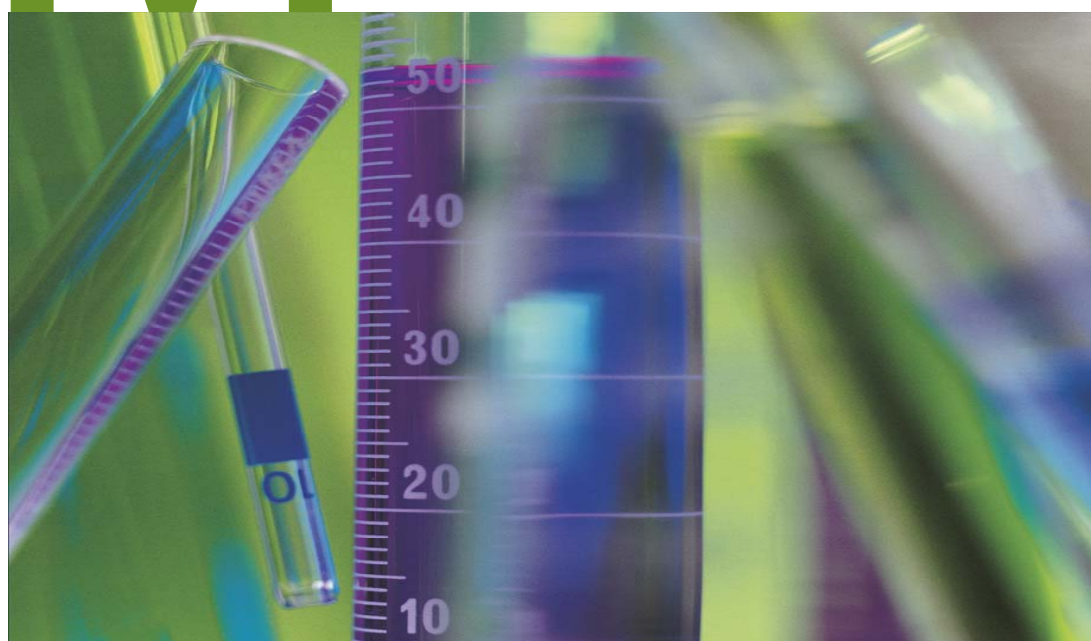


# M

## Analytical Method

**Determination of volatile organic compounds in the air by mass spectrometry**

**ANALYTICAL METHOD 369**



### **Applicability**

*This method is used for the determination of many volatile compounds in the air.*

### **Standard(s)<sup>1</sup>**

*TWAEV (time-weighted average exposure value): See Appendix I.*

*STEV (Short-term exposure value): See Appendix I.*

### **Sampling system**

*Glass tube, 7 cm x 6 mm O.D., containing two sections (100 mg/50 mg of activated charcoal).*

### **Recommended sampling flow rate and volume**

*TWAEV<sup>1</sup>: See Appendix II.*

*STEV<sup>1</sup>: See Appendix II.*

### **Analysis**

*Gas chromatography - mass spectrometry (GC-MS).*

### **Minimum reported value (MRV)**

*See Appendix III.*

### **Working range**

*See Appendix III.*

### **Reliability**

*See Appendix IV.*

### **Analytical uncertainty (CV<sub>A</sub>)**

*See Appendix VI.*



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en santé et en sécurité du travail,

2012

# Analytical Method

## Determination of volatile organic compounds in the air by mass spectrometry

ANALYTICAL METHOD 369

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This publication has been translated, only the original version shall prevail.

**IN CONFORMITY WITH THE IRSST'S POLICIES**

The results of the research work published  
in this document have been peer-reviewed.

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## Preamble

The aim of the [Act respecting occupational health and safety](#) in Québec is to eliminate, at the source, dangers to the health, safety and physical well-being of workers. Permissible exposure values (PEVs) for chemical substances have been established in Schedule I of the [Regulation respecting occupational health and safety](#) (ROHS). Section 44 of this regulation entitled "Methods" specifies that:

*" ...These dusts, gases, fumes, vapours and mists found in the workplace environment shall be sampled and analyzed to obtain an accuracy equivalent to that obtained by applying the [methods](#) described in the [Sampling Guide for Air Contaminants in the Workplace](#) published by the Institut de recherche Robert-Sauvé en santé et [en] sécurité du travail du Québec..."*

To achieve these objectives, analytical methods for quantifying the workers' degree of exposure are developed and written to establish appropriate means of control. In order to help health and safety professionals in workplaces, the IRSST publishes, periodically revises, and disseminates the [Sampling Guide for Air Contaminants in the Workplace](#) and the Laboratory Services and Expertise Department publishes contaminant analysis methods.

These methods must be used in combination with the following regulatory and normative references:

- ✓ *Act respecting occupational health and safety*. R.S.Q., chapter S-2.1. Éditeur officiel du Québec, (August 1, 2007).  
[http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=/S\\_2\\_1/S2\\_1\\_A.html](http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=/S_2_1/S2_1_A.html)
- ✓ *Regulation respecting occupational health and safety*. S-2.1, r.13, O.C. 885-2001. Éditeur officiel du Québec.  
[http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=3&file=/S\\_2\\_1/S2\\_1R13\\_A.HTM](http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=3&file=/S_2_1/S2_1R13_A.HTM)
- ✓ *Sampling Guide for Air Contaminants in the Workplace*. Operations Division, IRSST, T-015 Technical Guide, Montréal, Québec, (March 2005). <http://www.irsst.qc.ca/files/documents/PubIRSST/T-15.pdf>
- ✓ NIOSH, National Institute for Occupational Safety and Health.
- ✓ ISO Guide 30, Terms and definitions used in connection with reference materials, 2<sup>nd</sup> edition, 1992.
- ✓ ISO, International Vocabulary of Basic and General Terms in Metrology, 2<sup>nd</sup> edition, 1993.
- ✓ American Industrial Hygiene Association (AIHA), organization that certifies the IRSST laboratory in the field of workplace chemical and microbiological contaminant analysis.

