1,1-Dichloro-1-fluoroethane (Freon 141b)
1,1,2-Trichloro-1,2,2-Trifluoroethane (Freon 113)

_____

Method number:	113
Matrix:	Air

Target concentrations:	Freon 141b 1000 ppm	Freon 113 1000 ppm
OSHA PEL:		1000 ppm (7600 mg/m3)
ACGIH TLV:		1000 ppm (TWA) (7600 mg/m3) 1250 ppm (STEL) (9580 mg/m3)

Procedure: Samples are collected by drawing a known volume of air through two standard size (6-mm o.d., 150/75) Anasorb CMS tubes connected in series. Samples are desorbed with carbon disulfide and analyzed by GC using a flame ionization detector (FID).

Recommended air volume and sampling rate: 1 L at 50 mL/min (20 min)

Reliable quantitation limits:	Freon 141b 2.7 ppm (13 mg/m3)	Freon 113 3.1 ppm (24 mg/m3)
Standard error of estimate at the target concentration:	Freon 141b 5.6%	Freon 113 5.4%

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: November 1998   Chemist: Donald Burright

1. General Discussion

1.1 Background

1.1.1 History

There has been an assortment of samplers to collect chlorofluorocarbons (Freons). They include standard charcoal tubes (100/50 mg), Carbosieve S-III (130/65 mg), jumbo charcoal tubes (400/200 mg), and two charcoal tubes in series (400/200 mg followed by 100/50 mg). (Refs. 5.1-5.4) The following adsorbents were tested for their capacity to collect Freons: activated coconut charcoal, Carbosieve S-III, Carbotrap, Carboxen 1000, Carboxen 1003, Anasorb CMS and Anasorb 747. Fluorotrichloromethane (Freon 11), dichlorodifluoromethane (Freon 12), chlorodifluoromethane (Freon 22) and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) were selected for testing based on the number of samples analyzed at the Salt Lake Technical Center (SLTC). 1,1,1,2-Tetrafluoroethane (Freon 134a) and 1,1-dichloro-1-fluoroethane (Freon 141b) were added to the list as commonly used members of the new 'environmentally-safe' Freons. Freon 11 was later dropped from testing because SLTC did not have adequate equipment to produce an atmosphere of stable concentration. Anasorb CMS (carbon molecular sieve) had the most capacity to collect the five Freons tested. So that all of the Freons could have at least a 15-min sampling time, at least 225 mg of Anasorb CMS must be in the front section of the sampling device. Therefore, the sampling device consists of two Anasorb CMS tubes (each containing two sections, 150/75 mg) in series. A goal of this work was to find a common sampler with a common sampling time for all five of the selected Freons.

Attempts to desorb the Freons from Anasorb CMS resulted in low recovery. This was due to the amount of air displaced and heat generated when the desorbing solvent was added to the vial containing the absorbent. Several solvents and techniques were tried with poor results. An aluminum block had holes drilled into it to fit the desorption vial. One technique that had worked with other analytes was to cool everything. The block, vials containing adsorbent, pipettes and desorbing solvent were all cooled to -20°C. The recovery of Freon from Anasorb CMS with these chilled components was less than 65%. The 'boiling' action observed in the vial was allowing the Freon to be driven out of solution and escape from the vial before it could be sealed with a cap. A room-temperature solution to this problem was found. The Anasorb CMS and desorbing solution are placed inside a vial and are not permitted to mix until the vial is sealed. Freon can not escape but is dissolved into the desorbing solution after the bubbles stop forming.

This method covers only Freon 141b and Freon 113 because all five Freons being studied were not soluble in the same solvent. This procedure uses carbon disulfide to desorb the samples. Freon 12, Freon 22 and Freon 134a are more soluble in a desorbing solution consisting of 60/40 dimethyl formamide/carbon disulfide and will be described in a later method.

2

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Short-term exposure to Freon 113 may cause irritation of the eyes and throat or drowsiness. Breathing high concentrations may cause the heart to beat irregularly or to stop. Prolonged or repeated skin exposure to Freon 113 may cause skin irritation. (Ref. 5.5)

Exposure to Freon 141b may cause dizziness, eye irritation, difficulty in breathing, rapid heartbeat, and low blood pressure. (Ref.5.6)

1.1.3 Workplace exposure

Freon 113 has been used as a refrigerant, a heat transfer medium, a solvent for oils and gums, a film processing solvent, a degreasing and dry-cleaning solvent, and an intermediate in the manufacture of chlorotrifluoroethylene. The Montreal Protocol on Substances that Deplete the Ozone Layer is expected to cause an international decline in its use and production in the 1990s. (Ref. 5.7)

Freon 141b is one of the new 'environmentally-safe' Freons. It is used as a degreasing solvent and as a blowing agent for refrigerator insulation. The US Clean Air Act mandates the phase out of Freon 141b by 2003 as it also depletes the ozone. (Ref. 5.8)

1.1.4 Physical properties and other descriptive information (Refs. 5.6, 5.7 and 5.9)

	Freon 141b	**Freon 113**
CAS number:	1717-00-6	76-13-1
molecular weight:	116.95	187.38
boiling point, °C:	32	48
melting point, °C:	- 103	- 35
color:	colorless	colorless
specific gravity:	1.25	1.57
molecular formula:	$C_2H_3Cl_2F$	$C_2Cl_3F_3$
vapor pressure, kPa (mmHg):	2 (15)	44 (330)
odor:		slight ethereal
solubility:	insoluble in water	alcohol; ether; benzene; 0.02% in water
synonyms:	Freon 141b; FC-141b; HCFC-141b	Freon 113; CFC-113; F-113; TTE

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.12 and 0.26 ng for Freon 141b and Freon 113, respectively. These are the amounts of each analyte that will give a response that is significantly different from the background response of a reagent blank. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 4.0 (0.84 ppm or 4.0 mg/m^3) and 7.2 (0.94 ppm or 7.2 mg/m^3) µg per sample for Freon 141b and Freon 113, respectively. These are the amounts of each analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limits are 13 (2.7 ppm or 13 mg/m^3) and 24 (3.1 ppm or 24 mg/m3) µg per sample for Freon 141b and Freon 113, respectively. These are the amounts of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical Procedure)

