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Methodology for Analysis of Volatile Organic Compounds in Emission Testing of Building Materials

IRC-RR-254

Lusztyk, E., Yang, W., Won, D.Y.,

April 2005

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Methodology for Analysis of Volatile Organic Compounds in Emission Testing of Building Materials

Summary

The methodology for the analysis of compounds emitted from building materials applied in this phase of the project was generally similar to that used in Phase 1 of the CMEIAQ project (CMEIAQ-I), but it was further extended and enhanced.

Firstly, the list of 90 chemicals (IRC Target Compounds) was used as a basis for identification and individual quantification of VOCs in all tested building materials and in all samples taken during the progress of each test. As was used in Phase 1, GC/MS was the primary analytical technique. Some changes in operating parameters for GC/MS were introduced to improve separation and detection of Target Compounds. In addition to GC/MS, HPLC was applied for quantification of low molecular weight carbonyl compounds.

Secondly, the quantitative data analysis of Target Compounds was established using the extracted ion technique for identification and integration of peak areas, and individual response factors for concentration calculations.

Thirdly, a new data analysis approach was applied to the majority of data obtained in Phase 1 of the project, producing higher quality of data compatible with those obtained in the most recent experiments.

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Methodology for Analysis of Volatile Organic Compounds in Emission Testing of Building Materials

1. Introduction

Hundreds of volatile chemical compounds are emitted from building materials. They have different levels of toxicity and are in a wide range of concentrations. Their chemical and physical properties can be very different. The chemical analysis to identify and to quantify all of them could be very complex and expensive. Therefore, an analytical methodology has to set practical and economical criteria within the scope of its application.

In Phase 1 of this project the practical approach was to identify and to quantify ca. 20 most abundant compounds in one, usually 24h sample. Only 5 or 6 model compounds and TVOC (Total Organic Volatile Compounds) were quantified in all test samples. Toluene was used as a calibration standard for quantification of identified VOCs (Volatile Organic Compounds) and TVOC. Model compounds were calibrated individually using their own authentic samples (NRC, 1999).

In this phase of the project the methodology was further extended and elaborated. Most importantly, a list of 90 compounds (Target Compounds) was established to be quantified individually in all samples from emission tests (the list and the basis for its content are presented in Report 1.1). These data should provide more realistic foundations for predictions of cumulative effects of VOCs indoors where different materials and chemicals are present in varied quantities.

The list of Target Compounds to be identified and quantified is very diverse; it contains chemical compounds with very different physical and chemical properties. The quantitative analysis of these compounds cannot be achieved by applying a single technique. Two analytical techniques were selected in this study: GC/MS and HPLC. As was used in Phase 1, the principal methodology was GC/MS with thermal desorption. However, using Extracted Ion rather than Total Ion technique in data analysis and using individual response factors for mass calculations significantly enhanced the precision and accuracy of analytical methodology applied in GC/MS quantification.

This new approach was also used to reanalyze for the presence of Target Compounds from the stored data from Phase 1 of the project. The data from 43 out of total of 48 tests were reanalyzed using this approach. Other 5 were initially analyzed using FID detection and are not amenable for the new method.

Development of HPLC methodology was required for quantification of 5 compounds from Target Compound list, since they cannot be properly analyzed using GC/MS approach.

2. Gas Chromatography Mass Spectrometry Methodology

Exhaust air from a test chamber was pumped through multi-bed sorbent tubes where VOCs were trapped. The sampled tubes were tightly capped and stored in room temperature until they were analyzed, which were not later than two weeks. The exposed tubes together with a blank tube and a series of tubes with a calibration mixture were thermally desorbed and analyzed by GC/MS for individual VOCs and TVOC. The mass spectrometer was operated in the scan mode.

Quantitative data analysis of Target Compounds and TVOC were performed for all analyzed emission test samples. Data analysis for major VOCs emitted from tested materials, which may or may not be Target Compounds, was performed for a sample collected at approximately 24h from the start of one emission test.

2.1 Sampling

Supelco Carbotrap 300 tubes were used for air sampling. These three-bed tubes were designed to maximize the collection of VOCs in a wide range of volatility. The volume of the sample, depending on the concentration of the VOCs, was from 10 mL to 10 L with a sampling rate not higher than 200 mL/min.

2.2 Apparatus

Perkin-Elmer ATD400 thermodesorber connected with Gas Chromatography (Agilent GC 6890)/Mass Spectrometry (Agilent MSD 5973) system was used for all analyses. Operating parameters for the analytical system are summarized in Table 1.

2.3 Calibration of the Analytical System

A three-point calibration from the solution of toluene and 11 other standard compounds was performed daily at the beginning and at the end of a sequence of analyzed samples.

The solution of pure chemicals in methanol was injected directly into the Carbotrap B/C sorption tubes. Calibration tubes were purged for 2 min to remove solvent prior to desorption. Toluene Response Factor from Total Ion Chromatogram (RF_{TT}) and Ion 91 (RF_T) were calculated as a slope of the linear response of its peak area against the injected amount in ng. Ratios of response factors of other calibrated compounds to toluene were calculated and monitored for quality control purposes. List of standard compounds in a calibration mixture, and their properties are presented in Table 2. The standard compounds were selected to represent ten classes of compounds: ALD (aldehydes), ALOH (alcohols), CL (chlorinated compounds), EST (esters), HC-AL (aliphatic hydrocarbons), HC-AR (aromatic hydrocarbons), HC-CYC (cycloalkanes), KET (ketones), MISC (miscellaneous compounds), TERP (terpenes).

