96/3-28-90 JS ②

The Purity of Electronic Grade 1, 1, 2-Trichlorotrifluoroethane by Gas Chromatography

Kansas City Division

S. V. Dubiel

KCP-613-4202

Published March 1990

Final Report

DO NOT MICROFILM
COVER

Prepared for the United States Department of Energy Under Contract Number DE-AC04-76-DP00613.

Allied-Signal Aerospace Company

Allied
Signal

KCP-613-4202
Distribution Category 701

KCP--613-4202

DE90 008161

THE PURITY OF ELECTRONIC GRADE 1,1,2-TRICHLOROTRIFLUOROETHANE BY GAS CHROMATOGRAPHY

S. V. Dubiel

Published March 1990

Final Report
S. V. Dubiel, Project Leader

Project Team:
T. L. Harper

Technical Communications
Kansas City Division

Allied-Signal Aerospace Company

Allied Signal

MASTER

THE PURITY OF ELECTRONIC GRADE 1,1,2-TRICHLOROTRIFLUOROETHANE BY GAS CHROMATOGRAPHY

KCP-613-4202, Final Report, Published March 1990

Prepared by S. V. Dubiel

A gas chromatography (GC) method was developed to determine the purity of electronic grade 1,1,2-trichlorotrifluoroethane (TCTFE) for use in cleaning electronic components. High purity TCTFE is required to assure that the impurities would not inhibit or increase solvency characteristics. The low ppm chlorinated hydrocarbon (CHC) and chlorofluorocarbon (CFC) impurities were separated on a GC packed column containing a polydimethylsiloxane stationary phase and helium as the carrier gas. Flame ionization detected the resolved impurities as they eluted from the column. The standard addition method and computer intergration was used for quantitation. The concentration of known and unknown impurities were added together and subtracted from 100% to obtain the percent purity of TCTFE. The relative standard deviation (RSD) for ten replicate peak area determinations varied from 2 to 4% for most of the known impurities. The RSD for calculating ten replicate concentrations for two known impurities in the same sample was 2.8% for the 2.4 ppm (w/w) impurity and 1.3% for the 12.4 ppm impurity.

DC:ck

TRl/ai

A prime contractor with the United States
Department of Energy under Contract Number
DE-AC04-76-DP00613

Kansas City Division
P.O. Box 419159
Kansas City, Missouri
64141-6159

CONTENTS

Section Page

APPENDICES

ILLUSTRATION

TABLES

SUMMARY

A gas chromatography (GC) method was developed for determining the purity of electronic grade 1,1,2-trichlorotrifluoroethane (TCTFE). The solvent is suitable for cleaning electronic components. High purity TCTFE is required to assure that the impurities would not inhibit or increase solvency characteristics.

The present method was developed from procedures supplied by E. I. Du Pont De Nemours & Company (Inc.), Chemicals and Pigments Department, Wilmington, DE, and Allied-Signal Inc., Engineered Materials Sector, Morristown, NJ. The injection of known compounds assisted in identifying which of the low ppm chlorinated hydrocarbon (CHC) and chlorofluorocarbon (CFC) impurities were present in TCTFE. The standard addition method and computer intergration was used for quantitation. The TCTFE sample was first chromatographed. Known amounts of the impurities were added to a known amount of TCTFE. The solution was then chromatographed under the same condition. From these known amounts, the quantity of each impurity originally present in TCTFE was determined. The amount of unknown impurities were also calculated based on the total weight percents and total peak areas of the known peaks together with the total peak areas of the unknown impurities. The percent known and unknown impurities were added together and subtracted from 100% to obtain the percent purity of the TCTFE. In this work, the sample analyzed had a purity of 99.9983% by weight.

The analysis was performed using a GC packed column containing a polydimethylsiloxane stationary phase and helium as the carrier gas. A TCTFE sample was injected into the GC and transported by a continuous flow of helium carrier gas through the packed column. The packing separated the impurities which were detected by flame ionization. Only the procedure supplied by Allied gave consideration to calculating unknown peaks. The Du Pont procedure specifically stated that they did not account for unknown impurities.

