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**Reference method for the analysis
of 2-butoxyethanol (2-BE) and other glycol ethers (GEs)
in selected products (automotive and household
cleaners, paints, paint strippers and solvents)**

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Canada

Reader's comments

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1 INTRODUCTION

This analytical method was designed to support the 2-Butoxyethanol Regulations that were published in the Canada Gazette, Part II, on December 27, 2006, governing the concentration of 2-butoxyethanol (2-BE) in products set out in column 1 of Schedule 1 designed for indoor use. The method focuses on the measurement of 2-butoxyethanol (2-BE) and other common glycol ethers in indoor-use products, mainly household cleaners, paints, paint strippers and solvents, at the percentage levels specified by these regulations. This report provides detailed information, including sample preparation, the use of gas chromatography–mass spectrometry and isotope dilution techniques (carbon-13 and deuterium-(d-) labelled surrogates and standards) for detection and quantification, in addition to the quality assurance required to achieve reliable results.

The method is written in a performance-based format. Mandatory procedures, which are printed in bold type and underlined, must be followed. Procedures that are not highlighted in bold type and underlined may be modified by the user. There is a prerequisite to validate the analytical performance of the method to be used before the samples are processed.

Application of the reference method for compliance testing requires strict adherence to all mandatory procedures in this method. Throughout this report, such mandatory procedures are identified by bold type and underlining. Deviation from the mandatory procedures of this method may invalidate the test results and, therefore, any deviation must be approved in writing by Environment Canada before testing. If deviations are made without prior approval, the validity of the test results shall be determined by Environment Canada on a case-by-case basis.

2 ABBREVIATIONS

Chemicals

$^{13}\text{C}_2\text{-BE}$	2-butoxyethanol- $^{13}\text{C}_2$
2-BE	2- butoxyethanol (ethylene glycol butyl ether)
2-EE	2-ethoxyethanol (ethylene glycol ethyl ether)
2-HE	2-hexoxyethanol
2-ME	2- methoxyethanol (ethylene glycol methyl ether)
BEE	2-(2-butoxyethoxy)ethanol (diethylene glycol dimethyl ether)
CH_3OH	methanol
CH_2Cl_2	dichloromethane
$\text{d}_7\text{-ME}$	2-methoxyethanol- d_7
DCM	dichloromethane
DPGME	dipropylene glycol methyl ether
EEE	2-(2-ethoxyethoxy)ethanol (diethylene glycol ethyl ether)
HEE	2-(2-hexoxyethoxy)ethanol
MEE	2-(2-methoxyethoxy)ethanol (diethylene glycol methyl ether)
PE	2-phenoxyethanol
PFTBA	perfluorotributylamine (MS tuning and calibration compound)
PGBE	propylene glycol butyl ether
PGME	propylene glycol methyl ether
PGPE	propylene glycol propyl ether
PTFE	polytetrafluoroethylene
TPGME	tripropylene glycol methyl ether

Other terms

CEPA 1999	<i>Canadian Environmental Protection Act, 1999</i>
DCC	daily calibration check
DIG	distilled in glass
EI	electron impact (ionization)
FS	full scan
GC	gas chromatography
GC–MS	gas chromatography–mass spectrometry
ID	isotope dilution
IDL	instrument detection limit
IS	internal standard
LOQ	level of quantification
MDL	method detection limit
MS	mass spectrometer
MSD	mass selective detector
MV	mean value (arithmetic mean)
mL	millilitre, 10^{-3} litre
m/z	mass/charge ion ratio
μg	microgram (10^{-6} gram)
ng	nanogram (10^{-9} gram)
pg	picogram (10^{-12} gram)
ppm	part per million (10^{-6})
RS	recovery standard
RSD	relative standard deviation (also known as “coefficient of variation”)
RRF	relative response factor
$\overline{\text{RRF}}$	average relative response factor
RRF_{DCC}	relative response factor of daily calibration check standard
SA	spike amount (amount of analyte added to a sample)
SD	sample standard deviation
SIM	selective ion monitoring
SPE	solid phase extraction
v/v	volume/volume ratio
w/w	weight/weight ratio

3 SCOPE AND APPLICATION

The analytical methodology described in this method is applicable to the determination of 2-butoxyethanol (2-BE) in household cleaners, paints, paint strippers and solvents, at the level specified by the *Canadian Environmental Protection Act, 1999* (CEPA 1999) *2-Butoxyethanol Regulations* described in Part II of the *Canada Gazette*, Vol. 140, No. 26, 2006 (Table 1). In addition, the method can be used to analyze other common glycol ethers listed in Table 2. This method is suitable for this purpose.

4 SUMMARY OF THE METHOD

Sample preparation differs depending on the sample matrix. Different techniques are proposed for liquid (Section 4.1) and aerosol (Section 4.2) matrices. The same dilution step (Section 4.3) is used for both types of matrices.

4.1 Liquid samples: a small (0.5 mL to 1 mL) sample of the product to be analyzed is withdrawn from the sample container, weighed and then spiked with $^{13}\text{C}_2$ -BE-labelled surrogate to achieve a surrogate concentration of 1000 ppm. The sample is then mixed and left to stabilize for about 1 hr.

4.2 Aerosol samples: a small (100 mg to 500 mg) sample is injected through a septum into a sealed 20-mL volume vial filled with 4000 mg (~ 5 mL) of methanol. After the sample/methanol weight ratio is established, the sample is spiked with a $^{13}\text{C}_2$ -labelled surrogate to reach a concentration that, after final dilution, will be the same as the concentration in the calibration standard (1 ppm). For example, a sample of 100 mg is added to 3900 mg of methanol, resulting in a sample/methanol ratio of 1/40. In this case, 100 μg of $^{13}\text{C}_2$ -BE needs to be added so that the concentration after final dilution (Section 4.3) is 1 ppm.

4.3 Final dilution: a small subsample (5 μL to 10 μL) of spiked sample is withdrawn and mixed with methanol to achieve a final 1:1000 dilution and is then spiked with a known amount of recovery standard (d_7 -ME). The sample or a portion of it is then transferred to a Whatman Mini-UniPrep Syringeless Filter (0.4 mL, 0.2 μm pore size) and analyzed using gas chromatography–mass spectrometry (GC–MS) in electron impact (EI) ionization mode. Combined full scan/selective ion monitoring (FS/SIM) acquisition is recommended for best target compound identification (FS) and quantification results (SIM).

Note: Prior to concentration calculations, abundances of target analytes need to be corrected for instrument drift and sample losses using the appropriate internal standard (IS) and surrogate isotope dilution (ID) correction procedures. The final results will be automatically corrected for instrument instability and surrogate recovery.

To ensure that the glycol ether concentrations are reported as required by the Regulations (e.g. percentage (w/w)), **all steps in sample preparation (sections 10.1 and 10.2) must be gravimetric.** The volumes proposed here are for the sake of procedural simplicity; all calculations are based on the weight of the sample.

5 CONTAMINATION AND INTERFERENCES

Sources of interference will include, but not be limited to impurities in the standards, surrogates, solvents or glassware, high levels of background in the sample matrix and cross-contamination. Syringes should be thoroughly rinsed with solvents (distilled water and methanol) immediately after use. All glassware should be rinsed with solvents soon after use and then be washed with a detergent solution followed by solvent rinsing to remove most of the contaminants (Section 8.4). Use of a vacuum oven is recommended for drying glassware before subsequent use.

Depending on the nature of the sample matrix, interferences from samples will vary from source to source. Interferences may be present at a magnitude equal to or higher than that of the analyte concentration and therefore must be eliminated or reduced in order to ensure reliable quantification of the target analytes. The

procedure described in this method can remove some of the potential interferences but not all. It is always possible to come across sample matrices with interferences so high that they mask the response of an analyte. If this happens, a matrix specific cleanup procedure must be applied.

Ion interference must be taken into consideration when selecting monitoring ions in order to eliminate or minimize ion contributions from other target analytes. For example, the highest intensity ions in native 2-BE and its $^{13}\text{C}_2$ -BE surrogate are both of mass/charge ion ratio (m/z) = 57 and cannot be chosen as the monitoring ions due to their overlapping retention times and significant ion contribution. In such cases, the lower intensity ions that have the least ion contribution should be chosen instead of highest intensity ones.

Interferences may also arise from the use of surrogate standards containing native analytes as impurities. Surrogate standards must be assessed prior to use in sample processing to account for native contribution. Analyte concentrations originating from the surrogate standards must be subtracted from all processed samples.

6 SAFETY

All analytical work, including the preparation, handling and storage of all samples, must be carried out in an adequately equipped, ventilated laboratory.

Personnel in the laboratory should wear protective clothing consisting of safety glasses, a lab coat and disposable gloves as a minimum. The appropriate requirements of the applicable safety code must be followed.

Special care should be exercised when handling aerosol samples. Aerosol containers are under pressure and may quickly discharge a relatively large volume of product if handled improperly or carelessly. Only a small amount of aerosol sample is needed to be analyzed (Section 10.2). Injecting a larger volume of aerosol into a septum-sealed container should be avoided. Over-pressurizing the sample will result in sample loss, which not only invalidates the mass calculations and accuracy of the analysis, but may also result in sample ejection through a pierced septum seal, causing an unnecessary hazard for the operator.

Only experienced and trained personnel who are fully aware of the hazards associated with all the chemicals pertaining to sample processing should be involved in these analyses.

7 DEFINITIONS

- 7.1 Calibration standards:** standards containing the surrogate, recovery standard and target compound at different concentrations covering the full working range of the instrument. Calibration standards are used to calculate the average relative response factor(s) in the initial calibration.
- 7.2 Calibration check standard:** a calibration standard at a concentration near the midpoint of the calibrating concentration range. This standard is used to verify the state of the initial calibration.
- 7.3 Surrogate:** a compound that is expected to perform similarly to the compounds being analyzed. The surrogate is not naturally found in the environment (stable isotope labelling) and therefore can be used to monitor the recovery efficiency of the analytical processes used in the method. The surrogate is added to the samples in a precisely known amount at the beginning of sample preparation.
- 7.4 Recovery standard:** a compound added to the sample in a precisely known amount just prior to instrumental analysis. It is used as a reference for monitoring system performance and stability and for calculating surrogate recovery. Preferably, it should be similar to the compound being analyzed (stable isotope labelling) but different from the surrogate.

- 7.5 Solvent blank:** a solvent blank consists of the solvent used during sample preparation spiked with an internal standard. This blank is processed to demonstrate that any solvents and glassware used for sample preparation are free from compounds that could interfere with the analysis.
- 7.6 Method blank:** a method blank consists of a solvent used for sample dilution spiked with surrogate and processed through all preparation steps. A method blank is processed to demonstrate freedom from cross-contamination and the absence of other compounds that could interfere with the analysis of the target analytes.
- 7.7 Control sample:** a control sample consists of sample solvent of the highest solvent grade spiked with a known amount of native and surrogate analytes. It is processed to assess ongoing precision and accuracy.
- 7.8 Duplicates:** two separate aliquots of a sample processed to show repeatability of the sample preparation and analysis procedures (precision).