## 1 WORKING RANGE

This method applies to the determination of different volatile organic compounds (VOCs) present in the air by gas chromatography – mass spectrometry (GC-MS). The tests for method development were performed on an Agilent GC-MS (GC6890N-MS5975).

Analytical method linearity was initially verified for several VOCs and is found in Appendix III. Linearity is defined in total mg as well as in mg/m<sup>3</sup> for the sampling volume recommended for each of the compounds. The coefficient of determination ( $r^2$ ) then obtained was greater than 0.990 for all the validated compounds for a total of 30 samples distributed over five concentrations in the studied range, which necessarily include a concentration equivalent to the TWAEV (See Appendix VI).

**Note 1** – This method does not allow detection and quantification of all VOCs. Only substances that can be collected with activated charcoal, having an affinity with the desorption solution, and giving a positive signal with the given instrumental conditions have the possibility of being detected by this method.

This document also presents the method's procedure, performance controls, and proposes a routine analytical sequence. These aspects, presented mainly in sections 7.5 and 7.7, are not essential for the method in order to obtain the performance parameters presented in section 9.

## 2 PRINCIPLE OF THE METHOD

According to the procedure described in the Sampling Guide for Air Contaminants<sup>1</sup>, a known volume of air is aspirated through a tube containing activated charcoal to adsorb different Volatile Organic Compounds (VOCs). The activated charcoal is then transferred to a vial, and a given volume of the desorption solution is added to desorb the VOCs collected on the adsorbent. The resulting solution is analyzed by gas chromatography-mass spectrometry. The concentration of these VOCs in the air is calculated by taking into account a calibration curve, the area of the peak, the relative response of the compounds compared to the internal standard with which they are associated, and the air volume sampled.

### 3 INTERFERENCES

An activated charcoal tube field blank is used to verify the contamination possibilities during the entire sampling and analytical process. In this way, contamination occurring when the tube is opened, transported, or during the analysis itself, will be detected.

To cause analytical interference, a substance must be collected by the activated charcoal, be desorbed by the desorption solution, have the same retention time under the chromatographic conditions used, and have a fragmentation pattern similar to another substance of interest. If this situation occurs, the chromatographic conditions can be modified to obtain a better separation of the peaks on the chromatogram. Some chromatographic interference may be impossible to resolve, causing an underestimation or overestimation of the result, depending on the case, and a note will be included in the report to this effect if a possibility of interference has been detected. It is important that the people in charge of sampling bring to the laboratory's attention any relevant aspect about the sampled environment in order to identify the interferences as efficiently as possible before the sample is processed.

### 4 MATERIAL

- ✓ Activated charcoal tubes, 20/40 mesh, 7 cm x 6 mm O.D., two sections (100 mg/50 mg), (OSHA Equivalent 07)<sup>2</sup>;
- ✓ Vials, 2 mL, with Teflon-coated septum;
- ✓ Microsyringes, 10 to 5000 µL;
- ✓ Automatic dispensers;
- ✓ Set of laboratory glassware (volumetric flasks with tight cap and septum, beakers, etc.);
- ✓ Shaker for the desorption step;
- ✓ Gas chromatograph with mass spectrometer equipped with an automatic injector and a split mode injection port;
- ✓ Chromatographic column, type DB1-MS or equivalent, 40 metres long with an internal diameter of 0.18 mm and a film thickness of 0.4 µm;
- ✓ Electronic integrator or any other effective method for measuring the areas of the peaks;
- ✓ Hydrogen supply (purity > 99.99%)



## 5 REAGENTS

The chemical compounds used must be ACS (American Chemical Society) grade or better, unless otherwise specified.

- ✓ Carbon disulfide (CS<sub>2</sub>) with low benzene content [CAS 75-15-0];
- ✓ 2-Phenoxyethanol [CAS 122-99-6];
- ✓ Methyl alcohol [CAS 67-56-1];
- ✓ Internal standard 1,2-dichloroethane-d4 [CAS 3855-82-1], chlorobenzene-d5 [CAS 3114-55-4], toluene-d8 [CAS 2037-26-5] and 1-bromo-4-fluorobenzene [CAS 460-00-4];
- ✓ Mixtures for the calibration of custom-made solutions of VOCs prepared in CS<sub>2</sub> (example presented in Appendix V; the concentrations may vary);
- ✓ Mixtures for quality control of custom-made solutions of VOCs prepared in CS<sub>2</sub> by another supplier or from another lot than the calibration solution (example presented in Appendix V; the concentrations may vary).

## 6 SAMPLING

The VOCs in the air are sampled with activated charcoal tubes using a sampling pump whose flow rate has been previously adjusted. It is recommended that the pump flow rate be verified after sampling in order to guarantee the integrity of the air volume sampled. For each series of samples, there must be a field blank tube. It undergoes the same procedures as the other samples, except for the sampling step.

The sampling parameters recommended for the different VOCs are described in Appendix II (as found in the Sampling Guide for Air Contaminants in the Workplace).

These parameters take into account the exposure standards, the sensitivity of the analytical method, and the capacity of the sampling system. To adapt to the environmental constraints, a different sampling volume could be used, but must take into account the working range and the parameters already mentioned. For more details on the preparation of the sampling material, calibration and the strategy used, refer to the IRSST's Sampling Guide<sup>1</sup>.