The precision of the analytical procedure, measured as the pooled relative standard deviation over a concentration range equivalent to the range of 0.5 to 2 times the target concentration, is 0.93% and 0.45% for Freon 141b and Freon 113, respectively. (Section 4.5)

1.2.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage tests (at the target concentration) is ±11.0 and ±10.5 for Freon 141b and Freon 113, respectively. This includes an additional 5% for sampling error. (Section 4.6)

1.2.6 Recovery

The recoveries of Freon 141b and Freon 113 from samples used in the 15-18 day storage tests remained above 99.2% and 100.7% respectively when the samples were stored at 22°C. (Section 4.7)

1.2.7 Reproducibility

Six samples, for each analyte, were spiked with a solution containing one of the Freons after 1 L of humid air had been drawn through the sampling tubes. These samples were submitted for analysis by one of the OSHA Salt Lake Technical Center's service branch laboratories along with a draft copy of this procedure. The samples were analyzed after 15 days of storage at 4°C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.8)

2 Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, within ±5% at the recommended flow rate.

2.1.2 Samples are collected with two 7-cm x 4-mm i.d. x 6-mm o.d. glass sampling tubes, each packed with two sections of (150/75 mg) Anasorb CMS, connected in series. The sections are held in place with a glass wool plug and two urethane foam plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-121).

2.2 Reagents

None required.

2.3 Technique

2.3.1 Immediately before sampling, break off the ends of both sampling tubes. All tubes should be from the same lot. Connect the outlet end of one tube to the inlet end of the other tube with a 1-in. length of 3/16-in. i.d. silicone rubber tubing. Ensure that the connection is secure and that the broken ends of the tubes just touch each other. Be careful not to cut the silicone tubing with the sharp ends of the sampling tubes.

2.3.2 Attach the sampling device to the sampling pump with flexible, non-crimping tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tubes so that the sampled air first passes through the inlet of the sampling device.

2.3.3 Air being sampled should not pass through any hose or tubing before entering the sampling device.

2.3.4 To avoid channeling, attach the sampler vertically with the inlet pointing downward, in the worker's breathing zone. Position the sampler so it does not impede work performance or safety.

2.3.5 After sampling for the appropriate time, immediately remove the sampling device, separate the tubes and seal them with plastic end caps.

2.3.6 Wrap each tube end-to-end with an OSHA-21 form.

2.3.7 Submit at least one blank sample with each set of samples. Handle the blank sampling tube in the same manner as the other samples, except draw no air through it.

2.3.8 Record sample air volumes (in liters) for each sample, along with any potential interferences.

2.3.9 Ship any bulk sample(s) in a container separate from the air samples.

2.3.10 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at reduced temperature.

2.4 Sampler capacity

Sampler capacity is determined by measuring how much air can be sampled before the analyte breaks through the sampler, i.e., the sampler capacity is exceeded. Breakthrough is considered to occur when the effluent from the sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). Testing for breakthrough was performed by using a GC/FID to monitor the effluent from sampling tubes, each containing 225-mg of Anasorb CMS. Dynamically generated test atmospheres, which were about two times the target concentration of each analyte, were used for the capacity tests. The samples were collected at 50 mL/min and the relative humidity was about 75% at 25°C. The 5% breakthrough air volumes were calculated from the data of duplicate determinations and are 8.66 and 3.88 L for Freon 141b and Freon 113, respectively. (Section 4.9) A goal of this procedure was to develop a common sampling

device with a common sampling time for all five studied Freons. 1,1,1,2-Tetrafluoroethane had the shortest sampling time and that was the limiting factor in selecting the 20-min sampling time.

2.5 Desorption efficiency

2.5.1 The average desorption efficiencies for Freon 141b and Freon 113 from Anasorb CMS over the range of 0.5 to 2.0 times the target concentrations (TC) are 99.6% and 100.3%, respectively. (Section 4.10)

2.5.2 The desorption efficiencies at 0.05, 0.1 and 0.2 times the target concentrations (TC) were found to be very good and are listed below. (Section 4.10)

Table 2.5.2
Desorption Efficiencies at
0.05 to 0.2 times TC, %

TC	Freon 141b	Freon 113
0.05x	98.3	98.4
0.1x	99.0	98.8
0.2x	100.5	98.9

2.5.3 Desorbed samples remain stable for at least 24 h.

2.6 Recommended air volume and sampling rate

2.6.1 For long-term samples, collect 1.0 L at 50 mL/min for 20 min.

2.6.2 For short-term samples, collect 0.75 L at 50 mL/min for 15 min.

2.6.3 When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limits are 3.6 ppm (17 mg/m3) and 4.1 ppm (32 mg/m3) for Freon 141b and Freon 113, respectively, when 0.75 L is sampled.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of Freon 141b or Freon 113 on Anasorb CMS. In general, the presence of other contaminant vapors in the air will reduce the capacity of Anasorb CMS to collect both analytes.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.7.3 Safety precautions (sampling)

2.7.4 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.7.5 All safety practices that apply to the work area being sampled should be followed.

2.7.6 Protective eyewear should be worn when breaking off the ends of the glass sampling tubes.

3. Analytical Procedure

3.1 Apparatus

3.1.1 Gas chromatograph equipped with an FID. For this evaluation, a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a 7673A Automatic Sampler was used. A Forma Scientific Model 2006 refrigerated circulator was used to cool the sample tray of the HP 7673A to 10°C to minimize evaporation.

3.1.2 A GC column capable of separating the analyte of interest from the desorbing solvent, internal standard and any interferences. A 60-m x 0.32-mm i.d. fused silica DB-624 column with a 1.8-µm df (J&W Scientific, Folsom, CA) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters 860 Networking Computer System and an HP GC ChemStation were used in this evaluation.

