

GC/ECD Analysis of Chlorophenoxyacid Herbicides

Using Columns with Complementing Selectivity and New Reference Mixes

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- Optimized analysis on two stationary phases.
- Complete set of reference mixes for US EPA Method 515.4.
- Acids / methyl esters calibration mixes are at concentrations designed for GC/ECD.

Chlorinated phenoxyacid acid herbicides used to control broadleaf weeds are very persistent contaminants in the environment, particularly in drinking water. These strongly polar compounds readily contribute to hydrogen bonds, making them poorly volatile and strongly adsorptive to chromatographic stationary phases. As a consequence, chlorophenoxyacid herbicides are difficult to analyze by GC. To make these compounds suitable for GC analysis they must be derivatized to methyl esters. The most common derivatization reagent is diazomethane. US Environmental Protection Agency Method 515.4

describes a derivatization procedure using diazomethane and an analysis of the methylated esters using GC with an electron capture detector (ECD). The target list of Method 515.4 phenoxyacid herbicides consists of carboxylic acids and phenols.

When monitoring these methylated esters by GC/ECD two columns are needed, to provide identification and confirmation. Further, it is important to select stationary phases that have low bleed and high thermal stability, because the columns should be heated between analyses

to drive off any retained materials. The primary column chosen for this analysis is a 30m, 0.32mm ID, 0.25 μ m Rtx[®]-CLPesticides2 column. The Rtx[®]-CLPesticides2 stationary phase is highly selective for electronegative compounds and so is very effective in analyses of chlorophenoxyacid herbicides (Figure 1). We selected our new, intermediate-polarity Rtx[®]-440 column as the confirmation column because it has unique selectivity for chlorinated pesticides and is thermally stable to 340°C. Figure 2 shows an analysis of methylated chlorophenoxyacid herbicides on a 30m, 0.32mm ID, 0.25 μ m Rtx[®]-440 column. Resolution is good, and the column exhibits very low bleed at 340°C. In combination, the two columns resolve all target compounds, and the reverse in elution order helps ensure correct identifications. Both columns provide fast analyses.

To design a chlorophenoxyacid herbicide reference material suitable for GC/ECD, detection limits should be determined for each compound in the mix. Because the ECD is highly sensitive, and exhibits a narrow range of linear detection, concentrations of the target compounds must be determined carefully. Additionally, chlorinated phenoxyacid herbicides are photosensitive and heat-labile, so the materials must be packaged in amber ampuls and kept away from heat. Restek now offers a complete set of reference materials for Method 515.4: a chlorinated acids calibration mix, a methylated chlorinated acids calibration mix, a surrogate standard (2,4-dichlorophenylacetic acid), and an internal standard (4,4'-dibromo-octafluorobiphenyl). Note that the acids mix will degrade readily in the presence of alkaline compounds or strong oxidizers, and working solutions must be prepared in acidified glassware. The surrogate standard and internal standard are per recommendations in the EPA method. We selected the solvents for the surrogate standard and internal standard carefully, to ensure compatibility with the calibration mixes, and we prepare both standards at high concentrations, for more economical analysis.

If you are analyzing chlorophenoxyacid herbicides, and want fast analyses and reliable results, we highly recommend the combination of an Rtx[®]-CLPesticides2 column and an Rtx[®]-440 column, together with our complete set of reference materials.

Figure 1 Chlorophenoxyacid methyl esters are well separated on an Rtx[®]-CLPesticides2 column.