## 7 ANALYTICAL PROTOCOL

### 7.1 Preparation of solutions

- Internal standards and 2-phenoxyethanol solution;  
 Prepare a solution of 10 mg/mL of 1,2-dichloroethane-d4, chlorobenzene-d5, toluene-d8 and 1-bromo-4-fluorobenzene in benzene-free CS<sub>2</sub> containing 20% v/v of 2-phenoxyethanol.  
 Note 2: 2-Phenoxyethanol is added to the desorption solvent mixture to promote the efficiency of extraction of polar components. The final concentration of 2-phenoxyethanol in the desorption step is 2% v/v.
- Calibration solution for VOCs;  
 With the appropriate laboratory material, prepare 5 calibration solutions using the mixtures for the calibration of VOCs in CS<sub>2</sub> in order to cover the working range up to 100% of the standard. See Appendix III to determine the working range of the different components. The different solutions are added by means of microsyringes.
- Quality control solution for VOCs;  
 With the appropriate laboratory material, prepare the quality control solutions using the mixtures for quality control of VOCs in CS<sub>2</sub>. (See Appendix V for concentration suggestion.)  
 Note 3: The material used to prepare the solutions (examples: volumetric flasks and microsyringes) must be previously rinsed with methyl alcohol and air-dried.

### 7.2 Preparation of standards

Transfer 100 mg of activated charcoal from new tubes into a series of 2-mL vials (All of the 1<sup>st</sup> section (100 mg) or two 2<sup>nd</sup> sections (50 mg each)). Point 7.6 describes the procedure to be followed for processing the tubes.

Transfer 0.9 mL of each standard solution, by means of a microsyringe, as many times as necessary, into the 2-mL vials containing the activated charcoal. Add 0.1 mL of the internal standards and 2-phenoxyethanol solution. The calibration curve blank is prepared in the same way, except that benzene-free CS<sub>2</sub> replaces the standard solution.

Once transferred to the 2-mL vials, the standard solutions undergo the same procedure as the samples up to the analysis, meaning that they are placed on a mechanical shaker for 30 minutes to then be analyzed by gas chromatography-mass spectrometry.

### 7.3 Calibration of the mass spectrometer

Before beginning any new series of analyses, the mass spectrometer must be calibrated to adjust the signal obtained, the resolution of the different masses, as well as the accuracy of their weights using perfluorotributylamine (PFTBA). This process can be carried out automatically (Autotune). Check that the performances obtained comply with the criteria established by the manufacturer.

### 7.4 Calibration

The use of an internal standard reduces the impact of variation in the detector's response on the results obtained. With each series of analyses, the instrument's calibration is verified using a standard solution of concentration equivalent to the mid-point of the curve, and if the results obtained do not comply with the established criteria, the instrument is calibrated.

To do this, the standard solutions are analyzed at the start of the sequence in order to develop a calibration curve with the ratio of the concentrations of the analyzed substance/internal standard on the abscissa, and the ratio of the signal of the analyzed substance/internal standard (peak area) on the ordinate. The calibration curve is calculated by the acquisition software of the GC-MS, by linear regression, and is expressed in the form of the following equation:

$$S = m[\text{compound/internal standard}] + b \quad [1]$$

where

$S =$	Signal of compound/signal of internal standard (area under quantification ion)
$[\text{Compound/internal standard}] =$	concentration of the substance analyzed in the desorption solution, expressed in mg/mL
$m =$	slope of the calibration curve
$b =$	Ordinate at the origin

The calibration curve is considered to be valid when the coefficient of determination ( $r^2$ ) is  $\geq 0.990$ . Some calibration curve points can be eliminated to improve the performance (a minimum of 3 points must remain).

#### 7.4.1 Analytical conditions used in establishing this method

Generally, exposure to organic contaminants in the workplace is multiple in nature. The chromatographic conditions must consequently be adjusted to the nature and complexity of the sample. The conditions suggested for VOC analysis are:

Type of column	DB1-MS, 40 metres, 0.18 mm, 0.4 µm.
Type of injector	Split/Splitless
Split ratio	40:1
Injector temperature	210°C
Transfer line temperature	280°C
MS Quad temperature	150°C
Source temperature	230°C
Oven program	35°C (3 min.), 7.5°C/min., 115°C (0 min.), 15°C/min., 200°C (2 min.)
Injection volume	0.2 µL
Carrier gas	Hydrogen, constant flow (≈ 45 cm/sec)
Acquisition mode	Simultaneous SIM/SCAN
SCAN parameter	30 to 300 u.m.a
	Closing at ≈ 2.6 to 3.2 for CS <sub>2</sub>
	Closing at ≈ 17.0 for 2-phenoxyethanol

SIM parameters:

# Group	≈Start/ min.	Dwell*	Mass	1 <sup>st</sup> compound
1	0.0	10	31, 43, 45, 46, 49, 57, 58, 59, 72, 74, 84, 86	Ethyl alcohol
2	3.10	25	43, 57, 72	Methyl ethyl ketone
3	3.70	25	56, 57, 61, 70, 83, 85, 86, 88	Hexane
4	4.06	25	41, 42, 43, 65, 72, 74, 102	Isobutyl alcohol
5	4.60	15	41, 43, 56, 61, 69, 77, 78, 84, 86, 87	n-Butyl alcohol
6	5.56	25	95, 97, 130, 132	Trichloroethylene
7	6.04	25	61, 70, 71, 73, 100	n-Propyl acetate
8	6.53	25	58, 83, 85, 98, 100	Methyl isobutyl ketone
9	7.15	25	43, 56, 73, 87, 91, 92, 98, 100	sec-Butyl acetate
10	8.44	25	43, 56, 57, 85, 114, 129, 131, 164, 166	n-Butyl acetate
11	9.34	25	117, 119	Chlorobenzene-d5
12	9.98	25	58, 71, 78, 91, 103, 104, 106	Ethyl benzene
13	11.26	25	43, 55, 57, 85, 99, 128, 174, 176	n-Amyl acetate
14	11.75	25	91, 105, 120	Cumene

\*Dwell time in ms

Appendix VII presents the approximate retention times obtained using this acquisition method. In

addition, it presents the quantification and confirmation ions used to quantify and identify the different compounds.