3.1.4 Two- and four-milliliter vials with polytetrafluoroethylene-lined caps. Seven-milliliter scintillation vials with polytetrafluoroethylene-lined caps.

3.1.5 Three-fourths milliliter autosampler vials (8-mm x 30-mm) from Kimble Glass (catalog no. 60831D-830).

3.1.6 A dispenser capable of delivering 4.0 mL of desorbing solvent to prepare standards and samples. If a dispenser is not available, a 4.0-mL volumetric pipette may be used.

3.2 Reagents

3.2.1 1,1-Dichloro-1-fluoroethane (Freon 141b), reagent grade or better. The Freon 141b, 97%, used in this evaluation was purchased from PCR, Inc. (Gainesville, FL).

3.2.2 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113), reagent grade or better. The Freon 113, distilled in glass, used in this evaluation was purchased from Burdick & Jackson Laboratories, Inc. (Muskegon, MI).

3.2.3 Carbon disulfide (CS2), reagent grade or better. The CS2, 99.9+% - low benzene, used in this evaluation was purchased from Aldrich Chemical (Milwaukee, WI).

3.2.4 A suitable internal standard, reagent grade. The benzene, 99.94%, used in this evaluation was purchased from EM Science (Gibbstown, NJ).

3.2.5 Desorbing solvent. The desorbing solvent contains 200 µL of benzene per 1 L of CS2.

3.2.6 GC grade nitrogen, air, and hydrogen.

3.3 Standard preparation

3.3.1 Prepare concentrated stock standard of Freon 141b and Freon 113 in CS2. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 4-mL vials containing 4.0 mL of desorbing solvent delivered from the same dispenser used to desorb samples. Transfer the standard solution to 2-mL autosampler vials, if necessary. For example, to prepare a target level

standard of Freon 141b, inject 20 µL of a stock solution containing 246 mg/mL of Freon 141b in CS2 into 4 mL of desorbing solvent.

3.3.2 Bracket sample concentrations with working standard concentrations. If samples fall outside the concentration range of prepared standards, prepare and analyze additional standards or dilute the sample.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tube and carefully transfer both sections of the adsorbent (225 mg) to a 0.75-mL vial. Do not place any markings or tape on the 0.75 mL vial because it will be placed in the desorbing solvent. Discard the glass tube, urethane foam plugs and glass wool plug. Place the 225 mg of adsorbent from the back-up tube in a separate 0.75 mL vial.

3.4.2 Add 4.0 mL of desorbing solvent to each 7-mL scintillation vial using the same dispenser as used for preparation of standards.

3.4.3 Insert the 0.75-mL vial into the 7-mL vial and immediately seal the 7-mL vial with a polytetrafluoroethylene-lined cap.
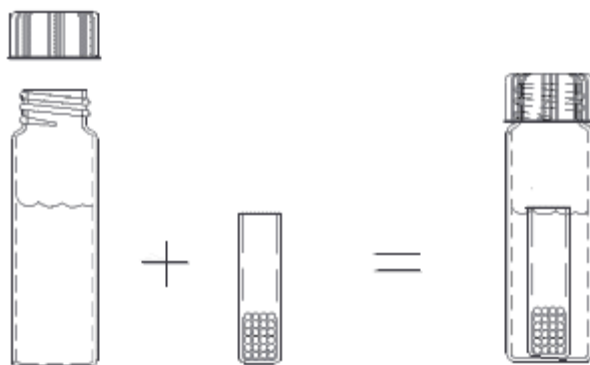
3.4.4 Shake the vial vigorously by hand several times while keeping the vial horizontally during the next 60 min. This will permit the solvent inside the small vial to mix with the solvent in the larger vial. Do not use a mechanical shaker to agitate the sample. The adsorbent beads will cause the small vial to become stuck in the neck of the larger vial and the result will be inadequate desorption.

3.4.5 Transfer the sample solution to a 2-mL autosampler vial, if necessary.

3.5 Analysis

3.5.1 Analytical conditions

GC conditions

zone temperatures:	35°C (column)
	250°C (injector)
	300°C (detector)
run time:	15 min

column gas flow:	2.5 mL/min (hydrogen)
septum purge:	1.5 mL/min (hydrogen)
injection size:	1.0 µL (10.2:1 split)
column:	60-m x 0.32-mm i.d. capillary DB-624 (df = 1.8 µm)
retention times:	6.03 min (Freon 141b)
	6.55 min (Freon 113)
	10.03 min (benzene)

FID conditions

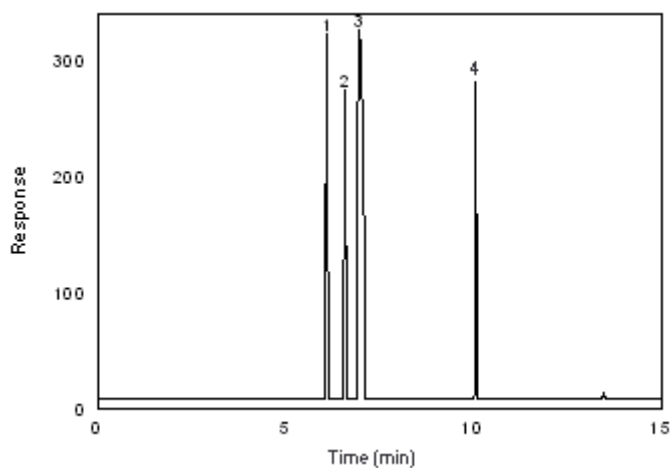|	
hydrogen flow:	34 mL/min
air flow:	450 mL/min
makeup flow:	33 mL/min (nitrogen)

Figure 3.5.1. Chromatogram of Freon 141b and Freon 113 at the target concentration. 1 - Freon 141b, 2 - Freon 113, 3 - CS2, 4 - benzene.

3.5.2 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting micrograms of analyte per sample versus ISTD-corrected response of standard injections. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an FID response and has a similar retention time as the analytes or internal standard is a potential interference. If any potential interferences were reported, they should be considered before the samples are desorbed.