2.4 General Analysis of VOCs Emitted from Tested Materials

A general analysis of emitted VOCs was performed for the sample taken at approximately 24h from the beginning of one test for all tested building materials. The purpose of the general analysis was to identify all chemicals emitted in a large amount while they may or may not be on the Target Compound list. The information may be used to update the Target Compound list in the future.

Compounds with chromatography peaks exceeding 1% of the TVOC were identified and quantified using the Toluene Response Factor for TIC (RF_{TT}). The sum of their concentrations represented usually more then 60 % of the TVOC concentration.

2.4.1 Identification of Compounds

Non-target compounds were identified by comparison of mass spectrum with NIST Mass Spectra library. Identification was confirmed by retention time and comparison with previously analyzed samples from different tests. In some cases, no strong match was obtained and the compound was flagged as "unidentified". Many isomers of hydrocarbons and cyclohydrocarbons were only identified to a class level, similarly as less-common terpenes and silioxy compounds. Target compounds identification was based on extracted ion analyses, in comparison with authentic sample mass spectra and their retention times.

2.4.2 Toluene Based Quantification of Identified VOCs

Concentrations of all identified compounds were calculated using the toluene response factor (RF_{TT}). Peak area used in Equation 1 was from the integration of Total Ion Chromatogram (TIC) peaks. In some cases peaks of eluted compounds overlapped one another and they were reported together.

Equation 1 was used for VOC calculations:

$$C_v = \frac{A_v}{RF_{TT}\ V} \tag{1}$$

Where:

C_V: Concentration of VOC in the air [µg/m^3]

A_V: Peak area of VOC from TIC [cts]

RF_{TT}: Response Factor for Toluene TIC [cts/ng]

V: Volume of the sample [L]

2.5 Quantification of Total Volatile Organic Compounds

TVOC were quantified for all analyzed emission test samples. Concentrations were calculated from the Total Ion Chromatogram by adding the areas of all peaks with the retention time between 5 and 40 min. Values calculated from Equation 1 were based on toluene response factor from TIC (RF_{TT}). In reported TVOC values, concentrations of carbonyl compounds not identified by GC/MS (but quantified by HPLC) were not included.

2.6 Analyses of Target Compounds

Target Compounds were analytically defined as compounds which presence was checked in all samples and which concentrations were calculated using their own response factors. A special procedure was established for identification and quantification of 90 Target Compounds.

2.6.1 Calibration of Target Compounds

All Target Compounds were calibrated using pure compounds (authentic samples) diluted in methanol as a solvent. In all calibrated mixtures toluene was used as an internal standard. Different volumes of the standard mixtures were injected directly onto two-bed sorption tubes. Tubes were next purged with dry nitrogen to remove the solvent and analyzed using the normal procedure. Mass response factors were determined from slopes of the computer-generated line from a multi-point (three to five points) calibration.

Ratios (RR_C) of the response factor of a target compound's primary ion (RF_C) to a response factor of toluene ion 91(RF_T) were calculated for all 90 Target Compounds. They are summarized in Table 3.

Variations in ratios of response factors for 12 chemicals (Standard Compounds) from different chemical classes were monitored daily by calibrations of the standard mixture. If the difference in response factors ratio to toluene (RR_C) exceeded 20%, old values were replaced with new ones in new concentration calculations. Ratios of response factors for all compounds were routinely checked (every few months). The diagram in the Figure 1 shows the calibration procedure for Target Compounds.

2.6.2 Identification and Quantification of Target Compounds in Air Samples

Identification of Target Compounds in air samples was based on analyses of extracted primary and secondary ions, which are specific for each compound. Ratio of these ions in mass spectrum (RRc) and retention time (RT) for Target Compounds were established from analyses of authentic samples.

Quantification of Target Compounds was based on the integrated peak area of the compound's primary ion. Selection of primary ion depended on interfering ions due to the co-elution of compounds as well as ion intensities. For some compounds a primary ion was significantly smaller then the most abundant ion, which had a negative effect on method detection limit (MDL) of those compounds. When the quantity of the Target Compound was below or close to MDL, only its presence was reported.

2.6.3 Calculation of Target Compounds Concentration in Air

Concentrations of Target Compounds were calculated using Equation 2:

$$C_c = \frac{A_c}{RF_c \; V} \tag{2}$$

Where:

C_C: Concentration of target compound 'C' in the air [µg/m^3]

A_C: Peak area of the primary ion of target compound 'C' [cts]

RF_C: Response Factor for the primary ion of target compound 'C' [cts/ng]

V: Volume of the sample [L]

Since not all Target Compounds were used for daily calibrations (see Table 2 for the standard calibration chemicals), the value of RF_c was calculated based on Equation 3.

The response factor for primary ion of target compound 'C' (RF_C) was based on response factor for ion 91 of toluene (RF_T) calculated from daily calibrations and the response factor ratio (RR_C) measured by calibrating the GC/MS system with 90 Target VOCs (see Section 2.6.1 and Table 4).

$$RF_c = RR_c \times RF_T \tag{3}$$

Where:

RF_C: Response Factor for Compound 'C' primary ion [cts/ng]

RR_C: Response Factor Ratio for Compound 'C' against toluene [RF_C / RF_T]

RF_T: Response Factor for Toluene ion 91 [cts/ng]

Calculated by this method, concentrations of Target Compounds were usually significantly different from and more accurate than values calculated using toluene response factor and TIC integration. Comparison of results from two calculation methods for some Target Compounds is presented in Table 4.