## 7.5 Preparation of quality controls

Several types of controls are analyzed during the analytical sequence to check the calibration and variation in sensitivity. Each control must meet the criteria established for this control, and any exceedence or deviation must be documented and appropriate actions in the quality system must be undertaken.

**Continuing Calibration Verification (CCV).** CCVs are the same solutions as the calibration solutions, representing approximately the concentration at the mid-point of the calibration curve. They undergo all the same preparation and analytical steps as a sample. CCVs are analyzed sequentially at the start of the sequence and every 15 samples.

**Minimum Reported Value (MRV).** MRV controls are control solutions analyzed after the CCV control. These controls verify the response of the analytical method at the minimum reported value of the analytical method. They undergo all the same preparation and analytical steps as a sample.

The commercial solutions used to prepare these control solutions must ideally come from a different manufacturer than the one used for preparing the calibration solutions, or otherwise from a different lot from the same manufacturer, or as a last resort, from a different intermediate solution from the same manufacturer.

**Quality Control Sample (QCS).** These control solutions are a mixture of VOCs at a concentration corresponding to 25% to 100% of the TWAEV of the recommended sampling volume. They undergo all the same preparation and analytical steps as a sample. The results are used to estimate the accuracy of the analytical method.

The commercial solution used to prepare these control solutions must ideally come from a different manufacturer than the one used for preparing the calibration solutions, or otherwise from a different lot from the same manufacturer, or as a last resort, from a different intermediate solution from the same manufacturer.

**Initial Blank Verification (IBV).** The IBV is the desorption solution that will be used for the samples. This solution contains only the reagents and does not come in contact with the charcoal before the analysis. It is analyzed after the QCS and the results must be below the MRV.

**Laboratory Reagent Blank (LRB).** The LRB control is a sample that contains only the reagents. It undergoes all the same preparation and analytical steps as a sample. It is used to verify whether the preparation steps result in contamination of the samples. The results must be below the MRV.

## 7.6 Preparation of samples

Score the tube (sample) with a glass cutter 1 cm before the first section of activated charcoal. Wear safety glasses.

Break the tube. Remove the glass wool.

Transfer section 1 of activated charcoal into a 2-mL vial. Throw out the glass wool separating section 1 from section 2 and transfer the latter into another 2-mL vial.

The field blank tubes are prepared in the same way as the samples except that the two sections of activated charcoal are transferred to the same vial.

Add 0.9 mL of CS<sub>2</sub> and 0.1 mL of the internal standard and 2-phenoxyethanol solution using the appropriate equipment. Cap the vials and place them for 30 minutes on the shaker plate for the desorption step. The field blank and other controls undergo the same procedure as the samples.

## 7.7 Analysis

Following calibration of the mass spectrometer (section 7.3), the desorption solution is analyzed in order to verify whether the response of the internal standards corresponds to those obtained during the last calibration. The power of the electron multiplier is adjusted if necessary so that the internal standard's signal is approximately the same as during calibration of the instrument.

The standard solutions, laboratory blanks, quality control solutions, sample field blanks, as well as the samples (sections 1 and 2) are analyzed by gas chromatography.

In addition, the standard solution of concentration equivalent to the curve mid-point is reanalyzed at a regular frequency during the analysis as well as at the end of the sequence to ensure calibration maintenance.

The analyses are done according to the following proposed sequence:

1. CCV or calibration solutions (if necessary)
2. IBV
3. LRB
4. MRV
5. QCS
6. 9 injections
7. CCV
8. 15 injections
9. Repeat steps 7 and 8 (for a larger number of samples)
10. QCS

## 11. CCV

### 8 CALCULATIONS

#### 8.1 Identification of volatile organic compounds

Identification of the quantified compounds is confirmed by the presence of quantification and confirmation ions, and by the expected retention time determined using the calibration solutions. The ratio of the signal of the quantification ion to the signal of the confirmation ion of an unknown must be similar to the one established using a very concentrated standard by taking into account the acceptability criteria established by the laboratory.

#### 8.2 Calculation of the results

The concentration of the different volatile organic compounds in the air of each section of the tube is calculated automatically by the acquisition software in the following way:

$$[\text{compound}]_{\text{section1}} = [\text{compound}]_{\text{extract 1}} \times V_{\text{extract 1}} \quad [2]$$

$$[\text{compound}]_{\text{section2}} = [\text{compound}]_{\text{extract 2}} \times V_{\text{extract 2}} \quad [3]$$

where

$[\text{compound}]_{\text{extract 1 or 2}}$	=	concentration in mg/mL of a compound in the extract from section 1 or 2 obtained from equation [1]
$[\text{compound}]_{\text{section 1 or 2}}$	=	mass in mg of a compound collected in section 1 or 2 of the tube
$V_{\text{extract 1 or 2}}$	=	Volume of the extract in mL

The final concentration of the compound in the air reported in the analytical report is calculated in the following way:

$$[\text{compound}]_{\text{air}} = ([\text{compound}]_{\text{section 1}} + [\text{compound}]_{\text{section 2}}) \div V_{\text{sampled air}} \quad [4]$$

where

$[\text{compound}]_{\text{air}}$	=	Total concentration in mg/m <sup>3</sup> of the compound in the air
$V_{\text{sampled air}}$	=	Sampled volume of air in m <sup>3</sup>

For all the analytical results for the samples, the analytical report also contains the relative quantity, expressed as a percentage, of the compound contained in section 2. The percentage is calculated in the following way:

$$\% \text{compound section2} = ([\text{compound}]_{\text{section2}} / ([\text{compound}]_{\text{section1}} + [\text{compound}]_{\text{section2}})) \times 100 \quad [5]$$

Interpretation of the percentage of the analyzed substance present in section 2 of the tube is described in the *Sampling Guide for Air Contaminants in the Workplace*<sup>1</sup>.

