

## Gas Chromatography

### Author

**Qianzhan. Yang**  
PerkinElmer, Inc.  
Chengdu, PRC

**Kira. Yang**  
PerkinElmer, Inc.  
Shanghai, PRC

# Determination of Chlorofluorocarbons and Hydrochlorofluorocarbons in Polyether Polyols by HS-GCMS

The photo-induced scission of the C-Cl bond in CFCs produces radical  $\text{Cl}\cdot$  which catalyzes the conversion of ozone into oxygen in the upper atmosphere. Owing to the contribution to ozone depletion, the manufacturing and use of CFCs and HCFCs have been phased out under the Montreal Protocol (1987)<sup>1</sup>.

CFCs, in the form of polyether polyol mixtures, have been widely used as blowing agents in the manufacture of rigid polyurethane foams (PU) used as insulation products. Although ozone depleting CFCs have been phased out per the Montreal Protocol, recent studies have found that atmospheric levels of CFCs are significantly higher than expected<sup>2</sup>. This finding suggests that production and use of CFCs are still on-going, with further evidence indicating that the manufacture of rigid PU foam insulation containing CFCs is still pervasive and widespread in countries such as China<sup>2</sup>. As such, the qualitative and quantitative analysis of CFCs and HCFCs in polyether polyols has important significance to protect the ozone layer.

### Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are fully or partially halogenated paraffin hydrocarbons, and have been utilized as aerosol propellants, foaming agents, solvents, and refrigerants.



In this study, trichlorofluoromethane (CFC-11), chlorodifluoromethane (HCFC-22) and dichlorofluoroethane (HCFC-141b) in a polyether polyol matrix are investigated using a PerkinElmer Clarus® GC/MS with a TurboMatrix™ HS-40. Instrument method parameters utilized in the study are presented herein, with detailed results demonstrating superior precision, linearity, sensitivity and recovery.

## Experimental

### Instrumentation

A PerkinElmer Clarus GC/MS and TurboMatrix HS-40 were used to perform these experiments, with the conditions presented in Table 1. A GS-GASPRO column (60 m x 0.32 mm) was used to separate the eluting compounds. The headspace transfer line was installed into the GC split injector port.

Table 1. Analytical parameters.

HS Parameters			
Needle Temperature	85 °C		
Transfer Line Temperature	95 °C		
Oven Temperature	60 °C		
Thermostatting Time	10 min		
Pressurization Time	1 min		
Injection Time	0.04 min		
Column Pressure	20 psi		
Vial Pressure	20 psi		
Operation Mode	Constant		
GC Parameters			
Headspace Connector	Split Mode Connection		
Inlet Temp	240 °C		
GC Injector	PSSI with a 1mm straight bore liner		
Carrier Gas	Helium		
Carrier Gas Flow Rate	1.2 ml/min		
Split Ratio	10:1		
Initial Oven Temp	40 °C		
Oven Hold	2 min		
Ramp	10 °C/min to 150 °C		
2 <sup>nd</sup> Oven Temp	0 min		
Ramp	5 °C/min to 200 °C		
3 <sup>rd</sup> Oven Temp	7 min		
Instrument Time Event	Time	Event	Value
	-1.0 min	Spl	Off
	1.0 min	Spl	20 ml/min
MS Parameters			
GC Inlet Line Temp	250 °C		
Ion Source Temp	230 °C		
Solvent Delay	5 min		
Function Type	Scan		
Mass Range	45-180 amu		

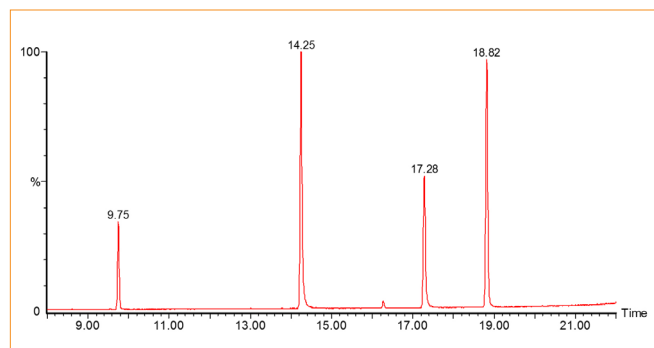


Figure 1. The chromatogram of a calibration standard. (The amount is 50 µg for standards and 200 µg for internal standard.)