2.7 Quality Control/Quality Assurance

2.7.1 Instrument Performance Quality Control

The analytical system was set up according to manufacturers' requirements. The mass calibration and resolution of the mass spectrometer were verified by the analysis of the instrument performance check standard PFDT. Parameters were checked daily. A non-exposed clean tube, as well as series of calibration tubes, was analyzed every time prior to a sequence of test samples as indicators of the instrument performance. Changes in retention times, peak shapes and response factor ratios of Standard Compounds against toluene were monitored.

2.7.2 Analytical Accuracy

Certified commercial standard tubes from European Community Bureau of Reference (CEC, 1989), which were preloaded with benzene, toluene and 1,3-dimethylbenzene, were used for auditing purposes to establish analytical quality. Their analytical results were compared with the results from a liquid calibration mixture prepared in the laboratory from authentic compounds. The results presented in Table 5 show a good accuracy level in all three standards.

2.7.3 Methodology Performance Criteria for Target Compounds Analysis

The procedure to measure and check the methodology performance criteria followed the routine established by US EPA for Compendium Methods TO-17 (EPA, 1999a) and TO-15 (EPA, 1999b).

Method Detection Limit (MDL)

The method detection limit is defined as the minimum level of the compound that can be measured with 99 percent confidence that its concentration is greater than zero. Studies of

MLD for Target Compounds were performed in accordance with the Code of Federal Regulations (40CFR136 Appendix B) (EPA, 2004).

MDL was calculated as a product of the standard deviation for seven replicate measurements of a concentration of the compound of interest near the expected detection limit (within a factor of five) and 3.14 (Student's "t" value for 99% confidence for seven values). Results of MDL studies for Target Compounds are listed in Table 3.

Analytical Precision

Analytical precision is defined as the absolute value of the relative difference between two samples.

$$\text{Precision (\%)} = \frac{X_1 - X_2}{X} \times 100 \tag{4}$$

Where:

X_1: First measurement value.

X_2: Second measurement value.

X: Average of the two values.

There are several factors that may affect the analytical precision of the measurement. A primary influence is the concentration level of the compound of interest in the sample, i.e. precision degrades as the concentration approaches the detection limit. An effect on the precision has the nature of the compound itself such as its molecular weight, solubility, polarizability, etc. In our analytical conditions polar compounds generally showed poorer precision then most of the non-polar VOCs.

Two types of analytical precision were checked and met the EPA-Compendium Method TO-17 performance criteria:

A) Precision of Duplicate Pairs (within 20% on synthetic samples of a given Target Compound), where X_1 and X_2 are measurement values for two identical samples, and

B) Precision for the Distributed Volume Pair (within 25% for two defined sample volumes), where X_1 and X_2 are measurement values for two different volume samples.

Audit Accuracy

Audit accuracy was defined as the relative difference between the measurement result and the nominal concentration of the audit compound.

$$\text{Audit Accuracy (\%)} = \frac{\left|\text{Spiked Value - Measured Value}\right|}{\text{Spiked Value}} \times 100 \tag{5}$$

A certified mixture of standard compounds was used as an audit material. EPA-Compendium Method TO-17 audit accuracy criteria of 30% was met for all measured compounds except for hexanal. For hexanal and other low molecular weight carbonyl compounds, quantification by HPLC was preferable.

Audit accuracy results for selected Target Compounds are presented in Table 6.

3. New Quantitative Analysis of Target Compounds from CMEIAQ-I Test Data

Analytical data collected in Phase 1 were recalculated using the routine similar to that described earlier. Compounds were identified and quantified using the extracted ion analytical technique. Operating conditions of GC/MS in Phase 1 were different from those in Phase 2. As a consequence retention times and mass spectrum for some compounds were different. Analytical parameters for Phase 1 are summarized in Table 1.

3.1 Identification of Target Compounds

All Target Compounds were identified by their primary and secondary ions as well as retention time. Some compounds were difficult to identify: they were too volatile and not separated at the beginning of the chromatogram (ethanol, 1-propanol, 2-propanol, acetone, 2-methyl-2-propanol, 2-methylpentane, 3-methylpentane, butanal, hexane) or their primary ions were not detected (ethanol, 1-propanol, 1,2-ethanediol).

3.2 Quantification of Target Compounds individually calibrated

During analyses in Phase 1, ca 20 different calibration mixtures were prepared and run in different times with tested samples. All calibration mixtures had toluene as an internal standard. From those data, ratios (RR_C) of the response factor of the primary ion of a target compound to the response factor of toluene ion 91 were calculated. Concentrations of identified Target Compounds were calculated using Equation 2 as in Phase 2. List of Target Compounds, their retention times, primary ions and Response Factor Ratios to toluene (RR_C), which were calculated from multi-point calibrations in Phase 1, are presented in Table 7.

3.3 Quantification of Target Compounds not individually calibrated

Some compounds were never individually calibrated in Phase 1 (list of them is in the Table 8). In these cases Equation 1 and toluene response factor (RF_{TT}) calculated from TIC were used for concentration calculations. For better precision, integrations of compounds were performed based on primary ions. Area of Total Ion (A_v) used in Equation 1 was calculated by dividing area of primary ions by its contribution in compound mass spectrum (I/TIC)(reported in Table 8).

4. HPLC methodology

The procedure, similar to ASTM D 5197-03 Test Method for "Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)" (ASTM, 2003) and EPA Method TO-11A (EPA, 1999c), was applied to the quantification of low molecular weight carbonyl compounds from the Target Compounds list. Table 9 summarizes target compounds analyzed by this method, their retention times and calculated method detection limit (MDL).

Among eight Target Compounds quantified by this method, only formaldehyde, acrolein and acetaldehyde were exclusively analyzed with HPLC. For butanal, pentanal, hexanal and acetone that were analyzed with both GC/MS and HPLC, HPLC data were preferable since the HPLC analysis was specifically designed for these chemicals and, therefore, produced more accurate results. For example, it was observed that GC/MS underestimated the amount of pure hexanal when it was analyzed with both GC/MS and HPLC.