3.6.2 Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.3 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data. (Section 4.11)

9

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for desorption efficiency. The back tube is analyzed primarily to determine if there was any breakthrough from the front tube during sampling. If a significant amount of analyte is found on the back tube (e.g., greater than 25% of the amount found on the front tube), this fact should be reported with the sample results. If any analyte is found on the back tube, it is added to the amount on the front tube. This amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulae.

$$\text{mg/m}^3 = \frac{(\text{micrograms of analyte per sample})}{(\text{liters of air sampled})(\text{desorption efficiency})}$$

$$\text{ppm} = \frac{(\text{mg/m}^3)(24.46)}{(\text{molecular weight of analyte})}$$

where   molar volume at 25°C and 101.3 kPa (760 mmHg) is 24.46

molecular weight of Freon 141b is 116.95

molecular weight of Freon 113 is 187.38

3.8 Safety precautions (analytical)

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Backup Data

4.1 Determination of detection limits

$$\text{YDL} - \text{YBR} = 3(\text{SDBR})$$

Detection limits, in general, are defined as the amount (or concentration) of analyte that gives a response (YDL) that is significantly different [three standard deviations (SDBR)] from the background response (YBR).

$$SEE = \frac{\sqrt{\Sigma\,(\text{Yobs} - \text{Yest})^2}}{n - k}$$

The measurement of YBR and SDBR in chromatographic methods is typically inconvenient and difficult because YBR is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SDBR and the precision of the data about curve are similar, the

standard error of estimate (SEE) for the regression curve can be substituted for SDBR in the above equation. The following calculations derive a formula for DL:

where

Yobs is observed response
Yest is estimated response from regression curve
n is total number of data points
k is 2 for linear regression curve

At point YDL on the regression curve

$$YDL = A(DL) + YBR$$

where A is analytical sensitivity (slope)

therefore

$$DL = \frac{(YDL - YBR)}{A}$$

Substituting 3(SEE) + YBR for YDL gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte actually introduced into the chromatographic column. Ten analytical standards were prepared in equal descending increments with the highest standard containing 19.2 and 30.7 μg/mL of Freon 141b and Freon 113, respectively. This is the concentration that would produce a peak approximately 10 times the baseline noise of a reagent blank near the elution time of the analyte. These standards, and the reagent blank, were analyzed with the recommended analytical parameters (1-μL injection with a 10.2:1 split), and the data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP.

Table 4.2.1.
DLAP Data for Freon 141b
A = 186 SEE = 7.16

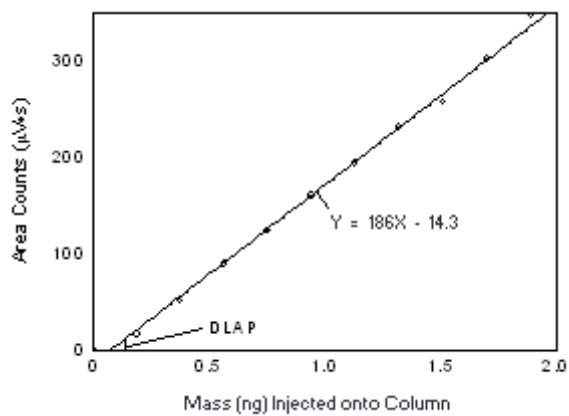| concentration (µg/mL)	mass on column (ng)	area counts (µV-s)
0	0	0
1.92	0.188	16
3.85	0.377	50
5.77	0.565	89
7.69	0.754	124
9.61	0.942	160
11.5	1.13	194
13.5	1.32	231
15.4	1.51	258
17.3	1.70	303
19.2	1.89	348

Figure 4.2.1. Plot of the data from Table 4.2.1 to determine the DLAP of Freon 141b, DLAP = 0.12 ng.

12

Table 4.2.2.
DLAP Data for Freon 113
A = 112 SEE = 9.87

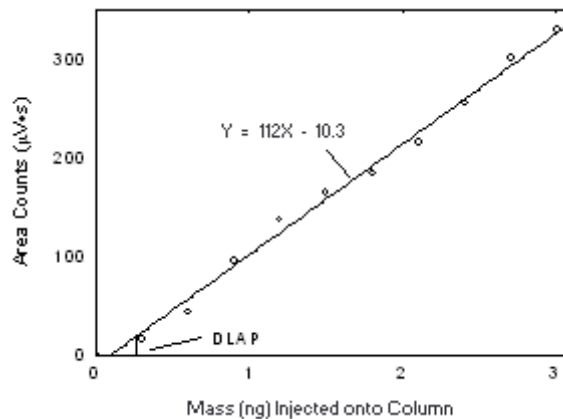| concentration (µg/mL)	mass on column (ng)	area counts (µV-s)
0	0	0
3.07	0.301	16
6.14	0.602	43
9.21	0.903	96
12.3	1.20	137
15.4	1.50	165
18.4	1.81	184
21.5	2.11	216
24.6	2.41	256
27.6	2.71	302
30.7	3.01	330

Figure 4.2.2. Plot of the data from Table 4.2.2 to determine the DLAP of Freon 113, DLAP = 0.26 ng.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 76.9 and 123 µg/sample of Freon 141b and Freon 113, respectively. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the baseline noise for a sample blank. These spiked samplers, plus a sample blank, were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required

parameters (A and SEE) for the calculation of the DLOP. For Freon 141b, the values of 4.12 and 44 were obtained for A and SEE, respectively and the DLOP was calculated to be 4.0 µg per sample (0.84 ppm or 4.0 mg/m³). For Freon 113, the values of 2.33 and 62 were obtained for A and SEE, respectively and the DLOP was calculated to be 7.2 µg per sample (0.94 ppm or 7.2 mg/m³).