### Sample Preparation

The chromatographic grade methanol was obtained from DUKSAN PURE CHEMICALS. Calibration standards (CFC-11, HCFC-22 and HCFC-141b) and internal standard (chlorobromomethane, CH<sub>2</sub>BrCl) were purchased from AccuStandard.

A sample solution was prepared by dissolving 1 g of a polyether polyol sample in 10 mL of methanol. 5 mL of sample solution and 200 µg of internal standard were transferred to a separate headspace vial. All vials were sealed immediately with the PTFE side of the septum facing toward the sample.

Method precision was investigated by analyzing six replicate sample solutions with 15.8 µg of HCFC-22, 18.0 µg of CFC-11 and 91.2 µg of HCFC-141b. Method detection limits (MDL) were determined by analyzing seven replicate standard solutions at an amount of 0.20 µg.

### Calibration

A standard solution was prepared by dissolving a certain volume of calibration standard in 5 mL of methanol. The calibration curve was prepared by adding the standard solution and 200 µg of internal standard to the headspace vials. The amount of target compounds in each vial is 5, 10, 20, 50 and 100 µg, respectively.

## Results and Discussion

The total ion chromatogram of a calibration standard (Figure 1) shows baseline resolution of the selected compounds and the internal standard. Utilizing a full scan of positive ions in EI mode, the selected compounds were quantitatively analyzed. Table 2 shows the retention time (RT), as well as the qualitative and quantitative ions of three external standards and the internal standard. Table 3 summarizes the results for repeatability, method detection limits and dynamic ranges.

Table 2. The qualitative and quantitative ions of 3 external standards and an internal standard.

RT (min)	Compound Name	Compound Type	Quantitation Ion	Qualitative Ion
9.75	HCFC-22	External standard	51	67, 69, 50
14.25	CFC-11	External standard	101	103, 105, 66
17.28	HCFC-141b	External standard	81	83, 61, 101
18.82	CH <sub>2</sub> BrCl	Internal standard	130	128, 49, 93

Table 3. Results for repeatability, method detection limit and linearity.

Compound Name	Repeatability	MDL	Linearity		
	(RSD %)	( $\mu\text{g}$ )	Slope	Intercept	$r^2$
HCFC-22	2.9	0.06	14.9678	-38.2784	0.9982
CFC-11	3.1	0.06	12.2053	-24.6074	0.9976
HCFC-141b	3.5	0.02	8.1348	-16.1299	0.9979

An internal standard method was used in this study. The internal standard calibration curves were plotted as the peak area ratio of the external standard to the internal standard, versus the ratio of the external standard to the internal standard. The coefficient of determination ( $r^2$ ) value for all compounds was over 0.997, showing the reliability of the analysis in the range of 5–100  $\mu\text{g}$ . The area repeatability measured by the relative standard deviation (RSD) was found to be between 2.9–3.5% for all compounds. Utilizing the approach described above, the MDLs per sample were calculated to be in the range of 0.02–0.06  $\mu\text{g}$ . The results for precision, linearity and method detection limit are excellent for all compounds.

## Summary

In this study, the determination of three CFCs in polyether polyols was easily performed using the PerkinElmer TurboMatrix HS 40 – Clarus GC/MS system. All target compounds analyzed exhibit superior detection limits, stability and linearity.

## References

1. United States Department of State. (2019). The Montreal Protocol on Substances That Deplete the Ozone Layer - United States Department of State. [online] Available at: <https://www.state.gov/key-topics-office-of-environmental-quality-and-transboundary-issues/the-montreal-protocol-on-substances-that-deplete-the-ozone-layer/> [Accessed 19 Aug. 2019].
2. Moore, Stephen. "Surge in atmospheric CFC-11 levels points to illegal Chinese use as blowing agent." *Plastics Today*, 19 July 2018, [www.plasticstoday.com/sustainability/surge-atmospheric-cfc-11-levels-points-illegal-chinese-use-blowing-agent/45400940959062](http://www.plasticstoday.com/sustainability/surge-atmospheric-cfc-11-levels-points-illegal-chinese-use-blowing-agent/45400940959062).