4.1 Sampling

Exhaust air from a test chamber was pumped through a SPE cartridge (Waters Sep-Pak XpoSure Aldehyde) coated with DNPH (2, 4-dinitrophenylhydrazine) at a rate of 100 mL/min for 120 min. Carboxyl compounds present in the air reacted with DNPH to form stable derivatives. The cartridge was washed with acetonitrile by gravity feed elution. The eluate was diluted volumetrically to 10 ml. Determination of DNPH derivatives was done by isocratic reverse phase HPLC with UV detection at 360nm.

4.2 Apparatus

The HPLC system consisting of Varian 9012 Solvent Delivery System/ 9050 Variable Wavelength UV-VIS Detector (at 360nm) / Prostar 410 Autosampler was used to analyze the extracted sample. Two Supelcosil LC-18 columns (25cm x 4.6mm, 5 µm) in series at 30^0C and, as a mobile phase, gradient of acetonitrile in water from 60% to 100% were used for separation of compounds.

4.3 Calibration

Six-point calibration from a commercial DNPH derivative mixture (TO-11/IP-6A Aldehyde/Ketone reference standard from Supelco, Inc) was performed.

4.4 Performance Criteria

Method Detection Limit (MDL) for HPLC was calculated in a similar manner as for Target Compounds quantified by GC/MS: as a product of the standard deviation for seven replicate measurements of a concentration of the compound of interest near the expected detection limit (within a factor of five) and 3.14 (Student's "t" value for 99% confidence for seven values).

MDL for HPLC are summarized in Table 9.

5. References

ASTM (2003) Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology), ASTM Standard D 5197-03, American Society for Testing and Materials, West Conshohocken, PA.

Commission of the European Communities (CEC) (1989) The Certification of Benzene, Toluene and m-Xylene Sorbed on Tenax in Tubes CRM 112, Report EUR 12308, Bureau of Reference.

EPA (1999a) Compendium Method TO-17, Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes, EPA/625/R-96/010b, Office of Research and Development, U.S. Environmental Protection Agency

EPA (1999b) Compendium Method TO-15, Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS), EPA/625/R-96/010b, Office of Research and Development, U.S. Environmental Protection Agency

EPA (1999c) Compendium of Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), EPA/625/R-96/010b, Office of Research and Development, U.S. Environmental Protection Agency

EPA "Code of Federal Regulations, Title 40, Part 136, Appendix B: Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11." [Online] 27 February 2004. <http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=7052affd1916e8e301b6f4538d0e7749&rgn=div5&view=text&node=40:20.0.1.1.1&idno=40#40:20.0.1.1.1.0.1.6.2>

National Research Council (1999) CMEIAQ Final Report 1.1, A Method for Sampling and Analysis of Volatile Organic Compounds in Emission Testing of Building Materials.

Table 1. Operating parameters for GC/MS analyses.

	Phase 1	**Phase 2**
Thermal Desorption		
Instrument	**Varian ATD 400**	**Varian ATD 400**
Primary Desorption	330^{0}C	330^{0}C
Cold Trap Low Temperature	1^{0}C	-20^{0}C
Cold Trap High Temperature	340^{0}C	340^{0}C
Gas Chromatography		
Instrument	**HP 5890**	**Agilent 5890N**
Column DB-5MS J&W Scientific	60m / 0.32mm / 25µm	60m / 0.32mm / 25µm
GC Temperature Program		
Initial Temperature	10^{0}C	-20^{0}C
Initial Time	4min	
Ramp1	5^{0}C/min to 170^{0}C	5^{0}C/min to 170^{0}C
Ramp 2	20^{0}C/min to 280^{0}C	25^{0}C/min to 280^{0}C
Final Time	5min	2 min
Mass Spectrometry		
Instrument	**HP MS Engine 5989**	**Agilent MSD 5973**
MS Quadruple	100^{0}C	150^{0}C
MS Source	200^{0}C	230^{0}C
Mass Range	35-350amu	30-350 amu

Table 2. List of standard compounds calibrated in CMEIAQ-II.

#	Class	Compound	CAS #	RT *	b.p. *	MW *
1	ALD	Hexanal	66-25-1	14.40	131	100.00
2	KET	Methyl ethyl ketone	78-93-3	6.51	80	72.11
3	ALOH	1-Butanol	71-36-3	9.04	118	74.00
4	EST	Butyl acetate	123-86-4	15.15	127	116.10
5	CL	1,4-Dichlorobenzene	106-46-7	27.70	173	146.00
6	HC-AL	Decane	124-18-5	22.34	110	92.14
7	HC-AR	Toluene	108-88-3	12.88	110	92.14
8	HC-AR	1,4-Dimethylbenzene	106-42-3			106.17
9	HC-AR	1,2,4-Trimethylbenzene	95-63-6	22.06	168	120.20
10	HC-CYC	Propylcyclohexane	1678-92-8	19.55	155	126.24
11	TERP	Limonene	138-86-3	23.38	175	136.24
12	MISC	n-Butyl ether	142-96-1	17.47	142	130.32

* RT: retention time (min), b.p.: boiling point, MW: molecular weight

Table 3. List of target compounds individually calibrated in CMEIAQ-II, their retention time (RT), primary and secondary ions, response factor ratio against toluene (RR_C), and method detection limit (MDL)*