Table 4.3.1.
DLOP Data for Freon 141b

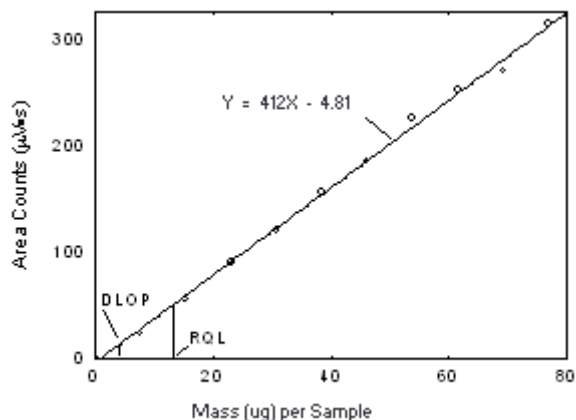| mass per sample (µg)	area counts (µV-s)
0	0
7.69	23
15.4	55
23.1	90
30.8	120
38.5	156
46.1	185
53.8	226
61.5	252
69.2	270
76.9	314

Figure 4.3.1. Plot of the data from Table 4.2.1 to determine the DLOP of Freon 141b on Anasorb CMS, (SEE = 5.44).

Table 4.3.2.
DLOP Data for Freon 113

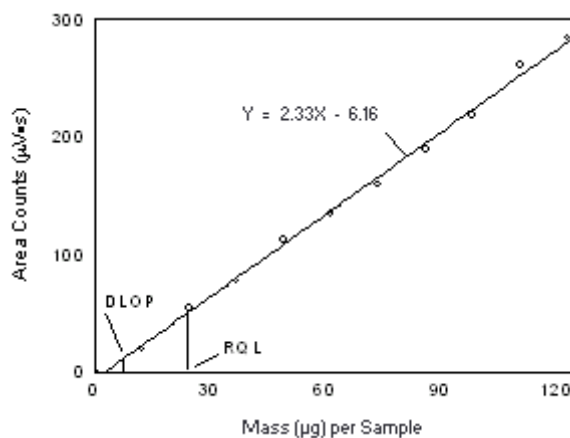| mass per sample (µg)	area counts, (µV-s)
0	0
12.3	19
24.6	54
36.8	77
49.1	112
61.4	135
73.7	159
86.0	189
98.2	218
111	261
123	284

Figure 4.3.2. Plot of the data from Table 4.2.1 to determine the DLOP of Freon 113 on Anasorb CMS, (SEE = 5.62).

4.4 Reliable quantitation limit (RQL)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculations of the DLOP (Section 4.3), providing at least 75% of the analyte is recovered. The RQL is defined as the amount of analyte that gives a response (YRQL) such that

$$YRQL - YBR = 10(SDBR)$$
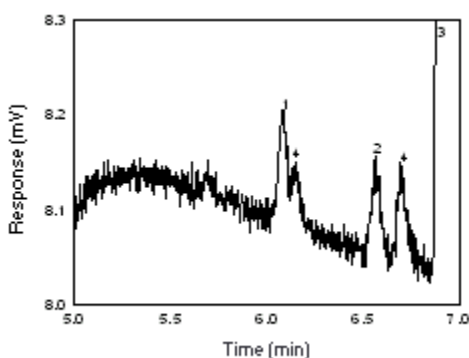
therefore

$$RQL = \frac{10(SEE)}{A}$$

Figure 4.4. Chromatogram of the RQL for both analytes on Anasorb CMS. 1 = Freon 141b, 2 = Freon 113, 3 = CS_2, 4 = interference.

Table 4.4
Reliable Quantitation Limits

Freon 141b	Freon 113
13 µg	24 µg
2.7 ppm	3.1 ppm
13 mg/m3	24 mg/m3

The RQL for each analyte was calculated and is listed above. The recovery of the analyte near the RQL was 99.5% and 96.3% for Freon 141b and Freon 113, respectively.

4.5 Precision (analytical method)

The precision of the analytical procedure is measured as the pooled relative standard deviation (RSDP). Relative standard deviations are determined from six replicate injections of analyte standards at 0.5, 0.75, 1, 1.5 and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, RSDP was calculated to be 0.93% and 0.45% for Freon 141b and Freon 113, respectively.

Table 4.5.1
Instrument Response to Freon 141b

x target concn (µg/mL)	0.5x 615	0.75x 923	1x 1230	1.5x 1845	2x 2460
area counts	157.23	235.20	295.72	441.19	574.19
(mV-s)	157.22	229.84	297.38	448.19	573.49
	159.56	230.53	296.14	437.30	571.21
	160.15	226.62	296.65	451.01	590.26
	156.29	229.93	300.30	444.80	585.16
	156.31	225.81	302.17	440.63	581.85
X	157.79	229.66	298.06	443.85	579.36
SD	1.375	2.293	2.117	4.147	6.396
RSD (%)	0.871	0.999	0.710	0.934	1.104

Table 4.5.2
Instrument Response to Freon 113

x target concn (µg/mL)	0.5x 981	0.75x 1472	1x 1963	1.5x 2944	2x 3925
area counts	117.04	175.15	234.08	341.46	453.08
(mV-s)	118.30	174.88	231.15	341.14	455.29
	119.16	173.80	231.67	345.79	454.31
	118.39	176.22	230.90	343.27	457.94
	118.97	177.26	231.56	342.88	454.54
	119.72	175.66	233.42	343.47	452.17
X	118.60	175.49	232.13	343.00	454.56
SD	0.686	0.885	1.082	1.175	4.372
RSD (%)	0.579	0.504	0.466	0.343	0.302

The Cochran test for homogeneity:

$$g = \frac{\text{largest RSD2}}{\text{RSD0.5x2} + \text{RSD0.75x2} + \text{RSD1x2} + \text{RSD1.5x2} + \text{RSD2x2}}$$

The critical value of the g-statistic, at the 95% confidence level, for five variances, each associated with six observations is 0.5065. The g-statistics are 0.2801 and 0.3301 for Freon 141b and Freon 113, respectively. Because the g-statistic does not exceed this value, the RSDs can be considered equal and they can be pooled (RSDP) to give an estimated RSD for the concentration range studied.

