PERCHLOROETHYLENE (portable GC)   3704
in exhaled breath and air

C_2Cl_4 MW: 165.8   CAS: 127-18-4   RTECS: KX3850000

METHOD: 3704, Issue 1	**EVALUATION: FULL**	**Issue 1: 15 January 1998**

OSHA : 100 ppm; C 200 ppm; P 300 ppm (5 min. max peak in any 3 h)
NIOSH: Ca; lowest feasible
ACGIH: 25 ppm, 100 ppm STEL; 10 ppm BEI, end-exhaled air
(1 ppm = 6.8 mg/m³ @ NTP)

PROPERTIES: colorless liquid with mild chloroform-like odor; d 1.62 g/mL @ 20 °C; BP 121 °C; VP 14 kPa (13 mm Hg) @ 22 °C; I. P 9.32 eV

SYNONYMS: tetrachloroethylene; perc

SAMPLING

SAMPLER: AIR BAG (Tedlar™) or direct injection

FLOW RATE: 0.02 to 5 L/min
sufficient volume in bag (greater than approximately 0.5 L) during sampling period of interest; fill bag ≤80% capacity

SAMPLE STABILITY: 8 h in Tedlar bags

BLANKS: clean air in bag from non-work area

ACCURACY

RANGE STUDIED: 0.1 to 100 ppm
0.05 to 0.3 ppm field validation [1]

BIAS: not significant

OVERALL PRECISION $(\hat{S}_{rT})$: ≤0.115

ACCURACY: ± 22.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE) / PHOTOIONIZATION DETECTOR (PID)

ANALYTE: perchloroethylene (perc)

INJECTION VOLUME: 0.5 mL (greater volume will increase sensitivity, smaller volume will extend upper range)

TEMPERATURE-INJECTION: ambient
    -DETECTOR: ambient
    -COLUMN: 40 °C

CARRIER GAS: air, ultra-pure @ 10 to 20 mL/min

COLUMN: macrobore capillary, 10 m, 0.53-mm ID, 2-µm polymethyl siloxane film, (CPSil 5CB™ or equivalent)

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.1 to 1000 ppm [1]

ESTIMATED LOD: 0.01 ppm

PRECISION $(\bar{S}_r)$: ≤0.115

APPLICABILITY: The working range is from 0.1 to 100 ppm for both air and exhaled breath samples by direct on-site analysis or by collection into inert sampling bags. Collection of exhaled breath into sample bags requires the use of a desiccant (see SAMPLING section) to remove humidity which may condense on the bag.

INTERFERENCES: Any compounds having similar retention times as perchloroethylene are potential positive interferences. The presence of a large number of compounds with retention times similar to perchloroethylene will cause a high background resulting in decreased sensitivity, possibly to the point where the LOQ approaches 1 ppm. Common human metabolites found in exhaled breath, as well as chemicals normally found in dry cleaning plants, do not interfere with the analysis of perchloroethylene. Specific compounds tested and shown not to interfere with this method include: acetone, isoprene, methanol, ethanol, acetaldehyde, carbon tetrachloride, chloroform, benzene, butane, styrene, toluene and xylenes.

OTHER METHODS: NMAM method 1003 for halogenated hydrocarbons [2] calls for collection of sample on charcoal sorbent, followed by laboratory desorption with carbon disulfide, and subsequent analysis by gas chromatography with a flame ionization detector. NMAM method 2549, volatile organic compounds (screening) [3], uses a multi-bed sorbent tube for sample collection, thermal desorption, and laboratory analysis by gas chromatography / mass spectrometry. Estimated limits of detection for Methods 1003 and 2549 are 1.5 and 15 ppm, respectively, for 1-L samples, which are typical for exhaled breath analysis.

REAGENTS:

1. Perchloroethylene* in air, commercial mixed gas standards, or liquid perchloroethylene.
2. Air, ultra-pure, or Nitrogen, purified.
3. Dry-Rite™ desiccant, indicating or equivalent.