The precision for most peak area determinations varied from 2 to 4% relative standard deviation (RSD) for ten replicate injections of a TCTFE sample. This was true for an as-received sample, a spiked sample, and a spiked solution containing all eleven impurities. The RSD for calculating ten replicate concentrations for two known impurities in the same sample was 2.8% for the 2.4 ppm (w/w) impurity and 1.3% for the 12.4 ppm impurity.

The impurities determined in this analysis were Freon 115, Freon 12, Freon 114, FC-216, FC-1112A, FC-123, FC-318, FC-122, FC-112, PCE, and FC-316.

DISCUSSION

SCOPE AND PURPOSE

This project was undertaken to develop a gas chromatography (GC) method for determining the purity of electronic grade 1,1,2-trichlorotrifluoroethane. The solvent is suitable for cleaning electronic components. High purity TCTFE is required to assure that the impurities would not inhibit or increase solvency characteristics.

PRIOR WORK

The method that was developed is similar to those supplied by E. I. Du Pont De Nemours & Company (Inc.), Chemicals and Pigments Department, Wilmington, DE, and Allied-Signal Inc. Engineered Materials Sector, Morristown, NJ.[1-2]

ACTIVITY

Introduction

The analysis was performed using a temperature programmed gas chromatograph (GC) with a flame ionization detector (FID). A packed column containing SP-2100 (polydimethylsiloxane) as the stationary phase on Supelcoport (Appendix A) was used to separate the impurities. Quantitation of the separated components was performed using the standard method of addition and computer integration. As an alternative, the analyst may use a fused silica capillary column of suitable length, internal diameter, and bonded stationary phase which will provide baseline or near baseline resolution of calibrating reagents.

The analytical method is suitable for determining the usual volatile chlorinated hydrocarbons (CHC) and chlorofluorocarbons (CFC) found in 1,1,2-trichlorotrifluoroethane (TCTFE).

The 3 μL amount of solvent used for injection saturated the detector, resulting in a TCTFE chromatographic peak with a flat top which could not be quantitated. Injection of smaller volumes of TCTFE, to help eliminate the peak flat top, resulted only in continued loss of sensitivity for the impurities and poor peak area reproducibility between injections. Adjustment of other instrument parameters such as flow of combustion gases to the FID and changes to the detector output interfacing to the computer integrator were not successful. The problem was solved by adding small, known amounts of each of the calibrating reagents to TCTFE (standard addition) and back calculating the amount that was originally present. The calculated known and unknown impurities were added together and subtracted from 100% to obtain the purity of TCTFE.

Gas Chromatograph (GC)

The equipment list used for the analysis is shown in Appendix A. The packed column was installed in the GC oven. The exit end was not connected to the base of the detector but was attached to a 6 ft. length of coiled 1/8 in. OD by 0.085 in. ID stainless steel tubing to preserve the column stationary phase characteristics by preventing back flow of air (oxygen) during column conditioning. The column was conditioned in the GC oven at 300°C for 2 h with a flow of about 60 mL/min of helium carrier gas. The 6 ft. section was removed and set aside. The column exit end was connected to the base of the detector and the GC parameters were adjusted as shown in Appendix B. Some adjustment in carrier gas and/or oven temperature may be necessary to achieve baseline separation of the impurities. Carrier gas, combustion gas connections, and optimization of the FID response were performed according to the GC operators manual. Appendix B lists the carrier and combustion gas requirements.

Locator

A locator is a sample of the original TCTFE to which a small amount of a calibrating reagent has been added (Appendix C) and mixed thoroughly. A portion of this solution was then injected into the GC to obtain a chromatogram. The increase in peak height or the appearance of a new peak, as compared to the chromatogram of the original TCTFE, assisted in identification of the impurities. A second impurity, suspected of being present, was added and the process was repeated until all of the knowns in the original TCTFE have been labeled. Figure 1 shows a chromatogram of all the expected impurities and can be used as a guide to the order of elution and approximate peak retention times.

About 230 mL of TCTFE was added to an amber bottle (Appendix A) and then sealed with a Mininert valve. The round red septum of the Mininert valve was replaced with a new one to assure a good seal. A 1 μL liquid sample (10 μL liquid syringe) and a 250 μL gas sample (250 μL gas tight syringe) was used for adding the reagents. This approach was satisfactory for developing a GC locator of calibrating reagents.

