

# Determination of Chlorinated Acidic Herbicides with a two-column System and Dual Electron Capture Detection

## Application Note

AN0026

### INTRODUCTION

The United States Environmental Protection Agency (US EPA) details a harmonised test method for the determination of chlorinated acids in water by gas chromatography with an electron capture detector (GC-ECD), EPA 515. The compounds included in the method are acidic and include phenols and carboxylic acids. The acidic herbicides require derivatisation, with the acid being converted to methyl esters. EPA 515 specifies that diazomethane is the derivatising agent to be used, however, it is vital that excess derivatising reagent is removed prior to analysis. This application note describes a derivatisation procedure using dimethylformamide dimethyldiacetal (Methyl-8), which is much easier to handle and also less hazardous than diazomethane. After derivatisation, the pesticides are separated on two columns for simultaneous analysis and confirmation using dual electron capture detectors.

### EXPERIMENTAL

A SCION 456 GC was equipped with a septum equipped programmable injector, dual ECDs, 8400 autosampler and CompassCDS for data handling and processing of results. A methylated herbicide mix was diluted to low nanogram levels in MTBE. Individual standards of each acidic compound were derivatised with Methyl-8 and injected into the GC system.

Eighteen compounds were individually injected into the GC before derivatisation. Compounds were then weighed and mixed with 100µL each of MTBE and Methyl-8 before being incubated at 65°C for 20 minutes. Each compound was then diluted to a concentration of 1-3ng/µL and injected into the GC to verify that derivatisation had occurred. The retention time of all peaks, on both columns, were determined. Retention times were compared with those of the methylated standard mix and the published times in the EPA method. Mixes were also prepared of all of the compounds with an internal standard recommended by the EPA; 4,4'-dibromooctafluorodiphenyl (DBOB). Precision, minimum detectable quantities and detector response at different concentrations were determined.

The analytical conditions of the instrumentation can be found in Table 1.

**Table 1.** Analytical conditions of the GC dual ECD system

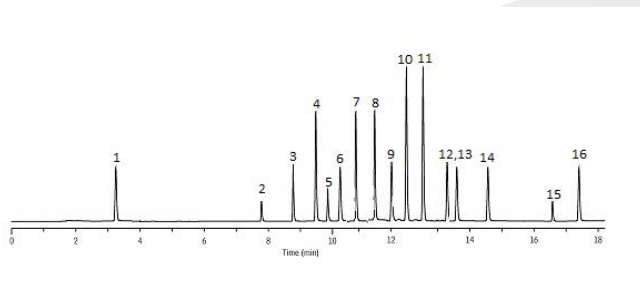
Conditions	
<b>Column 1</b>	SCION-5MS 30m x 0.25mm x 0.25µm
<b>Column 2</b>	SCION-Pesticides 30m x 0.25mm x 0.25µm
<b>Oven Programme</b>	40°C, 2°C/min to 240°C, 20°C/min to 300°C
<b>Carrier Gas</b>	Helium, 2mL/min
<b>Injector</b>	40°C, 100°C/min to 300°C (hold 50.4)
<b>ECDs</b>	320°C

### RESULTS

The retention times of all compounds are detailed in Table 2 with the chromatogram of the mixed standard, analysed on the SCION-5ms column, shown in Figure 1. The \* symbol notes that there was no compound response due to adsorption onto the column.

**Table 2.** Compound retention times on both columns

Peak	Compound	SCION 5-MS	SCION Pesticide
1	Dalapon	5.71	6.73
2	Nitrophenol	27.90	*
3	DCAA	27.04	29.28
4	Dicamba	27.51	29.96
5	Dichloprop	30.36	33.04
6	2,4-D	31.04	33.79
7	DBOB	32.53	34.37
8	Pentachlorophenol	34.38	*
9	2,4,5-TP	34.48	36.88
10	2,4,5-T	35.29	38.42
11	2,4-DB	37.00	39.78
12	Dinoseb	37.13	41.64
13	Bentazon	37.92	42.34
14	Picloram	39.23	45.20
15	Chloramben	44.69	48.88
16	Acifluorfen	46.56	50.88



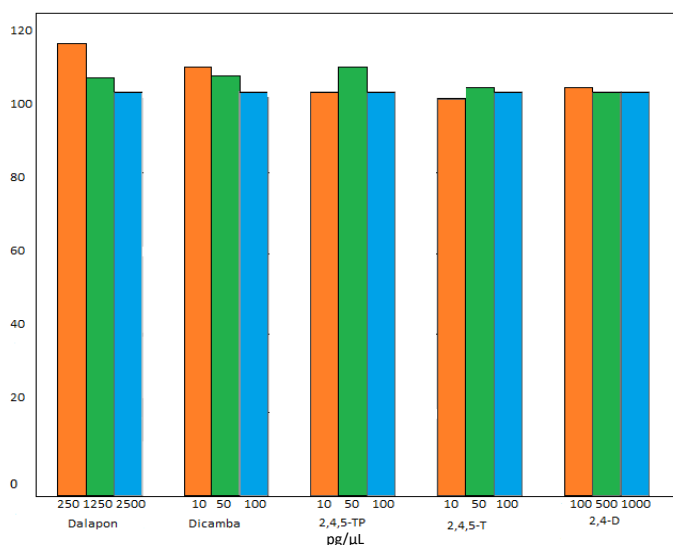
**Fig 1.** Chromatogram of mixed standard, analysed on a SCION-5MS column

The herbicides analysed had a wide range of volatilities. Table 3 details the precision data and minimum detectable levels (MDL) for selected compounds (n=8). The S/N for all MDLs stated was 5.

**Table 3.** Repeatability values of peak area and MDLs for selected compounds

Compound	Conc (pg/μL)	SCION-5MS		SCION-Pest		MDL (pg)
		Area Ave	RSD%	Area Ave	RSD%	
Dalapon	2940	4944	1.05	5708	1.30	7.5
Dicamba	115	976	0.94	1766	2.95	1.5
2,4,5-TP	110	1518	2.29	2892	3.38	1.0
2,4,5-T	105	1067	2.36	1788	2.46	1.5
2,4-DB	1020	2631	4.00	3615	2.58	6.5
Acifluorfen	140	748	2.36	881	3.03	3.5

Preparing calibration standards at several concentrations ensures linearity throughout the system. Detector responses for selected compounds, at varying concentrations can be found in Figure 2.



**Fig 2.** ECD response per picogram of selected methyl esters, at difference concentrations.

## CONCLUSION

The dual column and dual ECD system with SCION GC and programmable injector offers excellent chromatographic performance with compounds over a wide range of volatilities. Using Methyl-8 as a derivatizing agent was possible without compromising the results. The dual system shows excellent repeatability and low detection limits of acidic herbicides when analysed in accordance to EPA 515.