$$RSDP = \frac{\sqrt{5\,(\text{RSD0.5x2} + \text{RSD0.75x2} + \text{RSD1x2} + \text{RSD2x2})\text{Yobs} - \text{Yest}\,)^2}}{5+5+5+5+5}$$

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEER) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEER is similar to the standard deviation, except it is a measure of the dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE = \frac{\sqrt{\Sigma\,(\text{Yobs} - \text{Yest}\,)^2}}{n-k}$$

where

Yobs = observed % recovery at a given time
Yest = estimated % recovery from the regression line at the same given time
n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression

An additional 5% for pump error (SP) is added to the SEER by the addition of variances to obtain the total standard error of the estimate.

$$SEE = \sqrt{(SEER)^2 + (SP)^2} \qquad |^2$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1.1 through 4.7.2.2. The precisions of the overall procedure and the associated figures are listed below.

4.7 Storage test

4.7.1 Freon 141b

Storage samples were generated by sampling from a controlled test atmosphere containing 3400 mg/m3 of Freon 141b, about 0.7 times the 1000-ppm target concentration. Anasorb CMS tubes were used to sample for 20 min at 50 mL/min, the relative humidity was about 80% at 22°C. Thirty-six storage samples were prepared. Six samples were analyzed immediately after generation, fifteen tubes were stored at reduced temperature (4°C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22°C). At 2-4 day intervals, three samples were selected from each of the two sets and analyzed.

Table 4.7.1
Storage Test for Freon 141b on Anasorb CMS

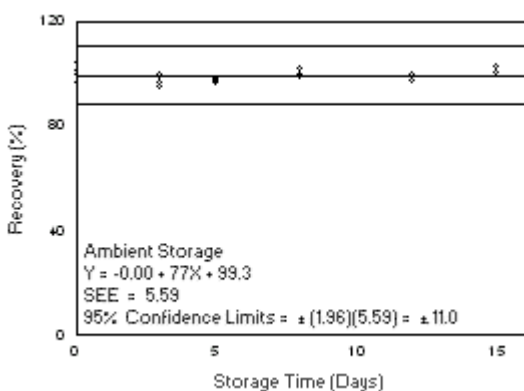| time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.2	101.6	100.5	97.2	101.6	100.5
	102.1	104.6	100.5	102.1	104.6	100.5
3	94.8	96.4	98.9	99.5	103.8	101.0
5	96.0	96.8	97.8	98.9	99.9	101.8
8	98.7	99.4	101.5	100.9	101.1	99.2
12	96.8	99.5	99.0	101.3	99.9	101.0
15	100.1	100.3	102.3	101.2	97.5	103.6

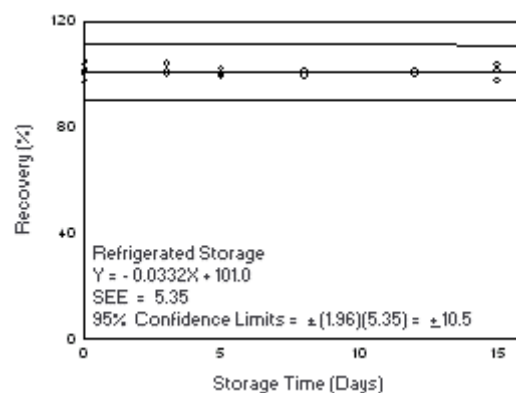Figure 4.7.1.1. Ambient storage test for Freon 141b.

Figure 4.7.1.2. Refrigerated storage test for Freon 141b.

4.7.2 Freon 113

Storage samples were generated by sampling from a controlled test atmosphere containing 6700 mg/m3 of Freon 113, about 0.9 times the 1000-ppm target concentration. Anasorb CMS tubes were used to

sample for 20 min at 50 mL/min, the relative humidity was about 80% at 22°C. Thirty-six storage samples were prepared. Six samples were analyzed immediately after generation, fifteen tubes were stored at reduced temperature (4°C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22°C). At 3-5 day intervals, three samples were selected from each of the two sets and analyzed.

Table 4.7.2
Storage Test for Freon 113 on Anasorb CMS

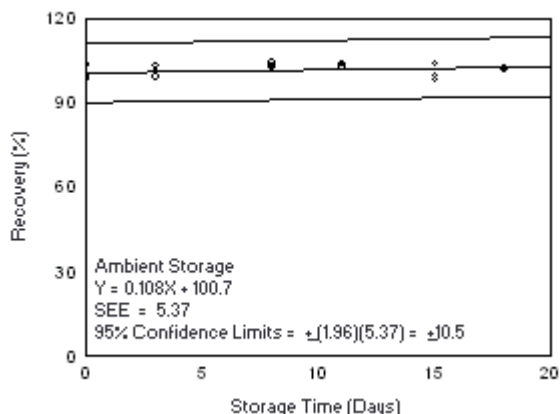| time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	103.4	98.7	100.3	103.4	98.7	100.3
	100.0	98.1	99.3	100.0	98.1	99.3
3	99.1	103.1	101.1	99.8	104.8	100.5
8	102.9	102.5	104.1	104.2	100.9	100.8
11	103.7	102.8	103.8	103.3	105.7	103.8
15	99.5	98.2	103.9	103.3	101.9	102.8
18	102.4	102.4	102.1	104.0	100.4	104.8

Figure 4.7.2.1. Ambient storage test for Freon 113.
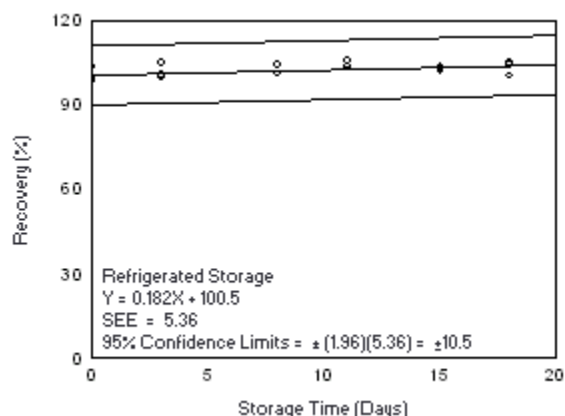

Figure 4.7.2.2. Refrigerated storage test for Freon 113.