Purity of Calibrating Reagents

The purity of all the calibrating reagents listed in Appendix C, with the exception of Freon 113, was determined to the nearest 0.01 percent. This was accomplished by injecting small amounts of each reagent into the GC and determining the peak area percent of the major peak, assuring that the main peak top has a normal type Gaussian shape and not a flat top. This purity determination

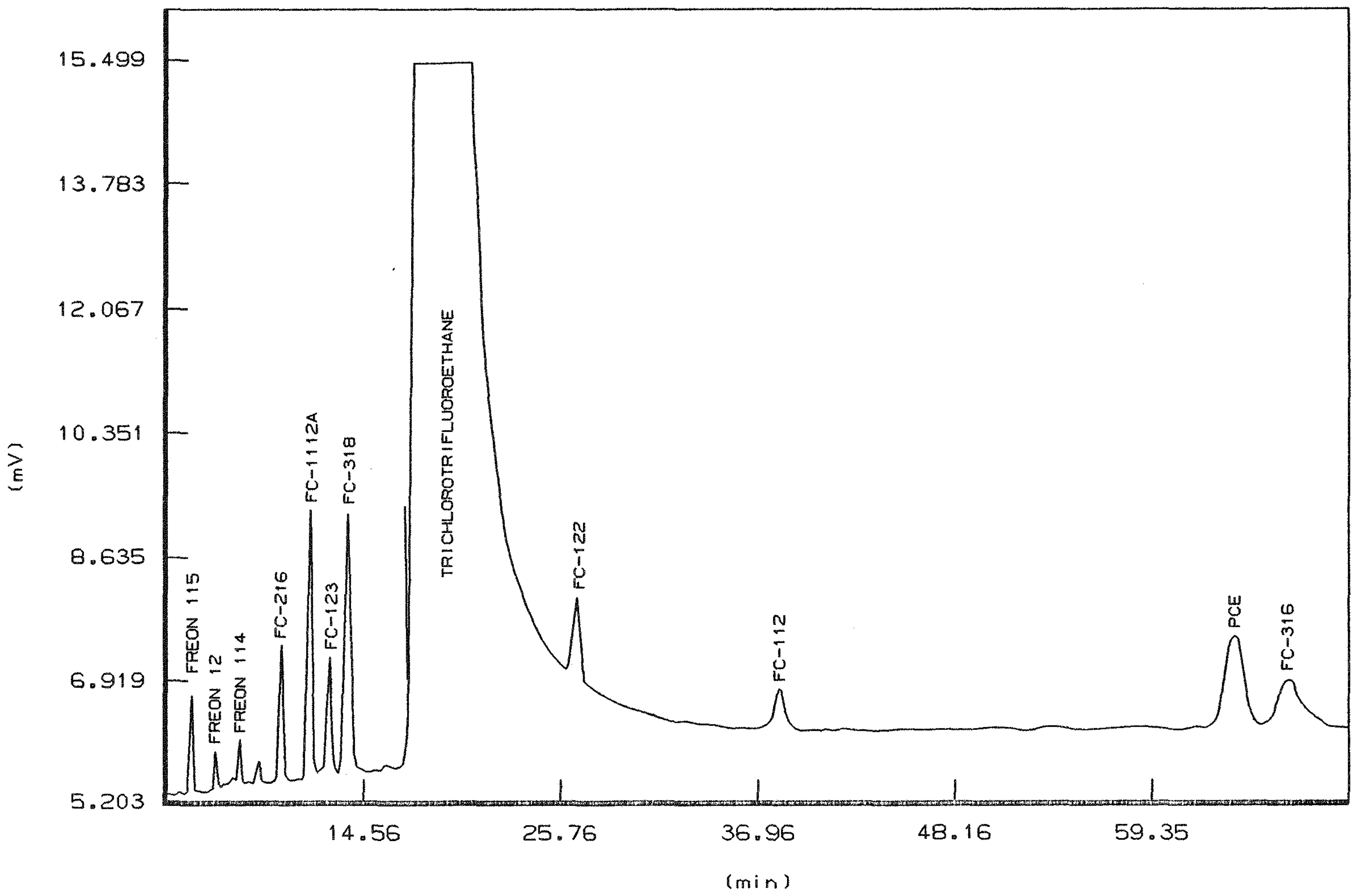

Figure 1. Chromatogram Showing the Elution Order of All Known Impurities in 1,1,2-Trichlorotrifluoroethane

is required to provide a means of correcting for the amount of reagents added later to TCTFE for calibration. A list of calibrating reagent purities determined for this present work is shown in Table 1.