No.	CAS #	Compound	Class	RT [min]	Primary Ion	Secondary Ions	RR_C	MDL [ng]
1	64-17-5	Ethanol	ALOH	6.02	31	45, 46	0.10	2.52
2	67-64-1	Acetone	KET	6.11	58	43	0.07	0.43
3	67-63-0	2-Propanol	ALOH	6.13	45	39, 59	0.33	1.27
4	75-65-0	2-Methyl-2-propanol	ALOH	7.09	59	41, 31	0.50	1.65
5	107-83-5	2-Methylpentane	HC-AL	8.13	43	71, 42, 41	0.26	0.29
6	71-23-8	1-Propanol	ALOH	8.59	31	59, 42	0.21	20.00**
7	96-14-0	3-Methylpentane	HC-AL	8.64	57	56, 41, 29	0.35	0.83
8	75-09-2	Dichloromethane	CL	7.03	49	86, 84	0.27	0.75**
9	123-72-8	Butanal	ALD	9.25	72	41, 39	0.09	21.82
10	110-54-3	Hexane	HC-AL	9.58	56	86, 57	0.11	0.39
11	78-93-3	Methyl ethyl ketone	KET	9.67	43	72, 57, 29	0.46	0.38
12	141-78-6	Ethyl acetate	EST	10.20	43	61, 88, 71	0.33	0.19
13	71-43-2	Benzene	HC-AR	11.78	78	77, 51	0.71	0.69
14	110-82-7	Cyclohexane	HC-CYC	11.79	84	56, 69, 55	0.23	1.03
15	108-21-4	1-Methylethyl acetate	EST	12.19	43	61, 87	0.56	13.65
16	71-36-3	1-Butanol	ALOH	12.41	56	41, 31	0.22	0.42
17	109-86-4	2-Methoxyethanol	ALOH	12.61	45	76, 31, 45	0.62	106.96
18	79-01-6	Trichloroethylene	CL	13.72	130	95, 132	0.31	0.45
19	110-62-3	Pentanal	ALD	13.60	58	44, 41	0.12	5.41
20	142-82-5	Heptane	HC-AL	13.77	71	100, 43, 70	0.17	0.43
21	107-98-2	1-Methoxy-2-propanol	ALOH	14.18	45	47, 75, 31	0.46	5.66
22	110-80-5	2-Ethoxyethanol	ALOH	14.99	59	31, 29	0.18	24.63
23	108-10-1	Methyl isobutyl ketone	KET	15.57	43	58, 100, 85	0.45	0.45
24	107-21-1	1,2-Ethanediol	ALOH	15.63	31	43, 62	0.34	107.00**
25	108-88-3	Toluene	HC-AR	16.44	91	92	1.00	0.31
26	57-55-6	1,2-Propanediol	ALOH	16.17	45	61, 43, 31	0.97	7.22
27	111-65-9	Octane	HC-AL	17.95	85	114, 71, 70	0.21	0.73
28	66-25-1	Hexanal	ALD	17.97	82	72, 56, 29	0.04	9.73
29	123-86-4	Butyl acetate	EST	18.71	43	56, 61, 73	0.45	0.81
30	98-01-1	Furfural	ALD	19.23	96	95, 36	0.15	24.00**
31	1678-91-7	Ethylcyclohexane	HC-CYC	19.37	83	112, 82, 55	0.59	1.72
32	100-41-4	Ethylbenzene	HC-AR	20.40	91	106	1.18	0.83
33	108-38-3	1,3-Dimethylbenzene	HC-AR	20.70	91	106	0.97	0.71
34	106-42-3	1,4-Dimethylbenzene	HC-AR	20.77	91	106	0.89	0.82
35	64-19-7	Acetic acid	MISC	12.42	60	43, 45	0.12	568.5
36	142-96-1	n-Butyl ether	MISC	21.35	57	87,56, 41	1.27	2.10
37	109-52-4	Pentanoic acid	MISC	24.18	60	73	0.85	871.6
38	95-47-6	1,2-Dimethylbenzene	HC-AR	21.67	91	106	0.92	0.75
39	100-42-5	Styrene	HC-AR	21.65	104	78, 103, 51	0.87	0.89
40	108-94-1	Cyclohexanone	KET	21.76	55	98, 69, 42	0.38	3.48
41	111-84-2	Nonane	HC-AL	21.97	85	128, 71, 57	0.18	0.44
42	111-71-7	Heptanal	ALD	22.12	81	70, 96	0.08	10.93
43	111-15-9	2-Ethoxyethyl acetate	EST	22.26	43	59, 72, 87	0.52	12.89