8 APPARATUS, REAGENTS AND SUPPLIES

8.1 Equipment and supplies

- 8.1.1 Gas chromatograph–mass spectrometer system (see Section 11 for details).
- 8.1.2 Electronic balance: accurate to 0.1 mg or better.
- 8.1.3 Pipettes: electronic or mechanical pipettes with capacities from 100 μL to 1000 μL , pipette tips from 100 μL to 1000 μL capacity.
- 8.1.4 Chromatographic syringes: 5 μL , 10 μL and 100 μL for sample injection and standard preparation.

8.2 Glassware

- 8.2.1 Volumetric flask: 5 mL, 10 mL and 15 mL.
- 8.2.2 Pasteur pipettes: 22 cm, disposable, glass.
- 8.2.3 Vials: various capacities from 3 mL to 20 mL, clear and amber glass, screw cap with Teflon-faced septum for standard and sample preparation.
- 8.2.4 Autosampler vials: Whatman Mini-UniPrep Syringeless Filters 0.45 μm pore size GMF or 0.2 μm PTFE, 1.5 mL standard glass vials, 0.2 mL glass insert vials of standard size.

8.3 Reagents and materials

- 8.3.1 **Standards:** 2-BE, 2-ME, 2-EE, 2-HE, HEE, BEE, EEE, MEE, DPGME, PE, PGBE, PGME, PGPE, TPGME, commercially available from several suppliers, with purity 98% or better. Isotopically labelled surrogates and standards ($^{13}\text{C}_2$ -BE, d_7 -ME) available from CDN Isotopes and may be available from other ISO 9001-registered suppliers.
- 8.3.2 **Standard storage:** All standard solutions must be sealed and refrigerated at $\leq 4^\circ\text{C}$ when not in use. Prior to use, standard solutions should be allowed to warm up to ambient temperature.

- 8.3.3 **Standard preparation:** Whenever possible, standards should be prepared from stock solutions purchased from ISO 9001-certified, reputable suppliers. When solutions are not available, the standards need to be prepared gravimetrically from pure compounds (at 98% purity or better) purchased from certified suppliers. Prior to use, standards identity **must be** confirmed by gas chromatography–mass spectrometry (GC–MS) analysis. Newly acquired or prepared standards should be verified by comparison with the previously used standard solution.

The following applies to the preparation of all standard stock solutions and secondary dilution standard mixtures (target analyte, surrogates and recovery standard):

- 8.3.3.1 **Stock solutions:** Stock solutions are prepared from pure standard materials (98% purity or better). The basic physical properties of selected glycol ethers are listed in Table 3 and can aid in solution preparation. Each compound is allowed to equilibrate to room temperature and is then transferred quantitatively into a pre-weighed volumetric flask. After each transfer, the exact amount of added compound is determined gravimetrically. After all transfers are completed, solvent is added to the graduation mark. The stock solution is mixed and allowed to equilibrate for a few minutes before being transferred to amber vials with Teflon-coated septum screw caps for longer storage. During the entire preparation process, care must be taken to minimize solvent loss through evaporation. Volumetric flasks should be kept closed all the times, except for the short moment when a new compound is added. The weight of the flask should be checked before and after each transfer. The preparation of the stock solution should be completed without any breaks or delays. Methanol is recommended as the stock solution solvent for glycol ethers.
- 8.3.3.2 **Standard mixtures:** Standard mixtures are prepared from stock solutions by combining a known volume of each stock solution and adjusting the final volume with a solvent accordingly. Each mixture is prepared in the same solvent that was used in the stock solution, with a final volume typically ranging from 10 mL to 20 mL. The vial is then capped and the standard solution is mixed thoroughly by shaking for at least 1 min to ensure homogeneity prior to use.
- 8.3.3.3 **Calibration standards:** Calibration standards are prepared from standard mixtures and/or stock solutions by combining the appropriate volumes of the surrogate and native standards solutions with solvent to the final concentration required. Calibration standards are prepared in clean vials at a typical volume of 1 mL to 10 mL. The vial is then capped and the standard solution is mixed thoroughly to ensure homogeneity prior to use. Calibration check standards should be prepared daily to verify the calibration curve. To obtain maximum accuracy and precision, it is recommended that the ratio of the response of the recovery standard and the surrogate be close to 1.
- 8.3.4 **Solvents:** All solvents should be of the highest purity, distilled-in-glass grade or better. Those required include methanol and/or dichloromethane.
- 8.3.5 **Gases:** High-purity grade pressurized nitrogen and helium.

8.4 Glassware preparation

All reusable glassware must be scrupulously cleaned as soon as possible after use. Glassware is sequentially rinsed with the last solvent contained in that glassware. This is followed by washing in a dishwasher using hot detergent solution and sequential rinsing with hot water, deionized water and 3 portions measuring 5 mL each of acetone and hexane. Severely contaminated glassware could be soaked overnight or treated in an ultrasonic bath with detergent. Care must be taken not to scratch the inner surface of the glassware if a brush is used. Glassware is either air-dried or dried in an oven and stored in a contaminant-free area.

9 PERFORMANCE VALIDATION

9.1 Precision and accuracy: Before sample analysis, the laboratory must demonstrate the ability to achieve acceptable precision and accuracy by validating the analytical performance as follows: Three spiked matrix samples similar to the samples being analyzed must be prepared, processed and analyzed according to the procedures used for actual samples. Each of these validation samples must be fortified as follows:

9.1.1 The amount of target analyte spiked must be close to the regulated limit or at an amount between the low end to the midpoint of the concentration range of the calibration standards used (Table 5).

9.2 Surrogate recovery: The labelled surrogate recovery for each sample must be within 40 to 130%. The target analyte recovery for each of the 3 samples must be within the range of 75 to 120% of the actual value.

9.3 Performance validation test: No samples shall be processed until the performance validation test yields acceptable results. This test should be repeated whenever extraction or cleanup procedures are modified, whenever the analyst has been changed, or if the performance validation test has not been conducted in the preceding 6-month period.

9.4 Control samples: The values obtained from control samples may be used instead of repeating the performance validation tests every 6 months if the following conditions are met:

9.4.1 No fewer than 3 control samples have been processed in the last 6 months.

9.4.2 Analyte recovery: The mean recovery corrected analyte value of all control samples within the last 6 months is within 75 to 120% of the actual value.

9.4.3 Mean surrogate recovery: The mean surrogate recovery of all control samples within the last 6 months is within 75 to 120% of the actual value.

10 SAMPLE PREPARATION PROCEDURES

10.1 Liquid samples

10.1.1 Transfer a known amount of sample (0.5 to 1 g) to a 1.5 mL screw-thread glass vial. Use a balance to verify the amount of sample transferred. Spike it with $^{13}\text{C}_2$ -BE surrogate so that the final concentration in the diluted sample will be 1 ppm. Samples containing elevated levels of 2-BE may need to be diluted and the concentration of surrogate should be adjusted accordingly. Cap the vial with a Teflon coated septum screw cap and mix for 1 to 2 min using a vortex shaker. After mixing, leave it for 1 hr to stabilize.

- 10.1.2 Withdraw a small subsample (2 to 10 μL) of surrogate labelled sample, calculate the weight added and mix it with solvent to achieve a 1:1000 dilution. Spike the solution with d_7 -ME recovery standard to the 1-ppm level and mix well. Close the vial tightly and leave it for a few minutes to stabilize. In our tests we used a 2- μL subsample diluted with methanol to 2 mL in 2.5 mL volume standard glass autosampler vials.
- 10.1.3 Transfer approximately 0.3 mL of the diluted sample to a Whatman Mini-UniPrep Syringeless Filter vial (0.4 mL capacity) with a 0.2- μm pore-size PTFE filter, fit the plunger and push it down to close the vial. Take care not to overfill the vial or the sample will overflow during filtration, which may result in contamination.
- 10.1.4 Move the vials with filtered samples to an autosampler for subsequent GC-MS analysis. The vials fit any autosampler accommodating 12 x 32 mm sample vials. Avoid storing samples in the vials; they are not gas-tight.
- 10.1.5 Remarks
- Solvents: methanol is recommended as a solvent as it was found to produce the best GC-MS results. Dichloromethane (DCM) can be used as alternative solvent if necessary (e.g. surrogate recovery from sample matrix is unsatisfactory).
 - Whatman Syringeless filter vials: use of 0.2- μm pore size PTFE filter inserts is recommended for sample filtration as these were found to produce the best results; 0.45- μm pore-size glass membrane filters (GMF) inserts can be used as an alternative as, in most cases, their performance was satisfactory.

10.2 Aerosol samples

- 10.2.1 Examine the aerosol container and determine the best way to achieve a clean sample transfer. Remove the nozzle. If the nozzle seats on a vent tube that is accessible, prepare a short piece of Tygon tubing that will fit tightly around it. Mount a stainless steel hypodermic needle at the other end of the tubing. If the tube is not accessible, you may have to fit a stainless steel needle directly into the nozzle. In this case, cut a part of the needle and drill a channel in the nozzle to accommodate it. Make sure the fit is tight; otherwise aerosol will spray through the needle and around it, which is **unacceptable**. Examples of the attachments are given at photos 1 and 2.
- Needles with gauges 26 to 30 (0.5 to 0.3 mm OD) usually work fine, but larger needle diameters should be avoided, as the septum in the sample vial may not seal properly after being punctured.
- 10.2.2 Prepare a 20 mL-volume glass autosampler vial and weigh it with the cap and septum that will be used to seal it. Fill the vial with 4000 mg (~ 5 mL) of methanol, then cap and reweigh it to determine the mass of the solvent.
- 10.2.3 Following the instructions on the aerosol can, shake the product for the specified period of time to ensure that the contents are evenly mixed with the propellant. Attach the previously prepared tubing or nozzle with the needle at the outer end of it.
- 10.2.4 Carefully pierce the septum at the top of the vial filled with solvent with the needle and gently squeeze the attachment to expel a small amount of aerosol sample. Withdraw the needle, gently mix the sample with solvent and weigh it again to find how much sample was added. Do not overfill the vial; 1 or 2 short squirts are usually enough. Injecting too much of the sample will over-pressurize the vial, resulting in some loss of sample through the septum.