4.8 Reproducibility

Six samples for each analyte were prepared by drawing humid air through the sampling tube for 20 min at 50 mL/min. The samplers were then liquid-spiked with an aliquot of a solution containing one of the Freons. The samples were submitted, along with a draft copy of this procedure, to an OSHA Salt Lake Technical Center service branch. The samples were analyzed after being stored for 15 days at 4°C. Sample results were

corrected for desorption efficiency. No sample result for Freon 141b or Freon 113 had a deviation greater than the precision of the overall procedure determined in Section 4.6.

Table 4.8
Reproducibility Data

	Freon 141b				Freon 113			
sample	expected (ppm)	reported (ppm)	recovery (%)	deviation (%)	expected (ppm)	reported (ppm)	recovery (%)	deviation (%)
1	1015	916.0	90.6	- 9.4	979	924.3	94.1	- 5.9
2	1015	964.4	95.4	- 4.6	979	894.0	91.0	- 9.0
3	1015	995.3	98.5	- 1.5	979	903.4	92.0	- 8.0
4	1015	1017.7	100.7	+ 0.7	979	926.3	94.3	- 5.7
5	1015	1010.1	99.9	- 0.1	979	929.4	94.6	- 5.4
6	1015	996.5	98.6	- 1.4	979	940.3	95.8	- 4.2

4.9 Sampler capacity

The sampling capacity of a sampling tube containing 225 mg of Anasorb CMS was tested by sampling from a dynamically generated test atmosphere of Freon 141b (9560 mg/m3 or 1999 ppm) or Freon 113 (15300 mg/m3 or 1998 ppm). The samples were collected at 50 mL/min and the relative humidity was about 75% at 25°C. A GC with a gas sampling valve was placed in-line behind the 225-mg front test section. The valve was rotated to measure the amount of Freon passing through the sampler at the time of rotation. The 5% breakthrough air volume was determined to be 8.66 and 3.88 L for Freon 141b and Freon 113, respectively.

Table 4.9.1
Capacity of Freon 141b on Anasorb CMS

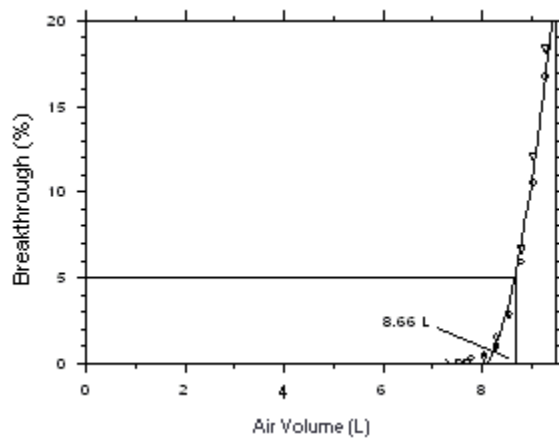| first test		second test	
air volume (L)	breakthrough (%)	air volume (L)	breakthrough (%)
7.30	0	7.54	0
7.55	0	7.80	0
7.80	0.27	8.05	0.36
8.05	0.48	8.3	1.0
8.30	1.5	8.55	2.9
8.55	2.7	8.80	6.7
8.80	5.9	9.05	12.1
9.05	10.5	9.3	18.4
9.30	16.7		

Figure 4.9.1. Five percent breakthrough air volume for Freon 141b on Anasorb CMS.

Table 4.9.2
Capacity of Freon 113 on Anasorb CMS

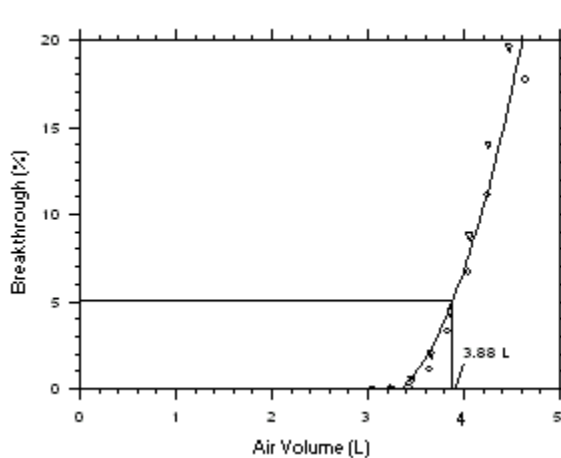| first test		second test	
air volume (L)	breakthrough (%)	air volume (L)	breakthrough (%)
3.24	0	3.05	0
3.44	0	3.25	0
3.64	1.1	3.46	0.60
3.85	3.3	3.66	2.0
4.05	6.7	3.86	4.4
4.25	17.7	4.26	14.0
		4.47	19.6

Figure 4.9.2. Five percent breakthrough air volume for Freon 113 on Anasorb CMS.

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Freon 141b

The desorption efficiencies (DE) of Freon 141b were determined by liquid-spiking 225-mg of Anasorb CMS in a vial with amounts equivalent to 0.05 to 2 times the 1000-ppm target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the working range of 0.5 to 2 times the target concentration is 99.6%.

22

Table 4.10.1.1
Desorption Efficiency of Freon 141b from Anasorb CMS

x target concn (µg/sample)	0.05x 246	0.1x 492	0.2x 984	0.05x 2460	0.1x 4920	0.2x 9840
DE (%)	98.0	98.5	100.3	98.2	99.3	99.2
	99.6	97.8	99.0	97.1	103.3	99.9
	98.8	97.9	103.0	96.7	101.9	102.3
	97.1	99.3	99.6	95.2	101.3	102.2
	99.6	99.2	100.7	96.4	101.6	100.4
	96.6	101.4	100.4	100.7	96.7	99.8
X	98.3	99.0	100.5	97.4	100.7	100.6

The stability of desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, three vials were recapped with new septa while the remaining three retained their punctured septa. The samples vials were stored in the refrigerated sampling tray (10°C) for the GC injector. The samples were reanalyzed with fresh standards. The average percent change was +1.6% for samples that were resealed with new septa, and - 0.3% for those that retained their punctured septa.