   * See SPECIAL PRECAUTIONS

EQUIPMENT

1. Sampler: air bags, Tedlar™, 1-L, or other appropriate size.
2. Drying tube for exhaled breath sampling. Plastic tubing, ca. 1-cm ID, containing approximately 5 g indicating Dry-Rite, held in place with glasswool plugs.
3. Personal sampling pump, 0.02 to 5 L/min, or other rate suitable for filling sample bag, with flexible connecting tubing.
4. Tubing, PTFE, ca. 6 ft. length.
5. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop, column (p. 3704-1), and (if appropriate) strip chart recorder.
6. Syringes, gas tight, various sizes appropriate to the GC.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.

SPECIAL PRECAUTIONS: Perchloroethylene is a suspect carcinogen as well as an irritant to the eyes, nose, and skin. Wear appropriate protective clothing. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC instrument and allow to warm up according to manufacturer's instructions. Select sampling mode.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. **Spot Sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
   NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
   (1) use a gas sampling loop for injections, if available;
   (2) make at least three replicate determinations per sample;
   (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.

3. **Integrated Air Sample.**
   a. Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags. Alternatively, purge used bags at least twice with clean air, then fill with clean air and analyze for perchloroethylene (step 6).
   b. Attach sample bag to outlet port of a personal sampling pump with a minimum length of flexible tubing. To the inlet port of the pump, attach a length of PTFE tubing sufficient to reach the desired site. When sample size is small, a rubber squeeze bulb may be used in place of a personal sampling pump. In either case, flush tubing and pump/bulb with sample air prior to, and clean air subsequent to, sample collection.
      NOTE: Tygon™ tubing has been shown to adsorb some materials in complex hydrocarbon mixtures and to off gas during later sample collection causing an increase in hydrocarbon

concentration in those subsequent samples.
  c. Pump air sample into bag at a rate calculated to fill ≤ 80% of the bag capacity over the sampling period.
     NOTE: The flow rate must be constant throughout the sampling period.
  d. As soon as practical, but within 8 h after completion of sampling, introduce an aliquot of the sample into the GC (step 2).
4. **Exhaled Breath Sample** (adapted from Toutonghi [4])
  a. Move subject to an area where ambient analyte concentrations are insignificant.
  b. Instruct subject to take 4 normal breaths followed by 1 deep inhalation.
  c. Hold the deep breath for 10 seconds.
  d. After 10 seconds, exhale the first half of the breath into the room and the last half through a tube filled with Dry-Rite into a sampling bag.
  f. Close the bag valve and queue the sample for analysis.
5. Obtain the perchloroethylene peak height or area of the injected sample (see Figure 1).

CALIBRATION AND QUALITY CONTROL:

6. Perform the following in the laboratory before field work begins:
  a. Establish a laboratory calibration graph with at least three replicate determinations of six or more working standards. Plot peak height or area vs. mass or concentration of perchloroethylene.
  b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
  c. Determine the ability of the GC column to separate the perchloroethylene peak from other substances known or predicted to be present in the field samples.
7. Establish a daily field calibration graph (peak height vs. mass or concentration of perchloroethylene).
  a. Fill Tedlar bags with standards, preferably commercially prepared and certified, or inject known amounts of pure perchloroethylene into Tedlar bags containing a metered volume of pure air or nitrogen. (See APPENDIX)
  b. Analyze working standards in triplicate under the same conditions as samples.
  c. Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

8. Determine mass, W (ppm), of perchloroethylene by comparison of sample peak height with daily calibration graph (step 7). Calculate concentration, C, of perchloroethylene in the sample volume injected, V (mL), applying the factor 6.8 to convert ppm to mg/m^3 at NTP.

$$C = \frac{6.8\ W}{V}, \ mg/m^3$$

NOTE 1: μg/mL ≡ mg/m^3
NOTE 2: Some GCs will perform this calculation electronically if programmed appropriately during the calibration phase.