Quantitation

The standard addition method was used for quantitation. The TCTFE sample was first chromatographed. Known amounts of the impurities were added to a known amount of TCTFE. The solution was then chromatographed under the same condition. From these known amounts, the quantity of each impurity originally present in TCTFE was determined.

About 230 mL (~360 g) of TCTFE was weighed to 0.1 g into an amber bottle (Appendix A) and sealed with a Mininert valve. A 3 μL (5 μL syringe) sample was injected into the GC to obtain a chromatogram of peak areas for the original TCTFE. All the known peaks were labeled. Another injection was made to obtain a second chromatogram.

One microliter (10 μL syringe) of each identified liquid impurity was accurately weighed to the nearest 0.00001 g (5th decimal place). The needle tip was sealed with a septum during the weighing process to prevent sample loss. Nylon gloves were worn to prevent adding weight to the syringe. Each calibrating reagent was injected through the Mininert valve of the bottle and mixed thoroughly with the TCTFE before adding the next calibrating reagent. The syringe was reweighed to determine by difference the amount added. This process was continued until all the identified liquid calibrating reagents were added.

The addition of calibrating reagent gases (Appendix C) required a different technique. The ambient temperature and pressure were recorded. The gas volume calculations are shown in Appendix D. The gas volume is arbitrarily selected to provide 4 ppm of the calibrating reagent. The graduation marks on the syringe, in most cases, will not be equal to the volume calculated. Therefore, the next closest graduation mark was selected and recorded and the calibrating reagent gas was injected into the bottle. Since most laboratories do not experience wide variations in temperatures and pressures, the analyst may select the set of precalculated gas volumes listed in Table 2 as a substitute for the upper calculation shown in Appendix D.

A fine metering valve, compatible with the pressure of the gas, was connected to the gas cylinder containing the calibrating reagent gas. A glass flowmeter with a glass or stainless steel float was connected to the metering valve. A 6 in. length of 1/8 in. OD Teflon tubing was added to the exit end of the flowmeter. The metering valve was closed.

Table 1. Peak Area Percent Purity for the Calibrating Reagents Used in This Work

Reagent*	Purity (percent)
Freon 115	97.67
Freon 12	97.49
Freon 114	99.84
FC-216	99.98
FC-1112A	97.24
FC-123	98.21
FC-318	99.12
FC-122	99.79
FC-112	99.55
PCE	99.81
FC-316	99.19

*Reagent properties are listed in Appendix C

The plunger of the selected gas-tight syringe was adjusted to zero and a volume of gas was taken of the vapors from inside the bottle, equal to the volume to be added by a gaseous calibrating reagent. The gas syringe plunger was removed and the syringe barrel was purged with lab air using the laboratory vacuum system (vacuum flow ~ 10 L/min) for at least 5 min. The plunger was replaced in the syringe and purged 4 to 5 times with dry nitrogen and adjusted approximately to the largest mark.

The valve on the gas cylinder was opened and the metering valve was adjusted to establish a flow of about 75 to 100 cm^3/min. The syringe plunger was discharged to remove dry nitrogen and the needle was immediately inserted to nearly its full length into the Teflon tube. The syringe was slowly purged with the calibrating reagent gas 4 to 5 times before adjusting the plunger to the desired mark. The contents of the syringe were discharged inside the bottle and mixed thoroughly. The syringe was purged again with ambient air to remove residual amounts of sample and

Table 2. Suggested Precalculated Gas Volume to be Added to the Bottle for Calibration at Ambient Temperatures and Pressures

Impurity	Volume (μL)
Freon 115	260
Freon 12	330
Freon 114	230
FC-1112A	300

then purged again with dry nitrogen. This process was repeated to add the other required calibrating gases. A partial vacuum in the bottle was necessary to prevent condensation of some of the gases inside the syringe when the plunger was depressed to discharge the gas sample inside the bottle. Appendix D shows the calculations for determining the weight of the calibration gas that was added to the bottle.