The concentration of the analyzed substance in the extract must fall in the concentration interval given by the working range (point 1). If a sample is more concentrated than this range, it must be diluted in the desorption solvent and again be analyzed by taking the dilution into account in the calculations. If dilution is impossible, as in the case when too much time passes between the first analysis and its repeat, a note will be added to the analytical report about a possible underestimation of the result because it is outside the curve's calibration range.

The results of the samples are not corrected in relation to the field blanks (subtraction). The result for the latter is reported in total mass ( $\mu\text{g}$ ), and interpretation of all of the results is not done in the analytical report.

## 9 PERFORMANCE PARAMETERS

### 9.1 Limit of detection, limit of quantification, and minimum reported value (MRV)

The limits of detection and quantification of the analytical method were evaluated initially and are presented in Appendix IV. The minimum reported value (MRV) is the minimum quantity of contaminant that is quantified in the IRSST laboratories. It takes into account one or more of the following aspects: linearity of the method under the experimental conditions used, the recovery efficiency, and the relevance of the determination at low concentration levels. The MRVs of the different volatile organic compounds are presented in Appendix III.

### 9.2 Extraction efficiency

The average percentage of the extraction efficiency initially evaluated for the different volatile organic compounds is presented in Appendix VI. These percentages were calculated using at least 30 samples distributed over 5 to 7 concentration levels. For this evaluation, the samples consisted of solutions of volatile organic compounds in phase equilibrium on activated charcoal and subjected to the entire analytical procedure.

The average extraction efficiency for styrene does not meet the acceptability criteria ( $\geq 75\%$ ). The desorption solvent is less efficient at low concentration for this compound. The average extraction efficiency is 86% for concentrations equivalent to 50%, 100% and 200% of the TWAEV for a recommended sampling volume of 5 litres.

No correction is applied for the desorption efficiency. The calibration procedure (section 7.2) takes into account this factor because the calibration solution is in the presence of the adsorbing medium, thus recreating the desorption step.



### 9.3 Reliability

The analytical method's replicability and repeatability data are found in Appendix IV. These values were determined in the laboratory from solutions containing all of the compounds (4 concentration levels, 6 replicates per level) and in phase equilibrium on activated charcoal and subjected to the entire analytical procedure.

### 9.4 Accuracy

The analytical method's accuracy is verified with each series of analyses by means of a control solution containing the analyzed substance prepared in the laboratory. This solution is prepared from a standard from a manufacturer different from the one used for preparing the calibration solutions, or from a lot different from the one used for calibration. When a different lot is unavailable, a different technician prepares the control solution. The concentration of this solution is from 25% to 100% of the standard. The results obtained are compiled in the context of an intra-laboratory quality control follow-up.

The laboratory also participates in an inter-laboratory study recognized by the accreditation organization, which allows it to confirm the validity of this analytical method.

The accuracy obtained during the initial validation of the method is presented in Appendix IV. These values were determined by analysis of a reference material analyzed 10 times. These data originate from different days and/or analysts.

### 9.5 Measurement uncertainty

Analytical measurement uncertainty, presented in Appendix VI, equals the analytical coefficient of variation  $CV_A$  of the method. It was determined on 30 samples or more, distributed over 5 to 7 concentrations levels in the working range, from solutions of volatile organic compounds in phase equilibrium subjected to the entire analytical procedure. Assuming a coefficient of variation for the sampling  $CV_s$  equal to 5%, and for a two-sided probability threshold of 95%, the expanded measurement uncertainty for the entire determination and sampling is presented in Appendix VI.

## 10 REFERENCES

- 1 *Sampling Guide for Air Contaminants in the Workplace*. Operations Division, IRSST, T-015, Technical Guide, Montréal, Québec, (February 2005).  
<http://www.irsst.qc.ca/media/documents/PubIRSST/T-15.pdf>
- 2 United States Occupational Safety and Health Administration (OSHA), OSHA Analytical Methods Manual, Method 07 — Organic Vapors, OSHA, Salt Lake City, UT, United States (2000).  
<http://www.osha.gov/dts/sltc/methods/organic/org007/org007.html>
- 3 National Institute for Occupational Safety and Health (NIOSH), *NIOSH Manual of Analytical Methods, Methanol Method 2000*, Cincinnati, OH, USA, 1998.

**APPENDIX I**  
**Permissible exposure values for air contaminants (ROHS)**

Compound	CAS	TWAEV mg/m <sup>3</sup>	TWAEV ppm	STEV mg/m <sup>3</sup>	STEV ppm
Ethyl alcohol	64-17-5	1880	1000	-	-
Acetone	67-64-1	1180	500	2380	1000
Isopropyl alcohol	67-63-0	983	400	1230	500
Diethyl ether	60-29-7	1210	400	1520	500
n-Pentane	109-66-0	350	120	-	-
Methyl acetate	79-20-9	606	200	757	250
Methylene chloride	75-09-2	174	50	-	-
Methyl ethyl ketone	78-93-3	150	50	300	100
n-Hexane	110-54-3	176	50	-	-
Ethyl acetate	141-78-6	1440	400	-	-
Chloroform	67-66-3	24,4	5	-	-
Tetrahydrofuran	109-99-9	300	100	-	-
Isobutyl alcohol	78-83-1	152	50	-	-
n-Butyl alcohol	71-36-3	-	-	-	-
Benzene	71-43-2	3	1	15,5	5
Isopropyl acetate	108-21-4	1040	250	1290	310
Cyclohexane	110-82-7	1030	300	-	-
Methyl propyl ketone	107-87-9	530	150	-	-
Trichloroethylene	79-01-6	269	50	1070	200
n-Propyl acetate	109-60-4	835	200	1040	250
n-Heptane	142-82-5	1640	400	2050	500
Methyl isobutyl ketone	108-10-1	250	50	307	75
Methylcyclohexane	108-87-2	1610	400	-	-
sec-Butyl acetate	105-46-4	950	200	-	-
Toluene	108-88-3	188	50	-	-
Isobutyl acetate	110-19-0	713	150	-	-
Perchloroethylene	127-18-4	170	25	685	100
n-Butyl acetate	123-86-4	713	150	950	200
Octane	111-65-9	1400	300	1750	375
Ethyl benzene	100-41-4	434	100	543	125
m,p-Xylenes	108-38-3; 106-42-3	434	100	651	150
Methyl n-amyl ketone	110-43-0	233	50	-	-
Styrene	100-42-5	213	50	426	100
o-Xylene	95-47-6	434	100	651	150
n-Amyl acetate	628-63-7	266	50	532	100
Nonane	111-84-2	1050	200	-	-
Cumene	98-82-8	246	50	-	-
1,3,5-Trimethyl benzene	108-67-8	123	25	-	-
1,2,4-Trimethyl benzene	95-63-6	123	25	-	-
1,2,3-Trimethyl benzene	526-73-8	123	25	-	-