EVALUATION OF METHOD:

This method was evaluated over the range 0.1 to 100 ppm perchloroethylene in air using a Photovac 10S portable gas chromatograph (Photovac International, Deer Park, NY). Certified standard gas mixtures of 1.0 ppm perchloroethylene in air were obtained from Scott Specialty Gases, Inc., (Troy, MI) These were verified by comparison with standards prepared from liquid and were then used to establish the calibration graphs. Analytical precision was determined by calculating the variation of replicate analyses of calibration standards and samples. Once calibration graphs were established, bias was assessed by analyzing a bag sample containing an unknown concentration and comparing the concentration obtained with that obtained from analysis of replicate charcoal tubes samples taken from the same bag. Additionally, a field evaluation was subsequently conducted in which results obtained using this method averaged 6% higher than results

obtained using conventional laboratory GC analysis by NMAM 1003 [2]. Sample bags should be analyzed as soon after collection as practical. Perchloroethylene (at concentrations of 5, 25, and 100 ppm) was found to be stable in Tedlar bags for more than 8 hours (loss of analyte <8%); storage for 24 hours resulted in a greater loss of analyte with increased concentration (20% loss of analyte at 100 ppm after 24 hours). Evaluation of this method, which uses a capillary column, indicated that perchloroethylene can be separated from acetone, isoprene, methanol, ethanol, acetaldehyde, carbon tetrachloride, chloroform, benzene, butane, styrene, toluene and xylenes. These compounds were selected for testing because they are either common human metabolites or substances which are frequently used in dry cleaning facilities with perchloroethylene.

Most permanent gases, including water vapor, carbon monoxide, and carbon dioxide, are not detected using a photoionization detector, and therefore, do not interfere with the analysis. However, water vapor at very high concentrations in exhaled breath was considered likely to condense in the bags subsequent to collection. To prevent condensation, exhaled breath was dried by passing it through a desiccant before entering the sample bag. The use of desiccant during the collection of exhaled breath samples was shown to decrease the perchloroethylene concentration by 7.0% at 1 ppm and 9.6% at 10 ppm, for an average 8.3% loss of analyte as a result of drying. Correction can be made for this loss either mathematically by increasing the measurement proportionally or by passing the calibration gas through the drying tube prior to calibration of the instrument.

REFERENCES:

[1] Sweet ND [1996]. A field method for near real-time analysis of perchloroethylene in end-exhaled breath [Dissertation]. Cincinnati, OH: University of Cincinnati, College of Medicine, Department of Environmental Health.
[2] NIOSH [1994]. Hydrocarbons, halogenated: Method 1003. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[3] NIOSH [1996]. Volatile organic compounds (screening): Method 2549. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed., 1st Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No.96-135.
[4] Toutonghi G, Echeverria D, Morgan M, et al [1994]. Characterization of exposure to perchloroethylene, with biological monitoring, in commercial dry cleaning workers, submitted for publication in Scandinavian Journal of Work and Industrial Health.

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APPENDIX

The volume of liquid perchloroethylene needed to create a calibration standard, if a commercial standard is not utilized, can be calculated as follows:

$$V_I = \frac{ppm \cdot MW \cdot L}{SpGr \cdot MV \cdot 10^6}$$

In the above equations:

ppm	=	parts per million, by volume, of perchloroethylene
MW	=	molecular weight of perchloroethylene
MV	=	molar volume (this value if 24.45 L at 25°C and 760mm Hg, but should be corrected if temperature or pressure vary significantly from these values.
V_I	=	volume of liquid perchloroethylene, in mL
L	=	volume of air in bag, in liters
SpGr	=	specific gravity of perchloroethylene, in g/mL

Concentrations in ppm can be converted to mg/m³ as follows:

$$mg/m^3 = \frac{(ppm)\ (MW)}{(MV)} = \frac{(ppm)\ (166)}{(24.45)} = (ppm) \times 6.8$$
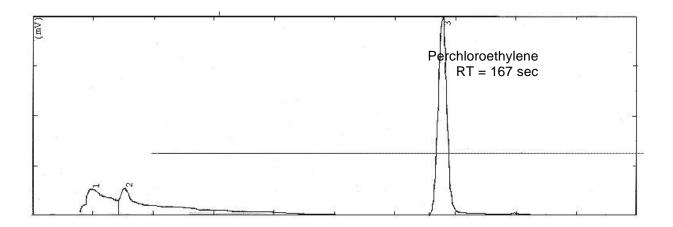

FIGURE 1 - Typical chromatogram obtained from the analysis of exhaled breath containing approximately 1.3 ppm perchloroethylene. Peak number 3 shows area of 598.1 mVs at a retention time of 167.4 sec. This is compared with a calibration curve in which a 1 ppm perchloroethylene standard produced a mean peak area of 452 mVs at a retention time of 167 sec.