After all the required calibrating reagents have been added to the bottle and mixed thoroughly, duplicate chromatograms were obtained to show peak areas using 3 μL (5 μL syringe) injections. All the known peaks were labeled.

The peak areas for the known original impurities were averaged for the two chromatograms from the original TCTFE and the two chromatograms from the bottle containing the added impurities. All the unknown peak areas in each of the two chromatograms for the original TCTFE were each totaled and the totals were averaged. The data in Appendix E were used to compute the weight percent purity of each known and unknown impurity. Table 3 shows the result of an analysis and the final calculation for determining the purity of TCTFE. The final results were recorded to the nearest 0.00001% (5 decimal) and reported to the nearest 0.0001% (4 decimal).

Statistics

Table 4 shows the precision that can be expected for peak area determination involving ten replicate injections for the analysis of four identified impurities contained in a sample of TCTFE used in this work. The range of relative standard deviations (RSD) was 1.58 to 3.65%. The sample, when spiked with the same impurities, produced the expected larger peak areas, and in some

Table 3. Purity of a TCTFE Sample

Impurity	Concentration (percent)
FC-216	0.00024
FC-123	0.00003
FC-318	0.00124
FC-112	0.00006
	0.00157 = percent known impurities
	+ 0.00016 = percent unknown impurities
	0.00173 percent total impurities

Record purity of TCTFE as "100% - 0.00173% = 99.99827%"

Report results as "purity = 99.9983%"

cases substantially higher, but the RSD range was relatively the same, 2.20 to 3.45%.

Table 5 shows the precision that can be expected for peak area determination involving ten replicate injections for a locator containing all known impurities in a sample of TCTFE. The RDS varied from 1.54 to 7.75%. More variation was recorded for the early eluting peaks (Freon 115, 12, 114) which are the gaseous components, compared to the remainder of the impurities which are nearly all liquid. This shows that it is more difficult to maintain a homogeneous mixture involving gases, especially during syringe sampling.

Table 6 shows the precision that can be expected for calculating ten replicate concentrations for the two higher concentrated impurities in the TCTFE sample, shown in Table 4.

ACCOMPLISHMENTS

A gas chromatography (GC) method has been developed to determine the purity of 1,1,2-trichlorotrifluoroethane (TCTFE). The polydimethylsiloxane stationary phase was found sufficient to separate all the known impurities that were readily detected by flame ionization. Known and unknown impurities were quantitated, added together and subtracted from 100% to obtain the percent purity of TCTFE. The relative standard deviation (RSD) for ten

Table 4. The Precision for Ten Peak Area Measurements for Unspiked and Spiked Impurities in the TCTFE Sample Shown in Table 3

Average for Peak Area Measurements	FC-216	FC-123	FC-318	FC-112
TCTFE sample as-received				
Average	2401	298	7006	219
Standard Deviation	49	9	111	8
Relative Standard Deviation (percent)	2.04	3.02	1.58	3.65
TCTFE Sample Spiked with the Impurities Above				
Average	5388	3462	8958	1520
Standard Deviation	162	94	197	52
Relative Standard Deviation (percent)	3.01	2.72	2.20	3.45

replicate peak area determinations was 2 to 4% for most of the known impurities. The RSD for calculating ten replicate concentrations for two known impurities in the same sample was 2.8% for the 2.4 ppm (w/w) impurity and 1.3% for the 12.4 ppm impurity.

FUTURE WORK

Time permitting, a capillary column will be evaluated to enhance resolution, shorten analysis time, and increase sensitivity.

Table 5. The Precision for Ten Peak Area Measurements for a TCTFE Spiked Locator Containing All the Known Impurities

Impurity	Average	Standard Deviation	Relative Standard Deviation (percent)
Freon 115	2687	209	7.78
Freon 12	1050	62	5.90
Freon 114	1264	60	4.75
FC-216	4457	135	3.03
FC-1112A	8858	307	3.47
FC-123	3899	119	3.05
FC-318	7667	118	1.54
FC-122	2929	90	3.07
FC-112	1444	47	2.91
PCE	3372	69	2.05
FC-316	1720	45	2.62

Table 6. The Precision for Determining PPM for Two Impurities Found in a TCTFE Sample Using the Standard Addition Method