- 10.2.5 After verifying the mass of an aerosol in the sample, spike it through the septum with the $^{13}\text{C}_2$ -BE surrogate so that the final concentration after dilution (Section 10.2.6) is 1 ppm. Samples containing elevated levels of 2-BE may need to be diluted and the concentration of surrogate adjusted accordingly. Mix and leave the sample to stabilize.
- 10.2.6 Using a chromatographic syringe, withdraw a small amount of liquid sample from the vial through the septum and mix it with methanol to achieve 1:1000 (final) aerosol dilution. For example, if a sample contains 100 mg of aerosol in 3900 mg of methanol, it is already diluted 1:40. In such a case, further dilution of 25 \times (e.g. 10 μL to 240 μL of methanol) is needed to bring its final dilution to 1:1000.
- 10.2.7 Spike the diluted (1:1000) sample with the recovery standard to the 1 ppm-level before analysis.
- 10.2.8 Remarks
- Calibrated pipettes may be used for measuring the amounts of solvent > 100 μL . Calibrated chromatographic syringes should be used for volumes \leq 100 μL .
 - The concentration of the surrogate spike and the recovery standard can vary between 1 ppm to 10 ppm, but should be consistent within the sample batch and calibration standards.
 - Method blanks are run with each batch of up to 10 samples.
 - Method control and/or replicate samples are run with each batch of up to 20 samples.

11 INSTRUMENTATION AND OPERATIONAL CONDITIONS

11.1 Gas chromatography

11.1.1 **Instrument:** HP 6890 GC interfaced directly to the mass selective detector (MSD).

11.1.2 **Carrier gas:** Helium.

11.1.3 **Injection:** 1 μL , splitless.

11.1.4 **Injector:** Split/splitless, operating temperature 260°C, purge gas to purge vent after 3 min, purge flow 30 mL/min.

11.1.5 **Column:** DB-624, 60 m x 0.32 mm ID, 1.80- μm film thickness. Carrier gas flow constant, 1.5 mL/min, initial head pressure 8.72 psi, outlet MSD.

11.1.6 **Oven temperature:** 40°C hold for 2 min, 6°C/min to 140°C, 12°C/min to 250°C hold for 2.17 min. Overall run time 30 min.

11.1.7 **GC-MS interface:** 290°C.

11.2 Mass spectrometry

11.2.1 **Instrument:** HP 5973N MSD.

11.2.2 **MSD operating parameters:** Source temperature 230°C, quadrupole temperature 150°C.

11.2.3 **Detection mode:** Electron impact ionization at 70eV operated in the full scan/selected ion monitoring (FS/SIM) combined mode.

- 11.2.4 **Instrument tuning:** Proper operation and calibration of the mass spectrometer is critical to the delivery of valid data. System leak checks and MSD tuning are performed routinely prior to sample analysis to monitor system performance and to optimize the mass spectrometer for analyte detection. Tune specifications are instrument-specific and the analyst should consult the manufacturers' operating manuals. The HP 5973N instrument is tuned using perfluorotributylamine (PFTBA).
- 11.2.5 **Acquisition:** A multi-step acquisition program with the time windows listed below was used. This program can be modified according to instrument performance and operator preferences. **As a general rule**, a minimum of 3 characteristic ions should be monitored per target analyte. A minimum 2 characteristic ions may be monitored for each isotopically labelled standard and 1 for the recovery surrogate if the surrogate shares another ion with a target analyte. Selected ions, their relative abundances and expected retention times under the conditions of the method are given in **Table 4**. **Figure 1** gives an example of a typical chromatogram.

Acquisition windows

Solvent delay:	0 to 10.0 min	
Group 1:	10.0 to 13.8 min	(d ₇ -ME, 2-ME, PGME)
Group 2:	13.8 to 19.8 min	(2-EE, PGPE)
Group 3:	19.8 to 22.5 min	(2-BE, ¹³ C ₂ -BE, PGBE, MEE)
Group 4:	22.5 to 24.0 min	(EEE, DPGME)
Group 5:	24.0 to 27.1 min	(2-HE, BEE)
Group 6:	27.1 to 28.9 min	(PE, TPGME)
Group 7:	28.9 to 30.0 min	(HEE)

- 11.2.6 **Criteria – the following criteria must be satisfied to confirm the presence of target analytes in samples**
- 11.2.6.1 **Response of the 2 most abundant characteristic ions must exceed the background noise level by a minimum of 3:1.**
- 11.2.6.2 **The abundance ratio of the target ion and the first confirmation ion must be within 20% of their corresponding ratios in the standard solution.**
- 11.2.6.3 **The second confirmation ion must be present unless masked by high background.**
- 11.2.6.4 **The peak maxima for each specified characteristic ion must be coincident within 3 sec.**
- 11.2.6.5 **Sample analyte retention time must be within 3 sec of the retention time of the corresponding standard component.**
- 11.2.7 **Quantification:** The isotope dilution quantification method is used for all target compounds. The relative response factors (RRFs) of target analytes to isotopically labelled internal standard(s) are used to determine analyte concentrations. RRFs of labelled surrogates to the recovery standard(s) are then used to calculate recoveries (Section 12).

11.3 Calibration

- 11.3.1 **Linear range:** The linear range should be established by using a minimum of 5 levels of calibration standards. However, the concentration range for 2-BE (0.1 to 22%) required by regulation for different products may be difficult to accommodate in a single calibration.

With a 1:1000 dilution, which is typically used in this method, this would translate into injecting between 1 to 220 ng of glycol ether. Such a dynamic range is likely to exceed the linear response of most MSDs. Several options are available to solve this problem when it occurs. The linearity of the detector response to the standards concentrations can be established separately for low and high concentration levels (Table 5); a non-linear fit can be used to relate the detector response to the concentration (Fig. 2); or the sample can be further diluted. While any of the above procedures produces valid results, sample dilution is likely to be most practical. The detector response is linear within the range of 0.1 ppm to 10 ppm (0.1 ng to 10 ng per injection), and fairly linear within the range of 10 ppm to 100 ppm for most of glycol ethers (Table 6). However, the calibration curve may have a different slope in each of these 2 ranges. Further details are discussed in Section 11.3.3.

- 11.3.2 **Initial calibration: To evaluate the linearity of the initial calibration, the average relative response factor (RRF) the standard deviation (SD) of that factor and the relative standard deviation (RSD) of the RRF are calculated using the following formulas:**

$$\overline{\text{RRF}} = \frac{\sum_{i=1}^n \text{RRF}_i}{n}$$

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (\text{RRF}_i - \overline{\text{RRF}})^2}{n-1}}$$

$$\text{RSD (\%)} = \frac{\text{SD}}{\overline{\text{RRF}}} \times 100$$

where:

RRF_i = RRF for each of the calibration standards

n = number of calibration levels and RSD is expressed as a percentage (%).

If the RSD is less than or equal to 15% over the calibration range, then linearity is assumed, and the average response factor may be used to determine sample concentrations. If this condition is not met, either a new calibration must be performed or the linear range modified.

- 11.3.3 **Daily calibration check: The initial calibration for each target analyte is verified by analyzing a daily calibration check (DCC) standard at a concentration near the midpoint concentration of the calibrated range. The DCC standard is run before and after each set of up to 7 samples. The validity of the initial calibration is checked by using the following percent difference formula:**

$$\% \text{ Difference} = \frac{\text{RRF}_{\text{DCC}} - \overline{\text{RRF}}}{\overline{\text{RRF}}} \times 100$$

where:

RRF_{DCC} = the RRF of the daily calibration check standard.

When the percent difference for each analyte is less than or equal to 10%, the initial calibration is assumed to be valid and options can be taken when choosing which RRF (average RRF or RRF_{DCC}) to use to calculate sample analyte concentrations.

Prior to sample analysis, the percent difference of ≤ 10% criterion must be met. If the criterion is not met, examine the instrument performance and reanalyze the daily calibration check standard. If still unable to meet the criterion, the analyst must recalibrate the system prior to further analysis (Section 11.3.2).

Quantification option 1: The \overline{RRF} s can be used to calculate the concentration of the target analyte and the recoveries of the surrogates as described in Section 12.

Quantification option 2: The RRF of the daily calibration check standard, RRF_{DCC}, can be used to update the calibration table that is used to calculate the concentration of the target analyte and the recoveries of the surrogates as described in Section 12.

- 11.3.4 **Recalibration: Whenever major instrument maintenance** (e.g. cleaning/replacing ion source, replacement of electron multiplier) **is required, the analyst must recalibrate the system prior to further analysis (Section 11.3.2).**
- 11.3.5 **Chromatographic performance: The chromatographic resolution is verified daily with the DCC standard. The daily calibration check standard must demonstrate good overall peak shape for all target analytes. Chromatographic problems such as excessive peak tailing, split peaks, unsymmetrical or broad peaks and poor sensitivity must be corrected prior to further analysis.**
- 11.3.6 **Surrogate and recovery standard spiking solutions: The sample spiking solutions (e.g. 13C₂-BE and d₇-ME) must be calibrated before use. These solutions must also be recalibrated or verified periodically against the daily calibration check standard.**
- 11.3.7 **Standard accuracy: The daily calibration check standard should be periodically verified against a certified reference solution if available.**
- 11.3.8 **Instrument sensitivity: The lowest calibration standard must be analyzed periodically to verify system sensitivity.**
- 11.3.9 **Detection limit:** Sample size, final volume and dilution as well as injection volume have a direct impact on detection limit. **For compliance testing, the limit must not be greater than 20% of the regulatory limit.** By following this method, the detection of target analytes between 0.01 ng and 1 ng per injection (1 µL) is typical, which, assuming 1000 x dilution of analyzed products, yields method detection limits between 0.001% to 0.1% (Table 7). For 2-BE, the method detection limit is 0.01%, which is 1/10 of its lowest regulatory limit.

