Application Note 20559

GC Analysis of Derivatized Chlorinated Acetic Acids

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Key Words

Derivatization reagent, extractive alkylation, pentafluorobenzyl bromide (PFBBr), chloroacetic acid (CA), dichloroacetic acid (DCA), trichloroacetic acid (TCA)

Abstract

Chloroacetic acid (CA), Dichloroacetic acid (DCA) and Trichloroacetic acid (TCA) are difficult to analyze by GC due to highly polar acidic groups and therefore must be derivatised to increase their detectability. This application note demonstrates derivatization is achieved using the alkylation reagent pentafluorobenzyl bromide (PFBBr) to form their corresponding fluorinated derivatives. Separation of the derivatized chlorinated acetic acids with highly symmetrical peak shapes was achieved using a 5% phenyl methypolysiloxane phase column.

Introduction

Chloroacetic acid (CA), Dichloroacetic acid (DCA) and Trichloroacetic acid (TCA) play important roles in chemical and pharmaceutical industries. CA is actively used in industrial processes such as in the production of dyes, insecticides and active pharmaceutical ingredients[1]. DCA has been used in cancer treatment[2] and TCA has been used in herbicides[3].

Trace levels of low molecular weight chlorinated acetic acids TCA, DCA and CA can be difficult to analyze by GC due to their highly polar acidic nature. Derivatization of chlorinated acetic acids improves the volatility and peak shapes on a chromatographic column.

Pentafluorobenzyl bromide (PFBBr) is commonly used for converting carboxylic acids, as well as mercaptans, phenols and sulphonamides to their respective fluorinated derivatives. In this case chlorinated acetic acid derivatives were obtained via an extractive alkylation procedure using the alkylation reagent PFBBr (Figures 1 and 2). PFBBr is manufactured to meet the exact needs for sensitive derivatization reactions. This procedure simultaneously combines extraction and derivatisation without the need for purification. In addition, the reaction time is fast and can take less than 30 min to complete.

Experimental Details

Sample Preparation

10 mg each of TCA, DA and CA were weighed into a 50 mL volumetric flask and made up to volume with Dichloromethane. A 1 mL aliquot was taken and placed into a Thermo Scientific Reacti-Vial containing a Reacti-Vial magnetic stirrer. To the Reacti-Vial, 1 mL of aqueous 0.1 M tetrabutylammonium hydrogen sulphate and 1 mL of 0.2 M NaOH were added. This was the followed by the addition of 20 µL of PFBBr. The vials were capped and placed in the Reacti-Therm Sample Incubation System and stirred for 30 minutes at 60 °C. The final sample was then transferred to a 2 mL autosampler vial and 1 µL was injected into the GC/FID.

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Reagents	Part Number
Thermo Scientific alkylation reagent PFBBr 5g	TS-58220
Fisher Scientific tetrabutylammonium hydrogen sulphate	16838-0250
Fisher Scientific sodium hydroxide	BPE359-500

Sample Handling Equipment	Part Number
Thermo Scientific Reacti-Therm III Heating/Stirring Module	TS-18823
Thermo Scientific Reacti-Vap III Evaporator	TS-18826
Thermo Scientific Reacti-Block Q-1 (Holds 8 × 10 mL Reacti-Vials)	TS-18814
Thermo Scientific Reacti-Vial clear glass reaction vials 10 mL	TS-13225
Thermo Scientific 2 mL amber vial and screw tops	60180-565

Separation Conditions		Part Number
Instrumentation:	Thermo Scientific TRACE GC Ultra	
Column:	TRACE TR-5 30 m × 0.25 mm × 0.25 µm	260E142P
Thermo Scientific BTO 17 mm septa		31303211
5 mm ID Focus Split Liner, 105 mm long		453T1905
Graphite liner seal		29033406
10 µL, 50 mm needle length gauge 25 Syringe		36500525
Graphite ferrules to fit 0.1-0.25 mm ID columns		29053488
Carrier gas:	Helium	
Split flow:	60 mL/min	
Column flow:	1.2 mL/min, constant flow	
Split ratio:	50:1	
Oven temperature:	40 °C (1 min), 10 °C/min, 300 °C (5 min)	
Injector type:	Split/Splitless	
Injector mode:	Split	
Injector temperature:	240 °C	
Detector type:	FID	
Detector temperature:	280 °C	
Detector Hydrogen flow:	35 mL/min	
Detector Air flow:	350 mL/min	
Detector Nitrogen flow:	30 mL/min	
Thermo Scientific TriPlus Autosampler		
Injection Volume:	1 µL	