No.	CAS #	Compound	Class	RT [min]	Primary Ion	Secondary Ions	RR_C	MDL [ng]
44	111-76-2	2-Butoxy ethanol	ALOH	22.35	57	87, 41, 75	0.60	35.51
45	1678-92-8	Propylcyclohexane	HC-CYC	23.32	83	126, 82, 55	0.67	1.73
46	80-56-8	alpha-Pinene	TERP	23.31	93	136, 121	0.64	0.61
47	79-92-5	Camphene	TERP	24.08	93	121, 136	0.49	1.01
48	103-65-1	Propylbenzene	HC-AR	24.12	91	120	1.43	1.05
49	620-14-4	3-Ethyltoluene	HC-AR	24.35	105	120	1.38	0.81
50	100-52-7	Benzaldehyde	ALD	24.53	106	105, 77	0.77	2.90
51	622-96-8	4-Ethyltoluene	HC-AR	24.48	105	120	1.31	0.69
52	108-67-8	1,3,5-Trimethylbenzene	HC-AR	24.67	105	120	1.16	0.65
53	611-14-3	2-Ethyltoluene	HC-AR	25.01	105	120	1.40	0.73
54	127-91-3	beta-Pinene	TERP	25.04	93	136, 121	0.40	0.81
55	98-82-8	Isopropylbenzene	HC-AR	23.10	105	120	1.04	7.73
56	3777-69-3	2-Pentylfuran	MISC	25.64	81	138, 82	1.37	4.76
57	95-63-6	1,2,4-Trimethylbenzene	HC-AR	25.62	120	105	0.66	0.71
58	142-62-1	Hexanoic acid	MISC	26.95	60	73, 87	0.48	400.1
59	124-18-5	Decane	HC-AL	25.78	71	142, 85, 99	0.20	0.62
60	124-13-0	Octanal	ALD	26.02	84	110, 100	0.11	8.80
61	13466-78-9	3-Carene	TERP	26.30	93	136, 121	0.60	0.52
62	108-95-2	Phenol	ALOH	25.26	94	66, 39	0.74	10.90
63	106-46-7	1,4-Dichlorobenzene	CL	26.45	146	148, 111	0.87	0.69
64	526-73-8	1,2,3-Trimethylbenzene	HC-AR	26.63	105	120	1.22	0.80
65	104-76-7	2-Ethyl-1-hexanol	ALOH	26.87	70	83, 98, 112	0.15	47.40**
66	99-87-6	4-Isopropyltoluene	HC-AR	26.89	119	134	2.24	0.35
67	99-86-5	alpha-Terpinene	TERP	26.89	93	121, 136	0.22	1.02
68	138-86-3	Limonene	TERP	26.93	68	93, 136	0.36	0.61
69	1678-93-9	Butylcyclohexane	HC-CYC	27.19	83	140, 82, 55	0.87	1.72**
70	95-50-1	1,2-Dichlorobenzene	CL	27.13	146	148, 111	0.92	0.69
71	872-50-4	1-Methyl-2-pyrrolidinone	MISC	27.41	99	98	0.46	16.54
72	99-85-4	gamma-Terpinene	TERP	28.09	93	136, 121	0.27	4.53
73	91-17-8	Decahydronaphthalene	HC-CYC	28.24	138	96, 67, 82	0.73	0.95**
74	98-86-2	Acetophenone	KET	28.31	105	120, 77, 51	1.22	27.90**
75	1120-21-4	Undecane	HC-AL	29.37	57	156, 85	0.56	0.65
76	124-19-6	Nonanal	ALD	29.65	57	98, 82, 70	0.15	3.98
77	95-93-2	1,2,4,5-Tetramethylbenzene	HC-AR	30.03	119	134	1.43	0.83
78	112-34-5	2-(2-Butoxyethoxy)ethanol	ALOH	32.62	45	75, 57, 87	0.36	36.72
79	91-20-3	Naphthalene	HC-AR	32.59	128	102	2.31	0.57
80	112-40-3	Dodecane	HC-AL	32.71	57	170, 71, 85	0.59	0.68
81	112-31-2	Decanal	ALD	33.05	57	128, 112	0.10	3.57
82	629-50-5	Tridecane	HC-AL	35.83	57	184, 71	0.55	0.68
83	4994-16-5	4-Phenylcyclohexene	HC-AR	37.23	104	155, 91	2.22	0.93**
84	629-59-4	Tetradecane	HC-AL	38.70	57	198, 71, 85	0.49	0.62
85	629-62-9	Pentadecane	HC-AL	40.72	57	212, 71, 85	0.66	1.21
86	6846-50-0	TM-PD-DIB***	EST	42.26	71	43, 56, 159	0.11	3.78
87	544-76-3	Hexadecane	HC-AL	42.37	57	226, 71, 85	0.69	2.47

* Method Detection Limit (Product of the standard deviation for seven replicate analyses and 3.14 (student's "t" test value for 99% confidence)

** Estimated value.

***2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

Table 4. Target compounds concentration calculated using individual and toluene response factor for OSB 4 -24h sample.

No.	Compound	Conc. [ng/L]	Conc. [ng/L]
	Based on	Individual RF	Toluene RF
1	Acetone	5.16	0.91
2	2-Methylpentane	0.68	
3	3-Methylpentane	0.26	
4	Butanal	3.11	1.15
5	Hexane	0.71	
6	Benzene	0.49	
7	Pentanal	5.67	
8	Heptane	4.71	3.81
9	Methylcyclohexane	0.07	
10	Toluene	1.46	1.57
11	Octane	1.95	
12	Hexanal	19.11	5.63
13	Ethylbenzene	0.37	
14	1,3-Dimethylbenzene	1.44	1.76
15	1,4-Dimethylbenzene	1.04	1.40
16	Acetic acid	0.09	
17	Pentanoic acid	1.40	
18	1,2-Dimethylbenzene	1.29	1.89
19	Nonane	3.40	2.87
20	Heptanal	1.13	
21	alpha-Pinene	0.24	
22	Propylbenzene	0.10	
23	3-Ethyltoluene	0.09	
24	Benzaldehyde	0.44	
25	1,3,5-Trimethylbenzene	0.30	
26	2-Ethyltoluene	0.05	
27	beta-Pinene	0.05	
28	Isopropylbenzene	0.04	
29	2-Pentylfuran	8.90	12.19
30	1,2,4-Trimethylbenzene	0.15	
31	Hexanoic acid	1.34	
32	Decane	1.50	1.71
33	Octanal	0.71	
34	1,4-Dichlorobenzene	1.37	2.11
35	1,2,3-Trimethylbenzene	0.03	
36	4-Isopropyltoluene	0.01	
37	Limonene	0.08	
38	Acetophenone	0.11	
39	Undecane	0.54	
40	Nonanal	1.44	0.98
41	Naphthalene	0.03	
42	Dodecane	0.19	
43	Decanal	1.27	0.89
44	Tridecane	0.31	
45	Tetradecane	1.56	1.77
46	Pentadecane	0.62	0.96
47	Hexadecane	0.13	
	Sum of TC	75.12	41.61
	Sum of identified comp.		54.11
	TVOC		107.31

Table 5. Analytical accuracy measurements.