12 CALCULATIONS

12.1 Native analyte RRF

Calculate the relative response factor RRF_x for each native (x) analyte relative to the corresponding surrogate in the calibration standard according to the following equation:

$$RRF_x = \frac{A_x C_s}{A_s C_x}$$

where:

RRF_x = relative response factor for analyte (x) to surrogate standard
 A_S = peak area of the quantification ion for the surrogate standard
 A_x = peak area of the quantification ion for the native analyte (x) in calibration solution
 C_S = concentration of the surrogate in the calibration standard
 C_x = concentration of the native analyte in the calibration standard

12.2 Surrogate RRF

Calculate the relative response factor RRF_s for surrogate(s) (e.g. $^{13}C_2$ -BE) relative to the recovery standard (e.g. d_7 -ME) in the calibration standard according to the following equation:

$$RRF_s = \frac{A_s}{A_{RS}} \frac{C_{RS}}{C_s}$$

where:

RRF_s = relative response factor for surrogate (s) in standard
 A_{RS} = peak area of the quantification ion for recovery standard
 A_s = peak area of the quantification ion for the surrogate
 C_{RS} = concentration of the recovery standard in the calibration standard
 C_s = concentration of the surrogate in the calibration standard

12.3 Analyte concentration

Calculate the concentration of the native analyte in the sample, C_N , as follows:

$$C_N = \frac{1}{RRF_x} \frac{A_N}{A_s} C_s$$

where:

C_N = concentration of native analyte in the sample
 RRF_x = relative response factor for analyte (x) in standard
 A_s = peak area of the quantification ion for the surrogate
 A_N = peak area of the quantification ion for the native analyte
 C_s = amount of surrogate added to the sample

12.4 Percent recovery of surrogate standard

Calculate the percent recovery of the surrogate standards, $\%R_x$, measured in the sample extract as follows:

$$\%R = \frac{1}{RRF_s} \frac{A_s}{A_{RS}} \frac{C_{RS}}{C_s} \times 100\%$$

where:

A_{RS} = peak area of the quantification ion for the recovery standard
 A_s = peak area of the quantification ion for the appropriate surrogate analyte
 C_s = amount of surrogate added to the sample
 C_{RS} = amount of recovery standard added to the sample

13 QUALITY ASSURANCE

The major elements of the analytical procedures used to assure acceptable method performance are as follows:

- 13.1 Calibration curve: The initial calibration is obtained from the analysis of standards containing the target compounds at a minimum of 5 different concentration levels within the working range of the instrument (Section 11.3).
- 13.2 Calibration verification standard: The daily calibration check standard containing the target analytes is periodically checked against commercially available mixtures whenever available.
- 13.3 Daily calibration check: The daily calibration check standard is run before and after each set of up to 7 samples that are injected on the GC-MS (Section 11.3.3).
- 13.4 Sample spiking: All samples are spiked with one or more isotopically labelled surrogate standard(s) (sections 10.1.1 and 10.2.5). In addition, recovery standard (e.g. d₇-ME) is added in exactly the same amount to each sample prior to GC-MS analysis to correct for instrument drift (Section 10.2.7).
- 13.5 Sample recovery: Surrogate is added to each sample, method blank, control and duplicates (sections 10.1.1 and 10.2.5) prior to sample reduction to produce individual known concentrations (e.g. 1 ng/μL) in the final volume. The acceptable level of surrogate recovery is from 40 to 130% for all surrogate analytes. Samples that fail to meet this criterion are reanalyzed.
- 13.6 Recovery correction: The percentage recovery of the labelled surrogate is calculated and reported. This serves to indicate the losses due to the sample workup and analytical procedures. The native concentration in the sample is corrected for surrogate recovery. The corresponding ¹³C-labelled surrogate is used to calculate the concentration of its native counterpart (Section 12.3).
- 13.7 Target analyte confirmation: The criteria to confirm the presence of target analytes in samples must be satisfied as described in Section 11.2.6.
- 13.8 Method blanks: A method blank consisting of solvent used for sample dilution (Section 10.2.8) spiked with surrogate mixture is processed along with each batch of up to 10 samples to demonstrate freedom from cross-contamination and the absence of other compounds that could interfere with the analysis of target analytes. The labelled surrogate recovery for each method blank must be within 40 to 130%. The level of contamination must not exceed 20% of the regulatory limit.
- 13.9 Control samples: A control sample consisting of sample solvent is spiked with surrogate and native analyte(s). The amount of target analyte spiked in the control must be close to the regulated limit or at an amount between the low end to midpoint of the concentration range of the calibration standards used (Table 1). Controls are processed along with each batch of up to 20 samples (Section 10.2.8). Ongoing precision and accuracy can then be assessed. The labelled surrogate recovery for each control must be within 40 to 130%. The target analyte recovery must be within the range of 75 to 120% of the actual value.
- 13.10 Duplicates: Duplicates may be processed along with each batch of samples. Ongoing precision can then be assessed.

14 METHOD VALIDATION

14.1 Objectives

The main objective of this method validation is to demonstrate performance characteristics with respect to selectivity, sensitivity, linearity, background, repeatability, accuracy, uncertainty and robustness, and to ensure that all the performance requirements specified in this method are adequate for the intent of the method.

14.2 Test design

Calibration solutions prepared from standard stock solutions (Section 8.3) were used to assess the selectivity, sensitivity, calibration linearity and precision of the method under ideal operating conditions under which no sample matrix interference was present. The precision of the method was further checked by spiking product samples with solutions of native standards and surrogates, and calculating analytes recoveries. Blank samples were used to assess background contamination.

Various commercial products (household cleaners, solvents and paints) were purchased and analyzed to assess the content of 2-BE and other glycol ethers (GEs). Samples that showed the presence of glycol ethers were run in triplicates to assess repeatability.

The robustness of the method was examined by changing some key operational conditions that could have an impact on the accuracy of results, such as final sample volume, injection volume, injection temperature, solvent, analytes concentration and surrogate spiking. Additional sample cleanup using reverse phase solid phase extraction (SPE) was tested as a way to minimize possible matrix interferences and system contamination.

14.3 Results and discussion

14.3.1 Selectivity

Results demonstrate that, with a carefully tuned temperature program, chromatographic separation of all 14 glycol ethers can be achieved on a 60-m DB-624 capillary column. While most of the potential interference can be removed or isolated (Fig. 1), potential problems may arise with 2-(2-methoxyethoxy)ethanol (MEE) and 2-(2-ethoxyethoxy)ethanol (EEE) at concentrations close to their detection limit. Under these circumstances, the separation between MEE and the adjacent coeluting peak is sometimes compromised. In such cases, monitoring the ion of m/z 57, which comes from the coeluting peak, would verify the peak purity. DPGME is typically a mixture of 4 isomers and 1 of them (Fig. 1) often coelutes with EEE. Examining the ion of m/z 59, which is the main fragment ion in DPGME isomer but a secondary ion fragment in EEE, and its ratio with the ion fragment of m/z 45, reveals both peaks purities. The above separation problems are responsible for a relatively high MEE and EEE detection limit and they impact the precision of measurements when these compounds are both present together in a sample in low quantities.

14.3.2 Background level

Solvent blanks (methanol) were run on the gas chromatograph at the beginning and the end of each day to ensure that the system was clean and free of contaminations. Additional solvent blanks were run after each batch of 8 to 10 samples with a concentration of analytes in the low-to-intermediate concentration and after every sample with a concentration of analyte in the high concentration range (Table 5). Results demonstrated that, if present, only negligible traces of target analytes were found in the blanks under typical conditions. Only when a very high concentration sample (> 100 ppm) is processed are there more significant amounts (~ 0.2 ppm) of some glycol ethers in the first blank, but typically not in the second. Blanks serve a dual purpose: first, as a quality assurance to check system performance and, second, as a means to clean a system and prevent accumulation of contaminants. If a second blank shows a significant amount of target

analyte, it is often connected with overall poor system performance and is a call for system maintenance.

14.3.3 Sensitivity and detection limits

The instrument detection limit (IDL) for each of the glycol ethers was established by subsequent injections of calibration solutions (1 μL) with gradually increasing concentrations from 0.001 ppm to 10 ppm (v/v). The criterion that the peak response for each of the characteristic ions must be at least 3 times the background noise level, and that the ion ratios between target ion and qualifying ions remain within 20% of their expected values was applied. The results are presented in Table 7.

The method detection limit (MDL) is typically established from the analysis of the replicate samples, which are individually performed throughout the entire sample preparation process. As a rule, the concentration of analytes in these samples, prior to injection into the instrument, should not exceed a value of 10 times the IDL. The MDL is then calculated from the standard deviation of the results using the following formula:

$$\text{MDL} = t_{(n-1)} \times \text{SD}$$

where:

MDL = method detection limit

$t_{(n-1)}$ = Student's test coefficient (1-tailed distribution, 95% confidence interval)

SD = standard deviation of the sample

n = number of replicates

The level of quantification (LOQ) is defined as the lowest concentration that can be accurately measured using sensitive but routine sampling and analytical methods (CEPA 1999, section 65.1). Measurement below the LOQ may not be quantifiable reliably.

The guideline recommended by the American Chemical Society's Committee on Environmental Improvement was adopted for the determination of LOQ. The American Society for Testing and Materials (ASTM) has also adopted this guideline as standard practice (ASTM D 6259-98, July 1998).

The calculation for LOQ is

$$\text{LOQ} = 10 \times \text{SD}$$

when replicate measurements of an analyte are done at concentrations near the detection limit. For a measurement at the LOQ, the uncertainty is $\pm 30\%$ ($10\text{SD} \pm 3\text{SD}$) at the 99% confidence level.

Whenever the original sample is diluted prior the analysis, the dilution factor F (in our case = 1000) needs to be accounted for in the calculations of MDL and LOQ to relate instrument uncertainties with product concentrations.

During method validation, we spiked 8 10-mL samples of each of 2 selected products (a water-based and an oil-based matrix) with native glycol ether standards and $^{13}\text{C}_2$ -BE surrogate. After mixing, we subsampled 2 μL of each spiked product sample and diluted the subsamples in 2 mL of methanol, spiked with a d_7 -ME recovery standard, and analyzed the subsamples. After dilution, the concentration of native glycol ethers in the sample remained below 10 x the IDL, while the concentration of surrogate and internal standard was fixed at 2.5 ppm and 1 ppm respectively. The use of surrogate allowed us to correct the concentration of the native analytes for recovery, while the recovery standard allows correction for instrument drift, matrix effects and volume changes during the injection.

The MDL for each of the glycol ethers calculated according the formula above ($n = 8$) is presented in Table 7. The LOQ calculated from the standard deviation of the results is also reported. Both MDL and LOQ calculations include the dilution factor ($F = 1000$) to relate them to product concentration rather than the concentration of the sample injected into GC. The dilution factor can be modified by the operator; however, lowering it may increase matrix interference.

The results show that the MDL and the LOQ for 2-BE in both water- and oil-based matrices are similar, suggesting that methanol extraction of glycol ethers from an oil-based matrix at this dilution is very efficient.

14.3.4 Linearity

The linearity of calibration for each analyte was examined within the concentration range of 0.1 ppm to 200 ppm. The full range spans 14 calibration levels, with 9 falling within the low 0.1 ppm to 10 ppm range, and 6 in the high 10 ppm to 200 ppm range (Table 5). Linear response for all analytes was the best in the low concentration range, as demonstrated by a high value of determination coefficient for linear regression (Table 6, Fig 2.1 and 2.2). At higher concentrations, non-linear effects are common. The only compounds for which the detector response remains linear over the entire calibration range are 2-EE, PGPE and TPGME. For the rest of glycol ethers a linear regression fit is upheld to a concentration of between 40 ppm to 100 ppm, with only a slight loss in the square value of the linear regression determination coefficient R . Above that range a second linear regression fit can be applied to compensate for non-linear effects for a majority of the glycol ethers (Table 6, Fig. 2.3), with the exception of BEE, 2-PE and HEE, for which the non-linear effects are too strong. Calibration above the lower linear range can be done with the use of a quadratic polynomial fit as demonstrated in Fig. 2.3, but it is usually more practical to dilute a sample.

