4-diet-benzene.
[a]Italic: NIST traceable VOCs.

H, I, and J. All other coelutions show either too little data to be intercompared or did not meet the DQO for deviation from the reference values.

According to Table 7 which listed the ranking of properly identified and quantified 28 GAW target VOCs. Table 11 shows the corresponding ranking for the total number of 76 unflagged compounds (resolved and unresolved compounds). The results are similar: propane, isoprene, benzene, ethylene and propylene are the top five NIST traceable VOCs. These compounds were accurately determined by at least 2/3 of the laboratories and almost 4/5 of the laboratories which identified these species also correctly quantified them. However, only 18 out of 76 unflagged compounds were accurately determined by at least 50% of the laboratories. Almost 17 unflagged compounds could not be determined accurately by any laboratory.

Including coeluting compounds did not change a lot the ranking of the overall performance of the labs ((Fig. 2(III)) which is based on the number of VOCs which meet the DQOs for both, uncertainty and repeatability. Overall the difference in the total score between the first (lab D) and the last place (lab B) is less than in the data interpretations made in the previous chapters. This is mainly due to the fact that considering coelutions usually leads to an increase of accurately determined compounds for low ranking labs whereas the increase of the total number of 76 unflagged compounds will lead to a slightly less total score for high ranking labs. Though somehow arbitrary, this procedure represents a first approach to account for unresolved peaks. Future work should focus on the development of advanced algorithms to handle properly coelutions problems.

## 4. Conclusions

The first VOC-GAW intercomparison considered world-wide for the first time offline and online VOC devices and integrated very different laboratories (e.g. programs, experience, infrastructure). The intercomparison focused on the assessment of the analytical performance status of these labs using a complex synthetic VOC mixture in $N_2$. As a first basic task it did not yet address real air samples. Due to the variety of analytical methods among the participants both the number of identified species (16–150 VOCs) and their proper quantification differed largely.

The results for a subset of 28 VOCs recognized as primary GAW target compounds show that the DQOs for repeatability are met in most cases. However, for the deviation from the WCC-VOC reference values the picture is different. For some VOCs the concentrations differed significantly among the different laboratories. Considering both uncertainty and repeatability a number of VOCs (e.g. propane, propylene, isoprene, and benzene) that are traceable to NIST were unambiguously identified and properly quantified by most labs. More problems occur with less volatile and more reactive VOC. There are also difficulties in the proper determination of important VOCs, e.g. aromatic compounds (apart from benzene), i-pentane, acetylene, and in general for low volatile VOCs. Coelution problems were observed more often with online GC-methods. Considering the entire suite of the GAW standard only 18 out of 76 compounds were accurately determined by at least 50% of the laboratories.

From the results of the intercomparison it appears imperative to strengthen harmonization

procedures. Future activities should include frequent intercomparisons with fewer VOC (5–10) on a more rigorous time schedule basis. It is strongly suggested to continue individual performance audits which have already been initiated based on the outcome of this first intercomparison. This includes comprehensive concurrent air sampling and subsequent mutual canister analysis which will further elucidate performance of sampling and storage procedures. In order to minimize calibration biases a uniform calibration gas mixture (e.g. NPL) must be made available to GAW and other participating groups.

The first GAW-VOC intercomparison also revealed that laboratories that report many VOCs do not necessarily quantify them accurately. On the other hand laboratories which identified only a small subset of the GAW standard compounds often quantified a large fraction of those species accurately. However, due to the limited number of VOCs reported by these laboratories this information only reflects partially the VOC mixture in ambient air and thus may not be representative enough. For this reason future guidelines should address proper criteria for a "good" measurement. They should evaluate whether the proper identification of as many as possible VOCs (including minor compounds) or the proper quantification of at least a few relevant VOCs ("standard compounds") should be considered important.

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