Name	**Standard**	**Source**	**Tube**	**Benzene [ng]**			**Toluene [ng]**			**1,3-Dimethylbenzene [ng]**		
				true	**found**	**AA***	**true**	**found**	**AA***	**true**	**found**	**AA***
CRM112	Certified Sorbed Standard	Community Bureau of Reference (BCR)	Tenax	1053	1180	**12%**	1125	1063	**6%**	1043	1116	**7%**
Cal. Mixture	Prepared in the Lab.	Aldrich Chemicals	cal tube	870	1069	**22%**	1188	1251	**5%**	975	1160	**19%**

AA* -Audit accuracy was defined as the relative difference between the measurement result and the nominal value of the audit compound.

Table 6. Audit accuracy* values for selected target compounds.

No.	Compound	True Value [ng]	Found Value I [ng]	Found Value II [ng]	Audit Accuracy** %
1	Methyl ethyl ketone	24.0	22.5	20.3	12
		60.1	59.3	45.0	17
		240.2	237.4	241.0	1
2	1-Butanol	24.0	29.0	20.8	18
		60.0	75.6	56.3	16
		240.0	278.9	277.6	15
3	Toluene	24.0	29.5	22.8	14
		60.0	67.2	57.5	8
		240.0	249.9	228.5	5
4	Hexanal	24.0	36.7	34.6	42
		60.1	87.4	80.5	35
		240.2	300.0	303.2	23
5	Butyl acetate	24.0	24.2	22.0	5
		60.1	60.6	61.7	2
		240.2	246.9	254.9	4
6	n-Butyl ether	24.0	24.1	21.3	6
		60.1	60.2	58.0	2
		240.2	243.1	226.9	4
7	1,2,4-Trimethylbenzene	24.0	23.6	21.6	6
		60.0	58.4	57.7	3
		239.8	250.6	233.3	4
8	Decane	24.0	24.5	23.8	1
		60.1	59.9	61.0	1
		240.4	249.2	243.6	2
9	Limonene	24.0	22.1	25.3	6
		60.1	54.4	60.3	5
		240.2	234.1	233.6	3
10	1,4-Dichlorobenzene	24.0	27.5	23.1	9
		60.0	68.2	59.7	7
		240.0	303.6	264.1	18

*Audit accuracy was defined as the relative difference between the measurement result and the nominal value of the audit compound.
** Average from two measurements

Table 7. List of target compounds individually calibrated in CMEIAQ-I, their retention time (RT), primary ion and response factor ratio against toluene (RR_C).

	CAS #	Compound	Class	RT [min]	Primary Ion	RR_C
1	67-63-0	2-Propanol	ALOH	4.14	45	0.94
2	75-65-0	2-Methyl-2-propanol	ALOH	4.50	59	0.85
3	107-83-5	2-Methylpentane	HC-AL	5.36	43	0.76
4	96-14-0	3-Methylpentane	HC-AL	5.68	57	0.68
5	123-72-8	Butanal	ALD	6.09	44	0.17
6	110-54-3	Hexane	HC-AL	6.31	56	0.39
7	78-93-3	Methl ethyl ketone	KET	6.38	43	1.24
8	141-78-6	Ethyl acetate	EST	6.85	43	1.17
9	71-43-2	Benzene	HC-AR	8.27	78	1.08
10	108-21-4	1-Methylethyl acetate	EST	8.60	43	1.23
11	71-36-3	1-Butanol	ALOH	8.97	56	0.56
12	109-86-4	2-Methoxyethanol	ALOH	9.06	45	1.15
13	79-01-6	Trichloroethylene	CL	9.75	130	0.20
14	110-62-3	Pentanal	ALD	9.83	58	0.21
15	142-82-5	Heptane	HC-AL	10.28	71	0.38
16	107-98-2	1-Methoxy-2-propanol	ALOH	8.99	45	1.01
17	108-10-1	Methyl isobutyl ketone	KET	11.60	43	1.16
18	108-88-3	Toluene	HC-AR	12.68	91	1.00
19	111-65-9	Octane	HC-AL	14.12	85	0.36
20	66-25-1	Hexanal	ALD	14.26	82	0.05
21	123-86-4	Butyl acetate	EST	15.09	43	0.97
22	98-01-1	Furfural	ALD	15.54	96	0.19
23	1678-91-7	Ethylcyclohexane	HC-CYC	15.45	83	0.65
24	100-41-4	Ethylbenzene	HC-AR	16.61	91	1.16
25	106-42-3	1,4-Ddimethylbenzene	HC-AR	16.96	91	0.96
26	108-38-3	1,3-Dimethylbenzene	HC-AR	16.96	91	0.96
27	142-96-1	n-Butyl ether	MISC	17.56	57	1.85
28	95-47-6	1,2-Dimethylbenzene	HC-AR	17.87	91	0.95
29	100-42-5	Styrene	HC-AR	18.00	104	0.79
30	108-94-1	Cyclohexanone	KET	17.85	55	0.55
31	111-84-2	Nonane	HC-AL	18.29	85	0.26
32	111-71-7	Heptanal	ALD	18.30	81	0.07
33	111-15-9	2-Ehoxyethyl acetate	EST	18.63	43	1.08
34	111-76-2	2-Butoxy ethanol	ALOH	18.48	57	1.13
35	1678-92-8	Propylcyclohexane	HC-CYC	19.39	83	0.76
36	80-56-8	alpha-Pinene	TERP	20.00	93	0.62
37	79-92-5	Camphene	TERP	20.56	93	0.52
38	103-65-1	Propylbenzene	HC-AR	20.28	91	1.43
39	100-52-7	Benzaldehyde	ALD	20.45	106	0.62
40	108-67-8	1,3,5-Trimethylbenzene	HC-AR	21.52	105	1.01
41	611-14-3	2-Ethyltoluene	HC-AR	21.59	105	1.30
42	127-91-3	beta-Pinene	TERP	21.63	93	0.34