	FC-216		FC-318	
	Area[1]	ppm	Area[1]	ppm
	2389	2.4	6903	12.2
	2478	2.5	7286	12.7
	2398	2.4	6935	12.2
	2466	2.5	6984	12.3
	2407	2.4	7037	12.4
	2418	2.4	6946	12.3
	2412	2.4	7059	12.5
	2353	2.3	6988	12.3
	2377	2.4	7004	12.4
	2312	2.3	6915	12.2
Av =	2401	2.4	7006	12.4
sd =	49	0.07	111	0.16
%RSD =	2.04	2.8	1.58	1.3

[1] Peak areas for ten replicate injections from a TCTFE sample.

REFERENCES

[1] Test Method No. F3297.165.01.CC, third revision: November 11, 1986, E. I. Du Pont De Nemours & Company (Inc.), Chemicals & Pigments Department. "Freon" 113 Fluorocarbon (1,1,2-trichlorotrifluoroethane). "Determination of Purity by Gas Chromatography."

[2] Test Method No. GSVD-1: Genesolv D, Fluorocarbons 112, 122, 1112A, and other organics, Allied Corporation, Chemical Sector.

Appendix A

EQUIPMENT
(Equivalent equipment may be used)

a. Gas chromatograph - Model Sigma 2000, with flame ionization detector and temperature programming, Perkin-Elmer, Norwalk, CT.

b. Integrator - an 80386 based computer system with Nelson Turbochrom 2700 software and NEC CP-7 printer or a Perkin-Elmer Chrom 2 or Chrom 3. A SP-4200 or SP-4270 integrator from Spectra Physics, San Jose, CA, would also be suitable for quantitation.

c. Column - 30 ft. stainless steel (304), 1/8 in. OD X 0.085 in. ID, packed with 20% SP-2100 on 80/100 mesh Supelcoport (diatomite, acid washed and dimethylchlorosilane treated) from Supelco, Inc., Bellefonte, PA.

d. Syringe, liquid, 5 µL, model 95, catalog no. 87920, Hamilton Co., Reno, NV.

e. Syringe, liquid, 10 µL, Hamilton, model 701, catalog no. 80300.

f. Syringes, side port removable needle, gas tight, Unimetrics, Shorewood, IL, 250 µL catalog no. TP5250R, 500 µL catalog no. TP5500R.

g. Vacuum system, 10^{-2} torr or better.

h. Bottle, 8 oz (237 mL), catalog no. 03-320-4C, Fisher Scientific Inc., St. Louis, MO. Although this bottle is sold as a 237 mL size, it will hold nearly 250 mL when completely full, more than enough additional volume available to add the calibrating reagents.

i. Mininert valve, catalog no. 10130, Pierce, Rockford, IL.

Appendix B

GAS CHROMATOGRAPH OPERATING CONDITIONS

Temperatures

Injection port = 250°C

Column = 40°C, 1.5°C/min to 65°C then program 20°C/min to 85°C and hold 62.2 min

Detector = 250°C

Gases

Carrier = 33 mL helium/min

Air Zero = 20 psig

Hydrogen = 20 psig

Detector

FID Range = 1X

Interface = 1V

GC Output = 0-10V (external terminal strip)

Appendix C

CHEMICALS FOR TCTFE ANALYSIS

<u>Reagents for Calibration</u> (in elution order)

a. Freon 115, gas, 1-chloro-1,2-pentafluoroethane, CClF2-CF3, MW=154.5, BP=-39.1°C, Du Pont

b. Freon 12, gas, dichlorodifluoromethane, CCl2F2, MW=120.9, BP=-29.8°C, Du Pont

c. Freon 114, gas, 1,2-dichloro-1,1,2,2-tetrafluoroethane, CClF2-CClF2, MW=170.9, BP=3.8°C, Du Pont

d. FC-216, liquid, 1,2-dichlorohexafluoropropane, CClF2-CClF-CF3, MW=221.0, BP=35.0°C, d=1.590 g/cm^3 (25°C), Specialty Chemicals, Gainesville, FL

e. FC-1112A, gas, 1,1-dichloro-2,2-difluoroethylene, CCl2=CF2, MW=133, BP=19.0°C, Specialty Chemicals

f. FC-123, liquid, 2-dichloro-1,1,1-trifluoroethane, CF3-CHCl2, MW=153, BP=27.1°C, d=1.475 g/cc (25°C), Specialty Chemicals

g. FC-318, liquid, 2,3-dichlorooctafluorobutane, CF3-CClF-CClF-CF3, MW=271.0, BP=63.0°C, d=1.680 g/cc (25°C), Specialty Chemicals