14.3.5 Precision

Precision is a measure of the reproducibility of the results collected under the same operating conditions and is usually measured at a concentration higher than $10 \times$ MDL. It describes the variability or spread of results around the mean. This was calculated using the following formula:

$$P = RSD \times t_{(n-1)} \times 100\%$$

where:

P = precision

RSD = relative standard deviation (coefficient of variation)

$t_{(n-1)}$ = Student's test coefficient (2-tailed distribution, 95% confidence interval)

n = number of measurements

The above definition implies that, with 95% probability, the results of n measurements fall within P% around their mean.

To evaluate the precision for the analysis of liquid samples, methanol, a water-based product and an oil-based product were spiked with native GEs and processed through all method steps according to the method procedure before injecting them into the GC–MS system. The initial concentration of glycol ethers varied from 0.1% to 1.5% to fulfill the criteria of being at least $10 \times$ MDL and at the same time to be on a par with the lowest proposed regulatory limit for 2-BE (0.1%). Results of the 7 independent measurements were used to determine the variability of data. Precision varied from 3.0% to 5.2% for methanol samples, from 3.5% to 7.7% for the water-based matrix, and from 7.2% to 11.5% for the oil-based sample (Table 8). Values obtained with the use of methanol represent a

scenario where no matrix effects are observed. In most cases, these values represent the best precision that the instrument and the method can reliably deliver. Depending on the product being analyzed and the amount of interference its matrix creates, these values may change. In our case, the water-based matrix product does not introduce significant interferences and the precision values obtained were similar to those obtained with pure solvent (methanol). Oil-based matrices interfere with the acquisition of several major ions and, as a result, yields were lower, but still gave an acceptable precision within the scope of method application (Table 8).

The precision of aerosol measurements (Table 9) were calculated from 2 sets of aerosol samples spiked with native glycol ether standards to concentrations of 10% of the lower regulatory limit and twice the upper regulatory limit (0.01% and 10% of aerosol content weight/weight respectively). Precision varied from 9% to 16% in the low concentration range (n = 9) and from 2% to 12% in the high concentration range (n = 8). Overall precision was better for samples with a higher initial concentration of glycol ethers.

14.3.6 Recovery

14.3.6.1 Liquid samples

Recovery of the glycol ethers from liquid products was assessed separately for water-soluble and oil-based matrices. Glycol ether standards were spiked onto blank sample matrices of water-soluble and oil-based samples. The concentration of spiked glycol ethers varied from 0.1% to 1.5% (Table 10) to fulfill the criteria of being on a par with the lowest proposed regulatory limit for 2-BE (0.1%). Sets of 7 independent samples, individually carried through the entire method, were used to calculate the percent recovery according to the following formula:

$$\text{Recovery} = (\text{MV}/\text{SA}) \times 100\%$$

where:

MV = mean value of replicate samples (n = 7)

SA = spike amount

The values obtained vary from 87 to 119% for water compatible matrices and from 92 to 116% for oil-compatible samples (Table 10). The majority of the results fall within $\pm 7\%$ of the spiked amount.

14.3.6.2 Aerosol samples

The recovery of glycol ethers from aerosol samples was tested using a fabric protector and an upholstery cleaner as blank matrices. A known amount of aerosol was injected through a septum into 9 40-mL glass vials filled with 5 mL of methanol (Section 10.2). Native glycol ethers were spiked individually at 0.01% of aerosol content by weight, resulting in a concentration between 3 ppm to 6 ppm (10% of the lower regulatory limit for 2-BE). Surrogate ($^{13}\text{C}_2\text{-BE}$) was added to achieve the concentration of 5 ppm. After both spikes were added, small amounts (100 μL) of each sample were withdrawn through the septum port using a chromatographic syringe, diluted in methanol (400 μL) and carried through the rest of sample preparation procedure. Recoveries of glycol ethers were calculated for each of the samples individually and then averaged. The original samples in the septum vials were then re-spiked with native glycol ethers to 10% of aerosol content by weight (2 \times upper regulatory limit for 2-BE) and surrogate to 0.1%, and carried through the rest of the sample preparation procedure (sections 10.2.5 to 10.2.7). Recoveries were calculated for each of the samples using the formula below and then averaged:

$$\text{Recovery} = (\text{MC}/\text{EC}) \times 100\%$$

where:

MC = measured concentration

EC = expected concentration

Recoveries of glycol ethers from aerosol matrices varied between 89 to 112% for low level spikes and between 94 to 107% for high level spikes (Table 11). Recoveries for 2-BE were 98% and 100% respectively.

14.3.7 Products analysis and reproducibility

The method was tested on samples of several selected products purchased from local suppliers (Table 12). Each product was analyzed for its GE content. Out of 8 liquid products tested, 5 were found to contain various glycol ethers at levels of 0.1% to 10%. Two products contained 2-BE at levels between 0.3% and 9%. Reproducibility of the results was relatively good, varying between 0.001 to 0.35% (SD of triplicate analysis).

In addition to liquid products, several aerosol products were tested (Table 12). Insect repellent and fabric and upholstery cleaner were found to be free of glycol ethers, while bathroom cleaner and glass and windshield cleaner contained 6.8 % of BEE and 4.6% of 2-BE respectively (Table 12).

The invisible glass and windshield cleaner aerosol was further tested to check the reproducibility of the sampling technique. Seven aerosol samples were withdrawn from the full can into 5 mL of methanol, spiked with the surrogate and processed according to sampling procedure (Section 10.2). The can was then emptied to half its content (by weight) and 7 additional aerosol samples were analyzed. The results show no statistical difference between the 2 sets of data, demonstrating the robustness and reproducibility of the method (Table 12).

14.3.8 Accuracy

Accuracy is defined as the difference between the measured value and the known true value, and describes any systematic error of the method. It is best estimated by analyzing multiple samples of reference material and comparing obtained results with the known reference value

$$\text{Accuracy} = (\text{MV}-\text{RV})/\text{RV} \times 100\%$$

where:

MV = mean value of concentration from replicate samples ($n \geq 7$)

RV = reference value of concentration

As no reference material is currently available, the true value remains uncertain.

14.3.9 Uncertainty

Different components attribute to the uncertainty of results. Measurements such as sample volume, amount of surrogate spike and gravimetric analysis, as well as the purity of reagents, cross-contamination, sample cleanup, calibration, GC-MS conditions and accuracy of standard solutions all introduce their own additive components. The above sources of uncertainty, except the accuracy of standard solutions, are normally included in the SD of replicate measurements and are listed in tables 10, 11 and 12 for different concentrations of the glycol ethers in different matrices, together with the number of measurements from which they were calculated.

The expanded uncertainty of products analysis at the 95% confidence level is presented in Table 13. The uncertainties that are presented are calculated from a limited number of samples. The quality of the reported uncertainties of the measurements will be improved as the number of control samples increases. This uncertainty is calculated as

$$U = t \times SD$$

where:

t = Student's t-distribution coefficient for n-1 degree of freedom for 2-sided test.

APPENDIX

TABLES, FIGURES AND PHOTOS

Table 1: Concentration limits of 2-butoxyethanol in products set out in column 1 of schedule 1 of the 2-Butoxyethanol Regulations
(*Canada Gazette*, Part II, Vol. 140, No. 26, p. 2227, December 27, 2006)

Item #	Product	Concentration limit (%) (w/w)
1	Automobile cleaner ¹	10.0
2	Rug or carpet cleaner	10.0
3	Floor or baseboard stripper	2.0
4	Paint stripper or thinner	0.5
5	Laundry stain remover	22.0
6	Any other aerosol ² cleaner ³	5.0
7	Any other non-aerosol cleaner ³	6.0
8	Aerosol paint or coating	0.1
9	Non-aerosol paint or coating	0.5

¹ Does not include automobile degreasers.

² Does not include pump sprays.

³ A product to be used to degrease and clean glass, floors and other surfaces, including bathroom and kitchen surfaces, but does not include automobile degreasers.

Table 2: Common names and abbreviations of selected glycol ethers

#	Chemical Name	Abbreviation	Alternative Name	Alternative Abbreviation
1	2-methoxyethanol	2-ME	Ethylene glycol methyl ether	EGME
2	2-ethoxyethanol	2-EE	Ethylene glycol ethyl ether	EGEE
3	2-butoxyethanol	2-BE	Ethylene glycol butyl ether	EGBE
4	2-(2-methoxyethoxy)ethanol	MEE	Diethylene glycol methyl ether	DEGME
5	2-(2-ethoxyethoxy)ethanol	EEE	Diethylene glycol ethyl ether	DEGEE
6	2-(2-butoxyethoxy)ethanol	BEE	Diethylene glycol butyl ether	DEGBE
7	1-methoxy-2-propanol		Propylene glycol methyl ether	PGME
8	1-propoxy-2-propanol		Propylene glycol propyl ether	PGPE
9	1-butoxy-2-propanol		Propylene glycol buthyl ether	PGBE
10			Dipropylene glycol methyl ether	DPGME
11			Tripropylene glycol methyl ether	TPGME
12	2-hexyloxyethanol	2-HE		
13	2-phenoxyethanol	2-PE		
14	2-2-hexyloxyethoxyethanol	HEE		

Table 3: Physical properties of selected glycol ethers (Abbreviation, CAS number, MF (molecular formula), MW (molecular weight), density, MP (melting point), BP (boiling point), VP (vapour pressure), K_{ow} (octanol/water partition coefficient))

Abbrev.	CAS #	MF	MW	Density g/mL	MP °C	BP °C	VP kPa	log K_{ow}
2-ME	109-86-4	C ₃ H ₈ O ₂	76.1	0.96	-85	125	0.83 at 20°C	-0.50
PGME	107-98-2	C ₄ H ₁₀ O ₂	90.1	0.92	-96	120	1.2 at 20°C	0.49*
2-EE	110-80-5	C ₄ H ₁₀ O ₂	90.1	0.93	-70	135	0.5 at 20°C	-0.54
PGPE	1569-01-3	C ₆ H ₁₄ O ₂	118.2	0.89*	-80*	150*	0.23* at 20°C	0.49*
2-BE	111-76-2	C ₆ H ₁₄ O ₂	118.2	0.90	-75	171	0.1 at 20°C	0.83
PGBE	5131-66-8	C ₇ H ₁₆ O ₂	132.2	0.88	-75	171	0.19 at 25°C	1.15
MEE	111-77-3	C ₅ H ₁₂ O ₃	120.2	1.04	-70	193	0.03 at 20°C	-1.14
EEE	111-90-0	C ₆ H ₁₄ O ₃	134.2	0.99	-76	196	0.02 at 25°C	-0.15
DPGME	34590-94-8	C ₇ H ₁₆ O ₃	148.2	0.95	-80	190	0.05 at 25°C	-
2-HE	112-25-4	C ₈ H ₁₈ O ₂	146.2	0.89	-45	208	0.007 at 20°C	1.57
BEE	112-34-5	C ₈ H ₁₈ O ₃	162.2	0.95	-68	230	0.003 at 20°C	0.3
2-PE	122-99-6	C ₈ H ₁₀ O ₂	138.2	1.10	14	245	0.001 at 20°C	1.2
TPGME	20324-33-8	C ₁₀ H ₂₂ O ₄	206.3	0.97*	-60*	243*	0.002* at 25°C	-
HEE	112-594	C ₁₀ H ₂₂ O ₃	190.3	0.94	-40	260	<0.001 at 25°C	1.7

Note: Unless otherwise noted, all data were obtained from the International Programme on Chemical Safety (IPCS), International Chemical Safety Card (ICSC) Database, WHO, Geneva, 2000–2009.