**APPENDIX II**  
**Recommended sampling volume and flow rate**

Compound	TWAEV		STEV	
	Volume (L)	Flow rate (L/min)	Volume (L)	Flow rate (L/min)
Ethyl alcohol	1	0.05	-	-
Acetone	2	0.2	1.5	0.2
Isopropyl alcohol	3	0.2	3	0.2
Diethyl ether	3	0.2	3	0.2
n-Pentane	4	0.2	-	-
Methyl acetate	7	0.2	3	0.2
Methylene chloride	3	0.2	-	-
Methyl ethyl ketone	10	0.2	3	0.2
n-Hexane	4	0.2	-	-
Ethyl acetate	6	0.2	-	-
Chloroform	15	0.2	-	-
Tetrahydrofuran	9	0.2	-	-
Isobutyl alcohol	10	0.2	-	-
n-Butyl alcohol	10	0.2	-	-
Benzene	12	0.2	3	0.2
Isopropyl acetate	10	0.2	3	0.2
Cyclohexane	3	0.2	-	-
Methyl propyl ketone	10	0.2	-	-
Trichloroethylene	10	0.2	3	0.2
n-Propyl acetate	10	0.2	3	0.2
n-Heptane	4	0.2	3	0.2
Methyl isobutyl ketone	10	0.2	3	0.2
Methylcyclohexane	4	0.2	-	-
sec-Butyl acetate	10	0.2	-	-
Toluene	5	0.2	-	-
Isobutyl acetate	10	0.2	-	-
Perchloroethylene	10	0.2	3	0.2
n-Butyl acetate	10	0.2	3	0.2
Octane	4	0.2	3	0.2
Ethyl benzene	10	0.2	3	0.2
m.p-Xylenes	12	0.2	3	0.2
Methyl n-amyl ketone	10	0.2	-	-
Styrene	5	0.2	3	0.2
o-Xylene	12	0.2	3	0.2
n-Amyl acetate	10	0.2	-	-
Nonane	4	0.2	-	-
Cumene	10	0.2	-	-
1,3,5-Trimethyl benzene	10	0.2	-	-
1,2,4-Trimethyl benzene	10	0.2	-	-
1,2,3-Trimethyl benzene	10	0.2	-	-

**APPENDIX III**  
**MRV and working range\* in µg and in mg/m<sup>3</sup> for the recommended sampling volume**

<b>Compound</b>	<b>MRV µg</b>	<b>MRV mg/m<sup>3</sup></b>	<b>Working range mg</b>	<b>Working range mg/m<sup>3</sup></b>
Ethyl alcohol	95	95	0.095 to 3.2	95 to 3200
Acetone	180	90	0.18 to 8.0	90 to 4000
Isopropyl alcohol	100	33	0.10 to 6.0	33 to 2000
Diethyl ether	72	24	0.072 to 6.9	24 to 2300
n-Pentane	21	5.2	0.021 to 2.5	5 to 625
Methyl acetate	215	31	0.215 to 9.0	31 to 1300
Methylene chloride	27	9.0	0.027 to 1.3	9 to 430
Methyl ethyl ketone	30	3.0	0.030 to 3.2	3 to 320
n-Hexane	15	3.8	0.015 to 1.3	3.8 to 325
Ethyl acetate	400	67	0.40 to 18	67 to 3000
Chloroform	22	1.5	0.022 to 1.4	1.5 to 93
Tetrahydrofuran	53	5.9	0.053 to 5.0	5.9 to 560
Isobutyl alcohol	75	7.5	0.075 to 3.2	7.5 to 320
n-Butyl alcohol	81	8.1	0.081 to 3.2	8.1 to 320
Benzene	2	0.17	0.002 to 0.090	0.17 to 7.5
Isopropyl acetate	475	48	0.475 to 21	48 to 2100
Cyclohexane	160	53	0.160 to 6.0	53 to 2000
Methyl propyl ketone	110	11	0.11 to 11	11 to 1100
Trichloroethylene	58	5.8	0.058 to 6.0	5.8 to 600
n-Propyl acetate	420	42	0.42 to 17	42 to 1700
n-Heptane	320	80	0.32 to 14	80 to 3500
Methyl isobutyl ketone	40	4	0.040 to 4.8	4 to 480
Methylcyclohexane	320	80	0.32 to 12	80 to 3000
sec-Butyl acetate	475	48	0.475 to 19	48 to 1900
Toluene	20	4	0.020 to 1.7	4 to 340
Isobutyl acetate	180	18	0.18 to 14	18 to 1400
Perchloroethylene	68	6.8	0.068 to 3.2	6.8 to 320
n-Butyl acetate	71	7.1	0.071 to 14	7.1 to 1400
Octane	290	72	0.29 to 11	72 to 2750
Ethyl benzene	43.3	4.3	0.043 to 2.7	4.3 to 270
m,p-Xylenes	100	8.4	0.10 to 10	8.4 to 830
Methyl n-amyl ketone	49	4.9	0.0049 to 5.0	4.9 to 500
Styrene	27	5.4	0.027 to 1.8	5.4 to 360
o-Xylene	100	8.4	0.10 to 5.0	8.4 to 420
n-Amyl acetate	265	27	0.265 to 11	27 to 1100
Nonane	210	53	0.053 to 8.8	53 to 2200
Cumene	86	8.6	0.086 to 5.2	8.6 to 520
1,3,5-Trimethyl benzene	62	6.2	0.062 to 1.7	6.2 to 170
1,2,4-Trimethyl benzene	62	6.2	0.062 to 1.7	6.2 to 170
1,2,3-Trimethyl benzene	62	6.2	0.062 to 1.7	6.2 to 170