Data Processing	
Software:	Thermo Scientific XCalibur™

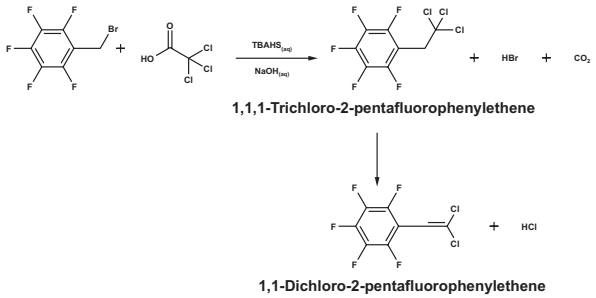

Figure 1: Reaction products of pentafluorobenzyl derivative of TCA[4]

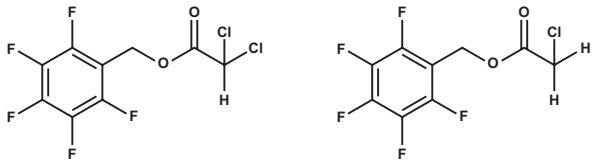

Figure 2 Pentafluoroderivative of (a) DCA and (b) CA

Results

Two peaks were observed for derivatised TCA-PFB; the product structures are shown in Figure 1. The reaction itself does not comprise of two products but one product 1,1,1-trichloro-2-pentafluorophenylethane decomposing to 1,1-dichloro-2-pentafluorophenylethene[4]. Each of the derivatized chlorinated peaks was identified by individually derivatizing the TCA, DCA and CA. Figure 1 shows the derivatization of TCA and Figure 2 shows the structures of the derivatized form of DCA and CA. Figure 3 shows the chromatograms of the corresponding esters of the derivatized TCA, DCA and CA.

Conclusion

PFBBr is an ideal derivatization reagent for increasing the detectability of low molecular weight chlorinated acetic acids. This enabled enhanced separation and detection with a TRACE TR-5 GC column.

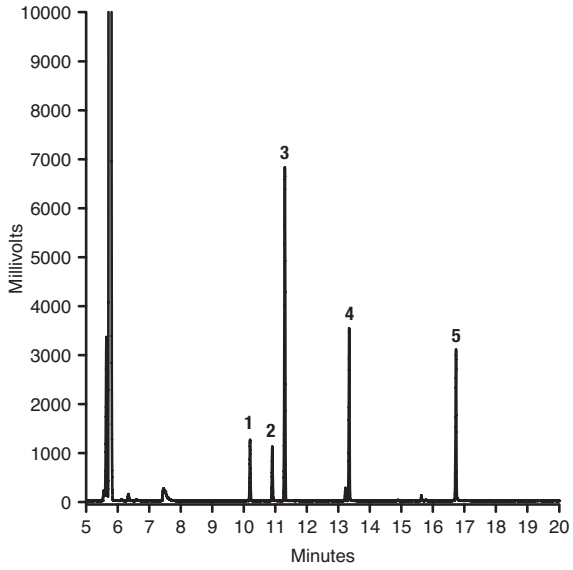

Figure 3: Chromatogram of PFB-derivatized acetic acids

Peak Number	Compounds	t_R (min)
1	Derivatized TCA	10.2
2	Derivatized TCA	10.9
3	PFB-by Product	11.3
4	Derivatized CA	13.3
5	Derivatised DCA	16.7

References

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3. Monaco T.J, Weller S.C, Ashton F. M, Weed science: principles and practices. 2002, Technology and Engineering.

4. Sinkkonen S, Kolehmainen E, Paasivirta J, Hamalainen S, Lahtipera M, Journal of chromatography A, 1995, 718, 391-396.

5. ACD labs software to draw chemical structures.

6. Thermo Scientific reagents, solvents and accessories brochure (Ref: BR20535_E 06/12S). Available upon request.

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