* Canadian Centre for Occupational Health and Safety (CCOHS), CHEMINFO Database, 2009.

Table 4: Monitored ions, their relative intensities* and expected retention times for selected glycol ethers

Analyte	Quantification Ion (m/z)	Confirmation Ion 1 (m/z)	Confirmation Ion 2 (m/z)	Relative Intensities (%)	Expected RT (min)
2-ME	45	76	58	100, 9, 5	11.8
PGME	45	47	75	100, 29, 5	12.8
2-EE	59	45	72	100, 36, 30	14.1
PGPE	45	73	59	100, 61, 31	18.1
2-BE	45	87	57	100, 85, 261	20.3
PGBE	57	45	87	100, 97, 67	21.0
MEE	45	59	90	100, 55, 25	21.4
DPGME**	59	73	103	100, 33, 54	22.6
EEE	45	59	72	100, 42, 37	22.9
2-HE	85	43	63	100, 95, 34	24.8
BEE	45	57	75	100, 113, 31	26.3
PE	94	138	77	100, 43, 30	27.3
TPGME	59	73	45	100, 28, 24	28.0
HEE	43	45	85	100, 84, 70	29.1
d ₇ -ME	50	49	83	100, 13, 9	11.7
¹³ C ₂ -BE	47	88	45	100, 81, 15	20.3

* Relative intensities as for the NIST Mass Spectral Library.

** DPGME standard was a mixture of 3 isomers: CAS 20324-32-7 (22.57 min); CAS 34590-94-8 (22.64 min) and CAS 13429-07-7 (22.9 min). The last compounds may interfere with 2,2-EEE analysis if peaks are not separated.

Table 5: Concentrations of calibration standards for glycol ethers analysis
(LCS = low concentration calibration standard; HCS = high concentration calibration standard)

Calibration Standards Concentration (ppm) in the Low Concentration Range (0.1 ppm to 10 ppm)									
Level	LCS-1	LCS-2	LCS-3	LCS-4	LCS-5	LCS-6	LCS-7	LCS-8	LCS-9
Natives	0.1	0.25	0.5	1	2	4	6	8	10
Surrogate 13C ₂ -BE	1	1	1	1	1	1	1	1	1
Internal standard d ₇ -ME	1	1	1	1	1	1	1	1	1

Calibration Standards Concentration (ppm) in the High Concentration Range (10 ppm to 200 ppm)						
Level	HCS-1	HCS-2	HCS-3	HCS-4	HCS-5	HCS-6
Natives	10	40	80	120	160	200
Surrogate 13C ₂ -BE	10	10	10	10	10	10
Internal standard d ₇ -ME	10	10	10	10	10	10

Table 6: Linearity of calibration (within the range 0.1 ppm to 200 ppm)

Compound	Lower Linear Range		Medium Linear Range		Upper Linear Range	
	ppm	R ²	ppm	R ²	ppm	R ²
2-ME	0.1 – 10	1.000	0.1 – 120	0.996	80 – 200	0.999
PGME	0.1 – 10	0.999	0.1 – 120	0.994	80 – 200	0.997
2-EE	0.1 – 10	1.000	0.1 – 120	0.999	0.1 – 200	0.999
PGPE	0.1 – 10	0.998	0.1 – 120	0.998	0.1 – 200	0.995
2-BE	0.2 – 10	1.000	0.2 – 120	0.993	80 – 200	0.995
¹³ C ₂ -BE	0.2 – 10	1.000	0.2 – 120	0.993	10 – 200	0.994
PGBE	0.2 – 10	0.997	0.2 – 120	0.993	80 – 200	0.993
MEE	2 – 10	0.998	4 – 120	0.993	80 – 200	0.995
EEE	2 – 10	1.000	4 – 120	0.994	80 – 200	0.994
DPGME	0.5 – 10	0.998	0.5 – 120	0.993	80 – 200	0.995
2-HE	0.2 – 10	0.998	0.2 – 80	0.995	80 – 200	0.992
BEE	0.2 – 10	0.996	0.2 – 40	0.995	quadratic fit > 40	
PE	0.2 – 10	1.000	0.2 – 40	0.990	quadratic fit > 40	
TPGME	0.5 – 10	0.999	0.5 – 120	0.999	0.5 – 200	0.999
HEE	1 – 10	0.999	2 – 40	0.999	quadratic fit > 40	

R² – coefficient of determination for linear regression.

Table 7: Instrument detection limit (IDL), method detection limit (MDL) and limit of quantification (LOQ) for water- and oil-based products (SD = standard deviation for MDL and LOQ measurements, t = Student's t-distribution coefficient, F = sample dilution factor = 1000; % calculations based on product density = 1 g/mL)

Water-based Matrix	IDL ng/ μ L	SD	MDL = t \times SD \times F		LOQ = 10 \times SD \times F	
			μ g/mL	% (w/w)	μ g/mL	% (w/w)
2-ME	0.01	0.005	9	0.001	46	0.005
PGME	0.01	0.002	3	0.0003	18	0.002
2-EE	0.01	0.008	16	0.002	83	0.008
PGPE	0.02	0.007	13	0.002	68	0.006
2-BE	0.09	0.016	29	0.003	155	0.016
PGBE	0.04	0.013	25	0.003	132	0.013
MEE	1.00	0.203	386	0.038	2035	0.204
DPGME	0.25	0.116	219	0.023	1156	0.116
EEE	1.00	0.246	466	0.047	2457	0.246
2-HE	0.45	0.158	299	0.034	1576	0.158
BEE	0.50	0.145	274	0.028	1446	0.145
PE	0.03	0.009	17	0.002	92	0.009
TPGME	0.50	0.223	423	0.044	2232	0.223
HEE	0.50	0.200	379	0.040	2000	0.200
Oil-based Matrix	IDL ng/ μ L	SD	MDL = t \times SD \times F		LOQ = 10 \times SD \times F	
			μ g/mL	% (w/w)	μ g/mL	% (w/w)
2-ME	0.01	0.009	18	0.002	93	0.009
PGME	0.01	0.003	6	0.001	30	0.003
2-EE	0.01	0.007	13	0.001	69	0.007
PGPE	0.02	0.008	15	0.002	80	0.008
2-BE	0.09	0.016	31	0.003	163	0.016
PGBE	0.04	0.015	29	0.003	155	0.016
MEE	1.00	0.140	265	0.026	1398	0.140
DPGME	0.25	0.104	197	0.021	1038	0.104
EEE	1.00	0.339	642	0.064	3390	0.339
2-HE	0.45	0.147	279	0.031	1474	0.147
BEE	0.50	0.131	249	0.026	1314	0.131
PE	0.03	0.012	23	0.002	123	0.012
TPGME	0.50	0.089	169	0.017	890	0.089
HEE	0.50	0.189	358	0.037	1888	0.189

Table 8: Precision of glycol ethers measurements for liquid samples (methanol, water- and oil-based products, Section 14.3.5)

Compound	Concentration % (v/v)	No. of Replicates	Precision (%)		
			Methanol	Water Base	Oil Base
2-ME	0.1	7	4.8	4.5	9.4
PGME	0.1	7	4.7	6.7	7.5
2-EE	0.1	7	4.9	4.8	8.8
PGPE	0.1	7	5.2	4.7	9.4
2-BE	0.1	7	4.5	4.3	10.5
PGBE	0.1	7	4.3	5.0	8.1
MEE	1.0	7	3.6	7.1	10.7
DPGME	1.0	7	4.1	7.7	11.5
EEE	1.5	7	3.5	7.5	11.2
2-HE	0.5	7	4.2	5.8	8.5
BEE	0.5	7	3.1	3.5	7.9
PE	0.1	7	3.7	5.4	7.2
TPGME	1.0	7	3.0	5.3	11.3
HEE	0.5	7	4.2	4.9	7.8

Table 9: Precision of glycol ethers measurements for aerosol samples
(upholstery and carpet cleaner)

Compound	Concentration % (w/w)	n	Precision %	Concentration % (w/w)	n	Precision %
2-ME	0.01	9	15.0	10	8	4.5
PGME	0.01	9	14.3	10	8	1.7
2-EE	0.01	9	14.1	10	8	3.3
PGPE	0.01	9	12.9	10	8	2.6
2-BE	0.01	9	9.4	10	8	2.9
PGBE	0.01	9	11.7	10	8	2.4
MEE	0.01	9	13.2	10	8	14.4
DPGME	0.01	9	12.3	10	8	3.1
EEE	0.01	9	13.3	10	8	12.0
2-HE	0.01	9	15.2	10	8	2.6
BEE	0.01	9	13.1	10	8	2.9
PE	0.01	9	12.8	10	8	2.3
TPGME	0.01	9	15.8	10	8	2.8
HEE	0.01	9	11.8	10	8	3.6

Table 10: Recoveries of glycol ethers from products with liquid matrices
 (SD = standard deviation of the results around the mean)

Compound	Concentration % (v/v)	Number of Replicates	Recovery from Product			
			Water- based %	SD %	Oil- based %	SD %
2-ME	0.1	7	97	1.8	116	3.8
PGME	0.1	7	94	2.8	107	3.1
2-EE	0.1	7	102	1.7	98	3.6
PGPE	0.1	7	95	1.9	113	3.8
2-BE	0.1	7	92	1.7	109	4.3
PGBE	0.1	7	93	2.0	109	3.3
MEE	1.0	7	104	2.9	92	4.4
DPGME	1.0	7	111	4.8	99	4.7
EEE	1.5	7	103	3.1	101	4.6
2-HE	0.5	7	101	2.4	107	3.5
BEE	0.5	7	119	1.4	111	3.2
PE	0.1	7	87	2.2	111	2.9
TPGME	1.0	7	109	2.2	96	4.6
HEE	0.5	7	102	2.0	97	3.2

Table 11: Recoveries of glycol ethers from aerosol samples (Conc.= concentration of glycol ethers in relation to aerosol, SD = standard deviation, n = number of measurements)