Freon 113, liquid, 1,1,2-trichloro-1,2,2-trifluoroethane, CCl2F-CClF2, MW=187.4, BP=47.6, d=1.565 g/cm^3 (25°C). This chemical is the main component of the sample received for analysis.

h. FC-122, liquid, 1,1-dichloro-1,2,2-trichloroethane, CClF2-CHCl2, MW=170.0, BP=72.0°C d=1.559 g/cm^3 (25°C), Specialty Chemicals

i. FC-112, liquid, 1,1,2,2-tetrachloro-1,2-difluoroethane, CCl2F-CCl2F, MW=203.8, BP=92.8°C, d=1.634 g/cm^3 (30°C), Specialty Chemicals

j. PCE, liquid, 1,1,2,2-tetrachloroethylene, CCl2=CCl2, MW=166.0, BP=121.0°C, d=1.623 g/cm^3 (25°C) Omnisolv, EM Science, Cherry Hill, NJ

k. FC-316, liquid, 1,1,3,4-tetrachloro-1,2,3,4-hexafluorobutane, CCl2F-CF2-CClF-CClF2, MW=304.0, BP=134.0°C, d=1.75 g/cm^3 (26°), Specialty Chemicals

Reagents for Gas Chromatography (or equivalent)

l. Helium carrier gas, 99.9950% minimum purity, Air products and Chemicals Inc.

m. Air zero for FID, maximum 1 ppm total hydrocarbons, Air Products and Chemicals Inc.

n. Hydrogen gas generator, model Mark V, 0-300 mL/min, impurities less than 10 ppb, LCD/Milton Roy, Riviera Beach, FL

Appendix D

GAS VOLUME AND WEIGHT CALCULATIONS FOR CALIBRATION

Gas Volume - at known ambient pressure and temperature.

$$V = \frac{A\ B\ (C+D)\ E\ F\ W}{P\ M}$$

V = volume in µL of gas calibration reagent
A = 0.000004, adding of 0.0004% of calibrating reagent
B = 82.054, gas constant (mL atmos/K mol)
C = 273.15°C, standard temperature
D = °C, temperature of room
E = 1000, conversion from mL to µL
F = 760, conversion from torr to atmospheres
W = weight in grams of TCTFE in bottle
P = ambient barometric pressure in torr
M = molecular weight of calibrating reagent

The volume calculated, in most cases, will not equal the graduation marks on the syringe. The next closest graduation mark was selected and this gas volume was recorded and injected into the bottle for calibration. Since most laboratories do not experience wide variations in temperatures and pressures, the analyst may desire to select a set of precalculated gas volumes listed in Table 2 as a substitute for calculating the gas volume previously shown.

Gas Weight - of the calibration reagent.

$$Q = \frac{M\ P\ V}{B\ G\ F\ (C+D)}$$

Q = weight in grams of gas volume
V = calculated volume from above or from Table 2
G = 1000, conversion from µL to mL

Appendix E

WEIGHT PERCENT OF KNOWN AND UNKNOWN IMPURITIES IN THE ORIGINAL TCTFE SAMPLE

$$\text{Percent Concentration} = \frac{H\,Q\,Z\,(100)}{(J - H)\,W}$$

H = average area of impurity in original TCTFE chromatogram

Q = weight in grams of the calibrating reagent that has been added (gas or liquid)

Z = percent purity (as a decimal) determined by GC and shown in Table 1 for this work

J = average increase area resulting from spiking impurities

W = weight in grams of TCTFE in bottle

Record the results to nearest 0.00001% (5 decimal places)

<u>Weight Percent of Unknown Impurities</u>

$$\text{Percent Concentration} = \frac{K\,L}{N}$$

K = total area of unknown impurities

L = total weight in percent (as percent, not decimal) of the known calculated impurities in the original TCTFE

N = total area of known impurities in the original TCTFE