Table 4.10.1.2
Stability of Desorbed Samples for Freon 141b from Anasorb CMS

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
99.3	102.6	+3.3	101.3	98.5	- 2.8
103.3	105.2	+1.9	101.6	99.1	- 2.5
101.9	101.6 (averages)	- 0.3	96.7	101.2 (averages)	+4.5
101.5	103.1	+1.6	99.9	99.6	- 0.3

4.10.2 Freon 113

The desorption efficiencies (DE) of Freon 113 were determined by liquid-spiking 225-mg of Anasorb CMS in a vial with amounts equivalent to 0.05 to 2 times the 1000-ppm target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the working range of 0.5 to 2 times the target concentration is 100.3%.

Table 4.10.2.1
Desorption Efficiency of Freon 113 from Anasorb CMS

x target concn (µg/sample)	0.05x 243.1	0.1x 486.2	0.2x 972.4	0.5x 2431	1x 4862	2x 9724
DE (%)	97.9	100.2	98.4	99.5	99.5	99.8
	98.9	98.7	98.5	100.3	100.6	101.0
	98.8	98.5	99.0	100.6	100.7	99.8
	99.7	98.5	99.2	99.6	100.4	101.4
	97.6	98.6	99.5	100.3	100.7	100.2
	97.6	98.2	99.0	99.5	101.3	100.4
mean	98.4	98.8	98.9	100.0	100.5	100.4

The stability of desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, three vials were recapped with new septa while the remaining three retained their punctured septa. The samples vials were stored in the refrigerated sampling tray (10°C) for the GC injector. The samples were reanalyzed with fresh standards. The average percent change was - 0.9% for samples that were resealed with new septa, and - 0.9% for those that retained their punctured septa.

Table 4.10.2.2
Stability of Desorbed Samples for Freon 113 from Anasorb CMS

punctured septa replaced			**punctured septa retained**		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
99.5	98.5	- 1.0	100.4	99.4	- 1.0
100.6	99.6	- 1.0	100.7	99.3	- 1.4
100.7	100.1 (averages)	- 0.6	96.7	101.3 (averages)	- 0.2
100.3	99.4	- 0.9	100.8	99.9	- 0.9

4.11 Qualitative analysis

Freon 141b and Freon 113 can be easily separated and identified by GC/MS. Mass spectra were obtained from an HP5973 Mass Selective Detector interfaced to an HP6890 GC.
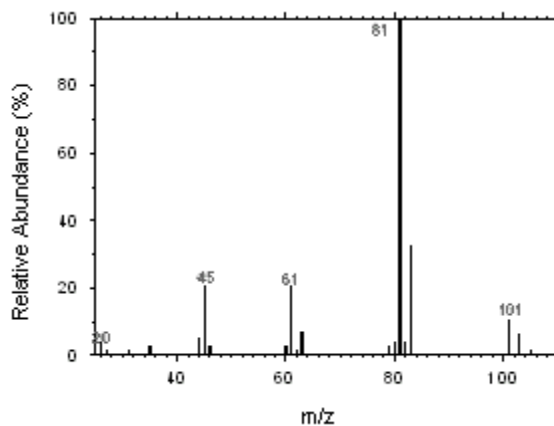

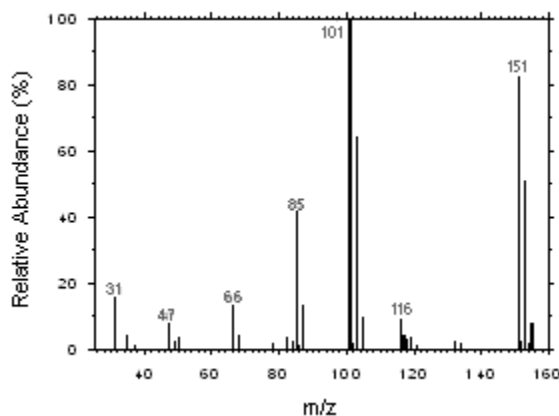Figure 4.11.1. Mass spectrum of Freon 141b.

Figure 4.11.1. Mass spectrum of Freon 113.

5. References

5.1 NIOSH Manual of Analytical Methods, Eller, P.M., Ed, 4th ed., US Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Science and Engineering, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, 1994; Method 1018. (Back to Text).

5.2 NIOSH Manual of Analytical Methods, Eller, P.M., Ed, 4th ed., US Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Science and Engineering, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, 1994; Method 1020.

5.3 NIOSH Manual of Analytical Methods, Eller, P.M., Ed, 4th ed., US Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Science and Engineering, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, 1994; Method 1006.

5.4 OSHA Computerized Information System Database, Chemical Sampling Information, Salt Lake Technical Center, Occupational Safety and Health Administration, Salt Lake City, UT, Sept 1998. (Back to Text)

5.5 Occupational Health Guidelines for Chemical Substances, NIOSH/OSHA, DHHS (NIOSH) Publ No. 81-123, Jan 1981. (Back to Text)

5.6 Material Safety Data Sheet: 1,1-Dichloro-1-fluoroethane, PCR, Inc., Gainesville, FL, Nov 1992. (Back to Text)

5.7 Documentation of the Threshold limits Values and Biological Exposures Indices, 6th ed., American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, Vol. III, pp. 1631-1635. (Back to Text)

5.8 Hileman, B.; A Chilling Battle. Chem. Eng. News, 1998, 76(31), 33-34. (Back to Text)

5.9 Material Safety Data Sheet; Trichlorotrifluoroethane, DuPont Canada, Inc., Mississauga, Ontario, Jan 1998. (Back to Text