	CAS #	Compound	Class	RT [min]	Primary Ion	RR_C
43	95-63-6	1,2,4-Trimethylbenzene	HC-AR	21.93	120	0.50
44	124-18-5	Decane	HC-AL	22.07	71	0.35
45	124-13-0	Octanal	ALD	22.18	84	0.13
46	13466-78-9	3-Carene	TERP	22.89	93	0.46
47	106-46-7	1,4-Dichlorobenzene	CL	22.64	146	0.53
48	104-76-7	2-Ethyl-1-hexanol	ALOH	23.18	70	0.22
49	99-87-6	4-Isopropyltoluene	HC-AR	23.39	119	1.55
50	99-86-5	alpha-Terpinene	TERP	22.89	93	0.32
51	138-86-3	Limonene	TERP	23.55	68	0.54
52	1678-93-9	Butylcyclohexane	HC-CYC	23.38	83	1.02
53	95-50-1	1,2-Dichlorobenzene	CL	23.17	146	0.48
54	99-85-4	gamma-Terpinene	TERP	24.62	93	0.44
55	91-17-8	Decahydronaphthalene	HC-CYC	24.22	138	0.46
56	98-86-2	Acetophenone	KET	24.40	105	0.75
57	1120-21-4	Undecane	HC-AL	25.50	57	1.00
58	124-19-6	Nonanal	ALD	25.76	57	0.33
59	91-20-3	Naphthalene	HC-AR	28.40	128	1.61
60	112-40-3	Dodecane	HC-AL	28.76	57	0.93
61	112-31-2	Decanal	ALD	29.04	57	0.21
62	629-50-5	Tridecane	HC-AL	32.32	57	1.13
63	31017-40-0	4-Phenylcyclohexene	HC-AR	33.18	104	1.38
64	629-59-4	Tetradecane	HC-AL	35.19	57	0.95
65	629-62-9	Pentadecane	HC-AL	37.68	57	0.88
66	6846-50-0	TM-PD-DIB*	EST	39.23	71	1.21
67	544-76-3	Hexadecane	HC-AL	39.55	57	0.62

*2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

Table 8. Target compounds analyzed by GC/MS in CMEIAQ-I, toluene TIC calibrated.

No.	CAS #	Compound	Class	RT [min]	Primary Ion	I/TIC
1	64-17-5	Ethanol	ALOH	4.09	45	0.56
2	67-64-1	Acetone	KET	4.41	58	0.22
3	71-23-8	1-Propanol	ALOH	5.52	59	0.18
4	75-09-2	Dichloromethane	CL	5.69	49	0.34
5	110-82-7	Cyclohexane	HC-CYC	8.21	84	0.16
6	110-80-5	2-Ethoxyethanol	ALOH	10.82	59	0.43
7	107-21-1	1,2-Ethanediol	ALOH	12.45	43	0.39
8	57-55-6	1,2-Propanediol	ALOH	12.37	45	0.74
9	64-19-7	Acetic acid	MISC	17.50	60	0.22
10	109-52-4	Pentanoic acid	MISC	17.90	60	0.38
11	620-14-4	3-Ethyltoluene	HC-AR	20.40	105	0.39
12	622-96-8	4-Ethyltoluene	HC-AR	21.49	105	0.41
13	98-82-8	Isopropylbenzene	HC-AR	19.39	105	0.35
14	3777-69-3	2-Pentylfuran	MISC	21.65	81	0.45
15	142-62-1	Hexanoic acid	MISC	22.10	60	0.29
16	108-95-2	Phenol	ALOH	22.50	94	0.35
17	526-73-8	1,2,3-Trimethylbenzene	HC-AR	22.80	105	0.36
18	872-50-4	1-Methyl-2-pyrrolidinone	MISC	23.52	99	0.21
19	95-93-2	1,2,4,5-Tetramethylbenzene	HC-AR	26.23	119	0.29
20	112-34-5	2-(2-Butoxyethoxy)ethanol	ALOH	28.47	45	0.24

Table 9. Target compounds analyzed by HPLC.

No.	CAS #	Compound	Class	RT [min]	MDL** [ng]
1	50-00-0	Formaldehyde*	ALD	9.95	0.03
2	75-07-0	Acetaldehyde*	ALD	11.79	0.02
3	107-02-8	Acrolein*	ALD	13.96	0.02
4	67-64-1	Acetone	KET	14.27	0.02
5	123-72-8	Butanal	ALD	19.09	0.05
6	100-52-7	Benzaldehyde	ALD	20.63	0.05
7	110-62-3	Pentanal	ALD	24.07	0.05
8	66-25-1	Hexanal	ALD	29.96	0.08

* Compounds quantified exclusively by HPLC
** Method Detection Limit (Product of the standard deviation for seven replicate analyses and 3.14 (student's "t" test value for 99% confidence).

Figure 1. Target compounds calibration procedure.