Compound	Conc. % (w/w)	n	Recovery %	SD %	Conc. % (w/w)	n	Recovery %	SD %
2-ME	0.01	9	96	6.3	10	8	103	2.0
PGME	0.01	9	93	5.8	10	8	106	0.8
2-EE	0.01	9	100	6.1	10	8	107	1.5
PGPE	0.01	9	99	5.5	10	8	106	1.2
2-BE	0.01	9	98	4.0	10	8	100	1.2
PGBE	0.01	9	98	5.0	10	8	102	1.1
MEE	0.01	9	106	6.1	10	8	94	5.7
DPGME	0.01	9	89	4.7	10	8	106	1.4
EEE	0.01	9	112	6.5	10	8	97	4.9
2-HE	0.01	9	95	6.3	10	8	105	1.2
BEE	0.01	9	104	5.9	10	8	104	1.3
PE	0.01	9	104	5.7	10	8	100	1.0
TPGME	0.01	9	103	7.1	10	8	98	1.1
HEE	0.01	9	101	5.2	10	8	105	1.6

Table 12: Concentration of glycol ethers in selected products
 (Conc. = concentration*, SD = standard deviation)

Product	Number of Samples	Glycol Ether	Conc. %	SD %
Liquids				
Glass cleaner	4	2-HE	0.85	0.02
Cleaning product	4	None detected		
Carpet stain remover	4	None detected		
General cleaner	3	PGBE	2.26	0.11
Dry paint solvent	3	2-BE	0.32	0.04
Oil wood finish	4	None detected		
Acrylic white paint	3	2-BE	8.79	0.35
Polyacrylic protective finish	3	PGBE	5.2	0.06
		EEE	0.01	0.001
		DPGME	1.7	0.007
		BEE	0.2	0.005
Aerosols				
Insect repellent	3	None detected		
Fabric and upholstery cleaner	3	None detected		
Bath cleaner	3	BEE	6.8	0.24
Glass cleaner	5	2-BE	4.6	0.30
	7	2-BE – full can	4.8	0.05
	7	2-BE – half can	4.7	0.06

* Concentrations reported here were acquired during the method validation from the analysis of a single product container, and are intended to demonstrate method performance only.

Table 13: Uncertainty of product analysis (n = number of measurements, SD = standard deviation, U = expanded uncertainty of the results at 95% confidence limit, MDL = method detection limit)

Product	Glycol Ether	Concentration %	n	SD %	U = k × SD %
Liquids					
Glass cleaner	2-HE	0.85	4	0.02	0.06
General cleaner	None detected		4	0	MDL
Carpet stain remover	None detected		4	0	MDL
Multipurpose cleaner	PGBE	2.26	3	0.11	0.47
Dry paint solvent	2-BE	0.32	3	0.04	0.17
Oil wood finish	None detected		4	0	MDL
Acrylic white paint	2-BE	8.79	3	0.35	1.5
Polyacrylic protective finish	PGBE	5.2	3	0.06	0.25
	EEE	0.01		0.001	0.004
	DPGME	1.7		0.007	0.030
	BEE	0.2		0.005	0.022
Aerosols					
Insect repellent	None detected		3	0	MDL
Fabric and upholstery cleaner	None detected		3	0	MDL
Bath cleaner	BEE	6.8	3	0.24	1.03
Glass cleaner	2-BE	4.6	5	0.30	0.83
	2-BE - full can	4.8	7	0.05	0.12
	2-BE - half can	4.7	7	0.06	0.15

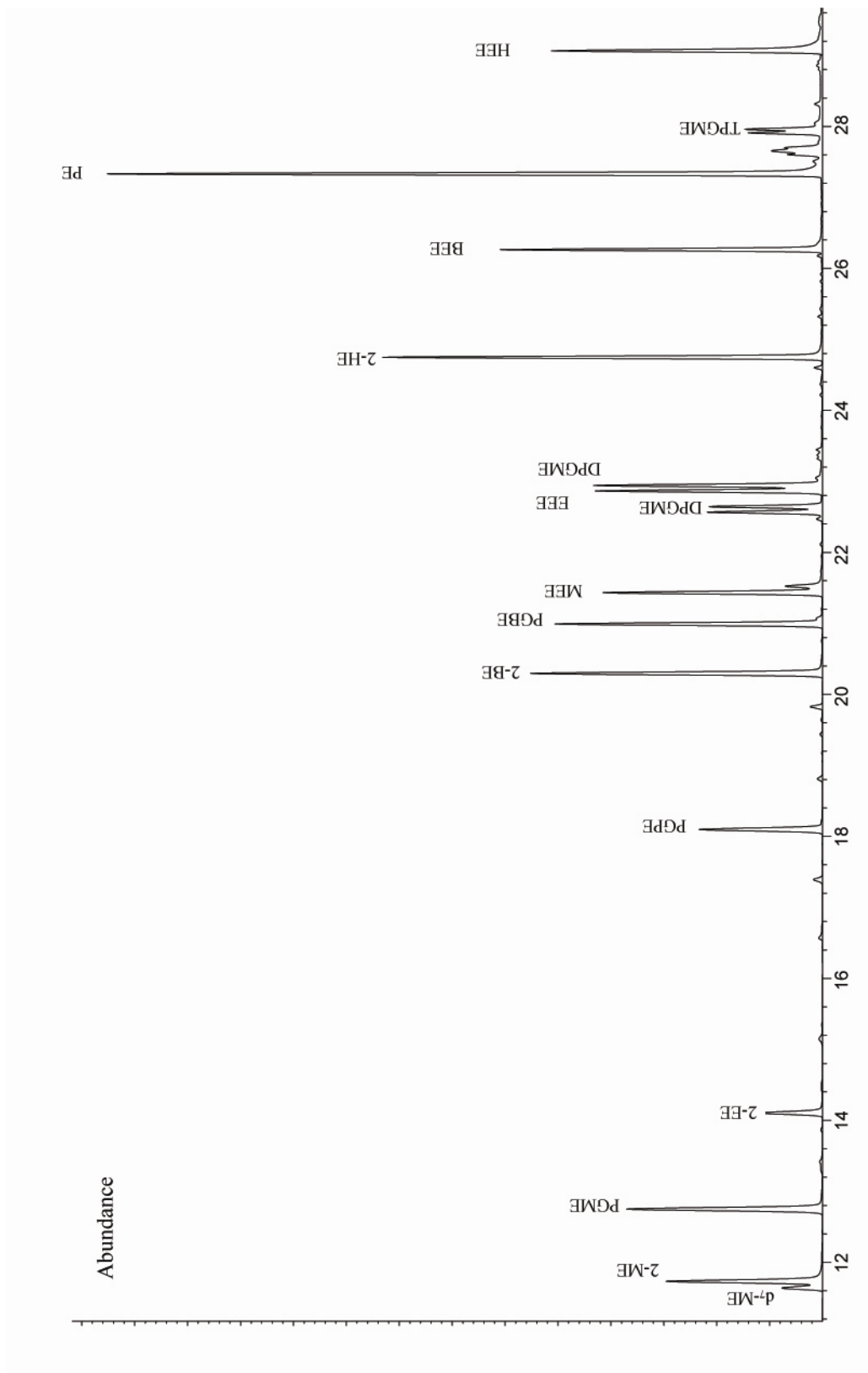


Figure 1: Example of glycol ethers chromatogram (40 ppm)

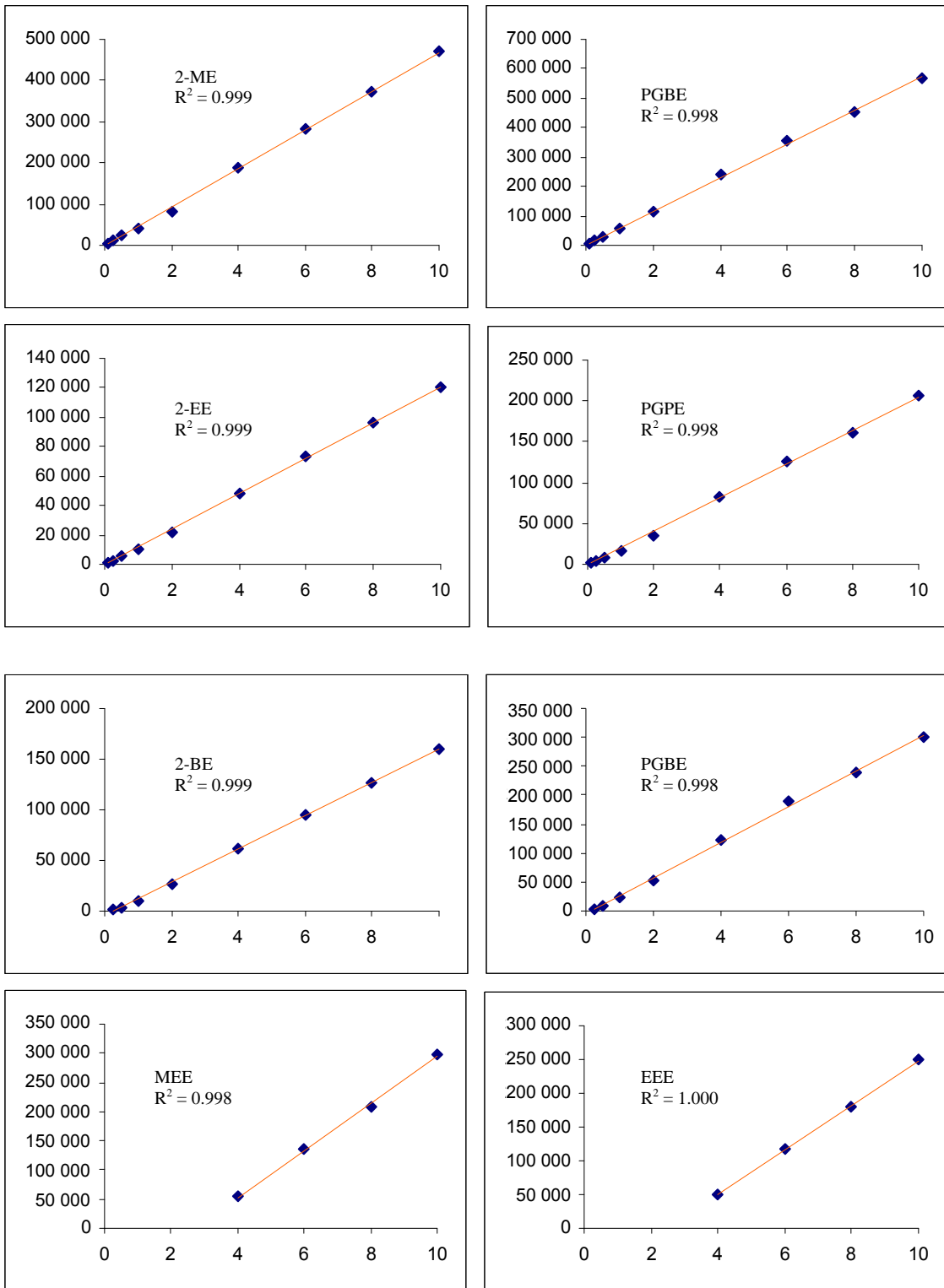


Figure 2.1: Calibration curves for selected glycol ethers (2-ME, PGME, 2-EE, PGPE, 2-BE, PGBE, MEE, EEE – concentration range, 0.1 ppm to 10 ppm)