\* The upper limit of the working range corresponds approximately to two times the TWAEV at the recommended sampling volume.

**APPENDIX IV**  
**Limit of detection (LDM) and quantification (LQM) of the method**  
**as well as the replicability, repeatability and accuracy\***

Compound	LDM in µg	LQM in µg	Replicability	Repeatability	Accuracy
Ethyl alcohol	15	50	1.3%	1.0%	94.5%
Acetone	15	50	0.49%	0.76%	98.7%
Isopropyl alcohol	3	10	2.0%	1.6%	97.7%
Diethyl ether	9	30	0.27%	2.1%	92.4%
n-Pentane	2	5	0.39%	0.40%	94.5%
Methyl acetate	20	70	0.24%	0.43%	99.0%
Methylene chloride	2	8	0.35%	0.53%	96.0%
Methyl ethyl ketone	3	10	0.55%	0.54%	99.9%
n-Hexane	2	7	0.58%	1.2%	94.9%
Ethyl acetate	9	30	0.26%	0.70%	92.0%
Chloroform	3	9	0.28%	1.4%	93.3%
Tetrahydrofuran	9	30	0.54%	2.4%	93.6%
Isobutyl alcohol	10	40	0.82%	0.69%	90.4%
n-butyl alcohol	10	40	0.68%	0.54%	95.7%
Benzene	0.5	1.6	1.0%	2.0%	97.3%
Isopropyl acetate	30	110	0.29%	1.9%	92.7%
Cyclohexane	8	30	0.24%	0.63%	98.2%
Methyl propyl ketone	8	30	0.27%	1.8%	95.9%
Trichloroethylene	3	10	0.25%	0.66%	97.4%
n-Propyl acetate	120	400	0.26%	2.0%	92.5%
n-Heptane	55	180	0.27%	1.4%	95.9%
Methyl isobutyl ketone	10	40	0.44%	2.1%	95.9%
Methylcyclohexane	9	30	0.25%	0.58%	94.1%
sec-Butyl acetate	70	240	0.27%	0.86%	94.0%
Toluene	1	2	0.19%	0.25%	94.8%
Isobutyl acetate	15	50	0.25%	0.94%	95.5%
Perchloroethylene	4	15	0.26%	0.34%	97.6%
n-Butyl acetate	9	30	0.26%	0.48%	91.1%
Octane	20	60	0.27%	0.34%	99.9%
Ethyl benzene	2	6	0.21%	0.28%	93.8%
m,p-Xylenes	5	6	0.17%	0.32%	95.5%
Methyl n-amyl ketone	10	30	0.35%	0.70%	92.0%
Styrene	6	20	0.55%	2.3%	98.6%
o-Xylene	2	6	0.15%	0.20%	95.4%
n-Amyl acetate	60	200	0.37%	1.2%	91.6%
Nonane	20	60	0.35%	0.38%	93.6%
Cumene	3	12	0.28%	0.20%	98.1%
1,3,5-Trimethyl benzene	3	9	0.31%	0.36%	98.4%
1,2,4-Trimethyl benzene	3	9	0.22%	0.31%	97.3%
1,2,3-Trimethyl benzene	2	7	0.24%	0.32%	95.7%

\* These validation data were obtained following the quantification in scan mode of the chromatograms.

**APPENDIX V**  
**Example of concentrations of standard solutions and quality control solutions  
 custom-made by a manufacturer**

Compound	Stock solution standard # 1* (mg/mL)	Stock solution standard # 2* (mg/mL)	Stock solution Quality control # 1** (mg/mL)	Stock solution Quality control # 2** (mg/mL)
Ethyl alcohol	3.2		1.6	
Acetone	8		3.6	
Isopropyl alcohol		6		0.6
Diethyl ether		6.9		1.4
n-Pentane	2.5		0.4	
Methyl acetate	9		4.2	
Methylene chloride	1.3		0.5	
Methyl ethyl ketone	3.2		0.6	
n-Hexane	1.3		0.3	
Ethyl acetate	18		1.6	
Chloroform		1.4		0.5
Tetrahydrofuran		5		1.1
Isobutyl alcohol	3.2		1.4	
n-Butyl alcohol	3.2		1.6	
Benzene	0.09		0.05	
Isopropyl acetate		21		8.5
Cyclohexane	6		3.2	
Methyl propyl ketone		11		2.2
Trichloroethylene	6		1.2	
n-Propyl acetate	17		8.4	
n-Heptane	14		6.2	
Methyl isobutyl ketone	4.8		0.8	
Methylcyclohexane		12		6.2
sec-Butyl acetate	19		8.7	
Toluene	1.7		0.2	
Isobutyl acetate	14		1.4	
Perchloroethylene	3.2		1.3	
n-Butyl acetate		14		1.4
Octane	11		5.5	
Ethyl benzene	2.7		0.34	
m,p-Xylenes	10		0.9	
Methyl n-amyl ketone		5		1
Styrene	1.8		0.45	
o-Xylene	5		0.5	
n-Amyl acetate	11		5.3	
Nonane	8.8		3.5	
Cumene	5.2		1.7	
1,3,5-Trimethyl benzene	1.7		0.8	
1,2,4-Trimethyl benzene	1.7		0.8	
1,2,3-Trimethyl benzene	1.7		0.8	

\* The concentrations of the standard solutions correspond to approximately 200% of the TWAEV at the recommended volume.