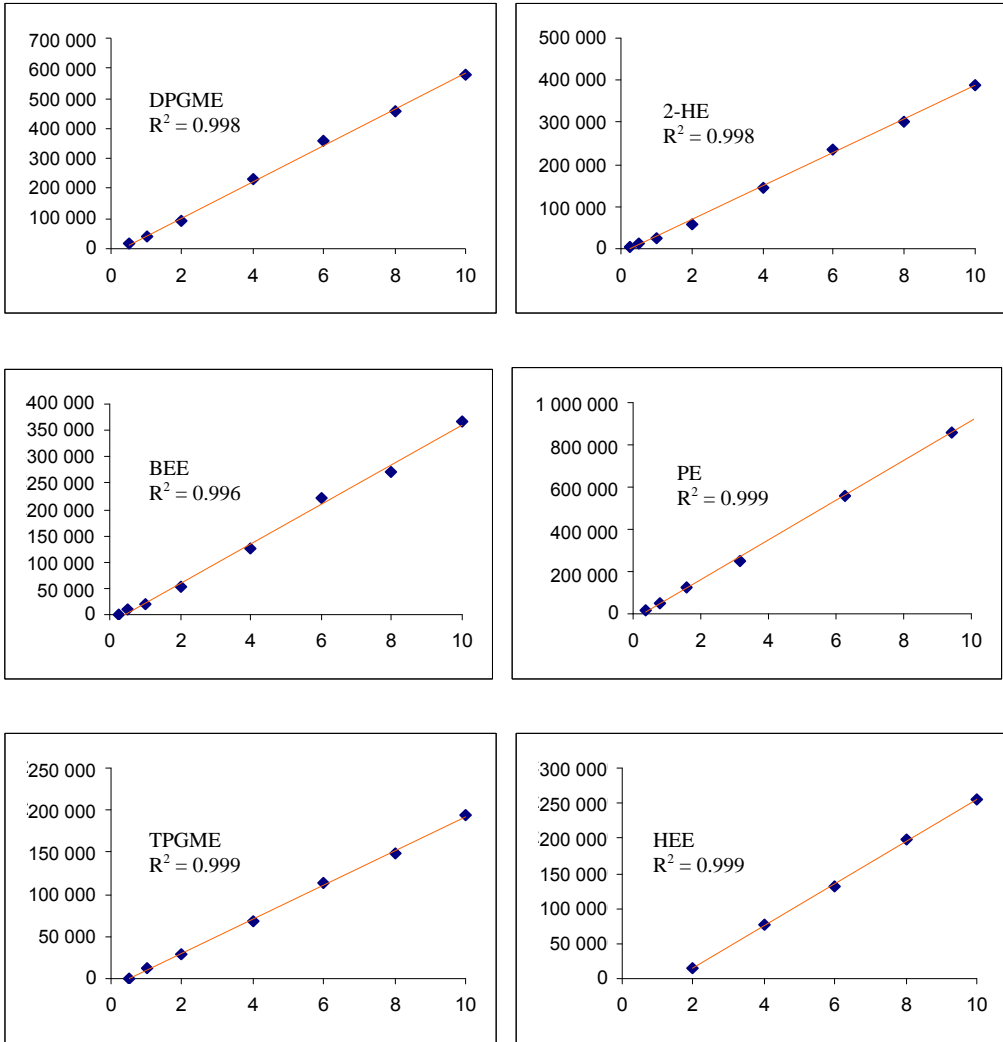


Figure 2.2: Calibration curves for selected glycol ethers (DPGME, 2-HE, BEE, PE, TPGME, HEE – concentration range, 0.1 ppm to 10 ppm)

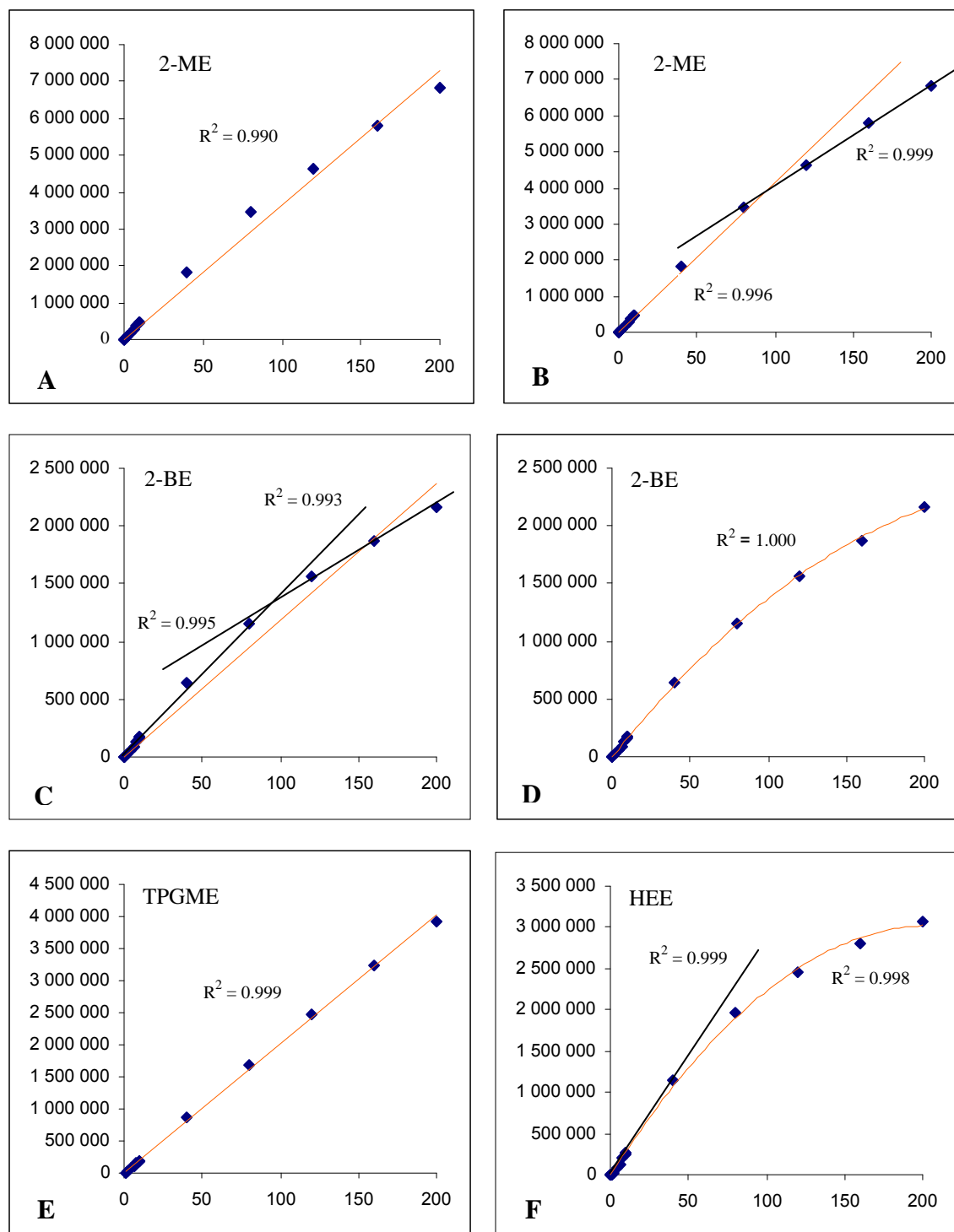


Figure 2.3: Examples of glycol ethers calibrations (within 0.1 ppm to 200 ppm range: A, B – 2-ME calibration with the use of one (A) and two (B) linear ranges; C – 2-BE calibration with the use of two linear ranges (thin line marks single 0.1–200 ppm linear fit); D – 2-BE calibration using quadratic polynomial fit (R^2 applies to the entire range); E – linearity of TPGME calibration; F – HEE calibration with the use of linear and polynomial fit. Note that in case of HEE, linear coefficient applies to the range 0.1–40 ppm; while quadratic polynomial coefficient is valid within entire range. Samples should be diluted so their concentration is within the linear range.)



Photo 1: Nozzle with needle attached for aerosol sampling

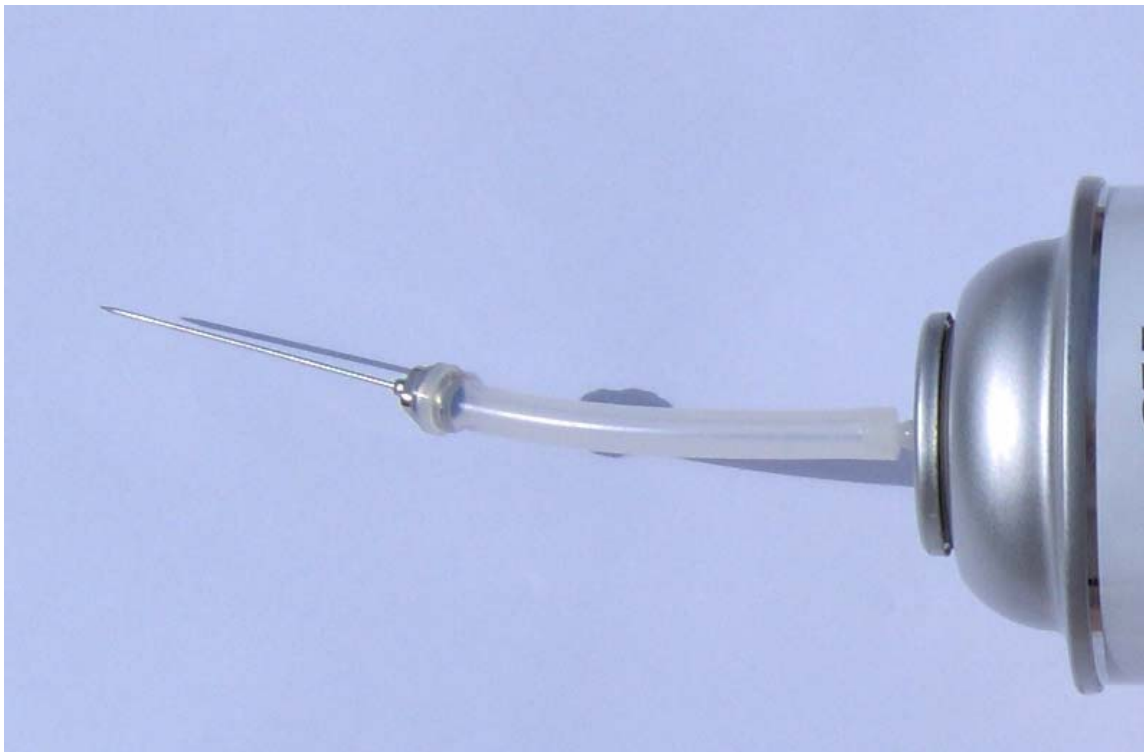


Photo 2: Tubing with needle attached for aerosol sampling

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