\*\* The concentrations of the quality control solutions are between 25 and 100% of the TWAEV at the recommended volume.

**APPENDIX VI**  
**Linearity, analytical uncertainty (CV<sub>a</sub>), expanded measurement uncertainty and % average extraction efficiency\***

Compound	Linearity data Coefficient of determination	Analytical uncertainty (CV <sub>a</sub> )	Expanded measurement uncertainty	% average of extraction efficiency
Ethyl alcohol	0.996	3.4%	12%	94.1%
Acetone	1.00	1.3%	10%	98.2%
Isopropyl alcohol	0.999	4.8%	14%	98.6%
Diethyl ether	0.997	0.67%	9.9%	103%
n-Pentane	0.999	1.5%	10%	104%
Methyl acetate	0.997	0.55%	9.9%	101%
Methylene chloride	1.00	0.96%	10%	102%
Methyl ethyl ketone	1.00	1.7%	10%	101%
n-Hexane	0.991	1.8%	10%	103%
Ethyl acetate	0.994	1.4%	10%	103%
Chloroform	0.999	0.93%	10%	100%
Tetrahydrofuran	0.998	1.9%	10%	101%
Isobutyl alcohol	1.00	3.6%	12%	101%
n-butyl alcohol	1.00	2.1%	11%	99.2%
Benzene	1.00	3.6%	12%	99.3%
Isopropyl acetate	0.994	0.74%	9.9%	102%
Cyclohexane	0.996	0.56%	9.9%	104%
Methyl propyl ketone	0.998	0.79%	9.9%	101%
Trichloroethylene	0.999	0.78%	9.9%	101%
n-Propyl acetate	0.995	0.91%	10%	101%
n-Heptane	0.993	0.71%	9.9%	104%
Methyl isobutyl ketone	1.00	1.3%	10%	101%
Methylcyclohexane	0.991	0.54%	9.9%	104%
sec-Butyl acetate	0.996	1.1%	10%	103%
Toluene	1.00	0.56%	9.9%	102%
Isobutyl acetate	0.995	0.69%	9.9%	104%
Perchloroethylene	1.00	0.75%	9.9%	101%
n-Butyl acetate	0.996	1.1%	10%	104%
Octane	0.999	0.63%	9.9%	104%
Ethyl benzene	1.00	0.53%	9.9%	101%
m,p-Xylenes	0.998	0.38%	9.8%	101%
Methyl n-amyl ketone	1.00	1.1%	10%	101%
Styrene	1.00	3.0%	11%	64.1%
o-Xylene	0.999	0.43%	9.8%	101%
n-Amyl acetate	0.999	1.4%	10%	104%
Nonane	0.994	0.76%	9.9%	104%
Cumene	0.997	0.61%	9.9%	103%
1,3,5-Trimethyl benzene	1.00	0.74%	9.9%	101%
1,2,4-Trimethyl benzene	1.00	0.53%	9.9%	98.6%
1,2,3-Trimethyl benzene	1.00	0.62%	9.9%	96.2%

\* These validation data were obtained following the quantification of the chromatograms in scan mode.



**APPENDIX VII**  
**Retention time and quantification ion of VOCs**

Compound	Approx. retention time (min)	Quantification ion (m/z)	Confirmation ion (m/z)
Ethyl alcohol	2.07	31	45
Acetone	2.25	58	43
Isopropyl alcohol	2.38	45	43
Diethyl ether	2.47	59	74
n-Pentane	2.47	43	57
Methyl acetate	2.62	43	74
Methylene chloride	2.63	84	86
Methyl ethyl ketone	3.43	43	72
n-Hexane	3.88	86**	56
Ethyl acetate	3.88	88**	70
Chloroform	3.90	83	85
Tetrahydrofuran	4.20	42	72
Isobutyl alcohol	4.19	43	41
1,2-Dichloroethane-d4*	4.34	65	102
n-Butyl alcohol	4.98	56	41
Benzene	4.96	78	77
Isopropyl acetate	4.98	61	87
Cyclohexane	5.20	84	56
Methyl propyl ketone	5.37	43	86
Trichloroethylene	5.89	130	132
n-Propyl acetate	6.21	61	73
n-Heptane	6.24	100**	71
Methyl isobutyl ketone	6.79	100	85
Methylcyclohexane	6.80	83**	98
sec-Butyl acetate	7.48	43	87
toluene-d8*	7.60	98	100
Toluene	7.70	91	92
Isobutyl acetate	7.83	43	56
Perchloroethylene	8.95	166	164
n-Butyl acetate	8.88	43	56
Octane	8.97	85	114
Chlorobenzene-d5*	9.68	117	119
Ethyl benzene	10.25	91	106
m,p-Xylenes	10.51	91	106
Methyl n-amyl ketone	10.77	58	71
Styrene	10.93	104	103
o-Xylene	10.07	91	106
n-Amyl acetate	11.47	43	55
Nonane	11.60	57	85
Bromofluorobenzene*	11.66	174	176
Cumene	11.92	105	120
1,3,5-Trimethyl benzene	13.00	105	120
1,2,4-Trimethyl benzene	13.60	105	120
1,2,3-Trimethyl benzene	14.23	105	120

\* Internal standard, \*\* Secondary ion (chromatographic interference present for the main ion)