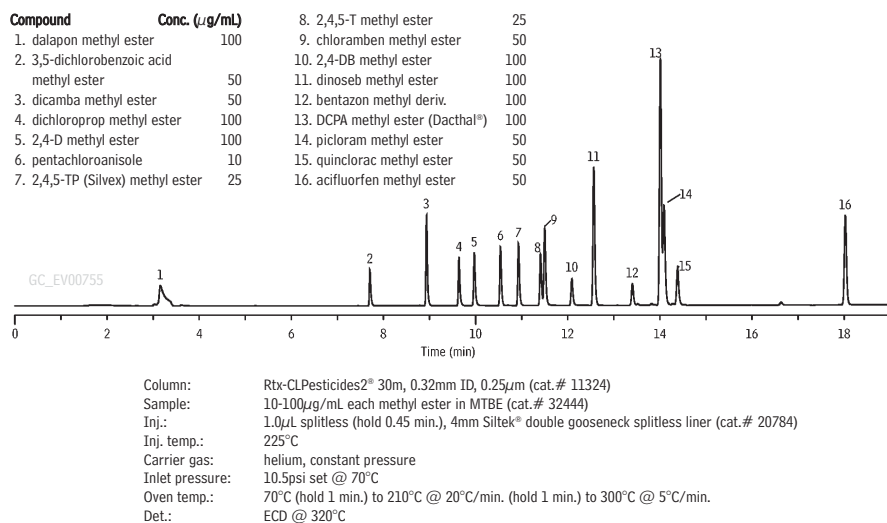
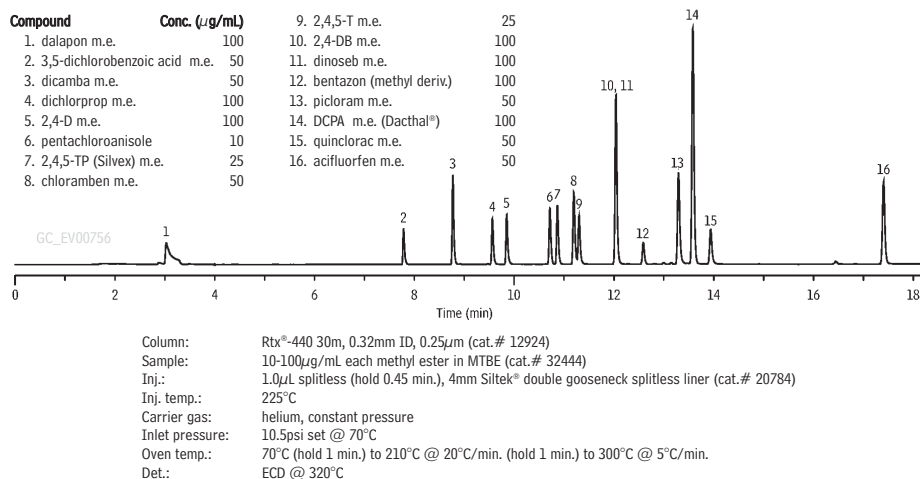


Figure 2 Good resolution of chlorophenoxyacid methyl esters on an Rtx[®]-440 column.

In combination, an Rtx[®]-CLPesticides2 column and an Rtx[®]-440 column resolve all target compounds and provide fast results.





Rtx[®]-440 Column (fused silica)

(proprietary intermediate-polarity Crossbond[®] phase)

Temp. limits: -60 to 310/330°C

ID	df (μm)	length	cat. #
0.32mm	0.25	30-Meter	12924

Rtx[®]-CLPesticides2 Column (fused silica)

Temp. limits: -60 to 320/340°C

ID	df (μm)	length	cat. #
0.32mm	0.25	30-Meter	11324



515.4 Calibration Mix

acifluorfen (Blazer [®])	50μg/mL	3,5-dichlorobenzoic acid	50
bentazon	100	dichlorprop	100
chloramben	50	dinoseb	100
2,4-D	100	pentachlorophenol	10
dalapon	100	picloram	50
2,4-DB	100	quinclorac	50
DCPA diacid (tetrachloro-terephthalic acid)	50	2,4,5-T	25
dicamba	50	2,4,5-TP (Silvex)	25

In acetone, 1mL/ampul

cat. # 32443 (ea.)

515.4 Methylated Chlorinated Acids Mix

acifluorfen methyl ester	50μg/mL	3,5-dichlorobenzoic acid	50
bentazon methyl ester	100	dichlorprop methyl ester	100
chloramben methyl ester	50	dinoseb methyl ether	100
dalapon methyl ester	100	pentachloroanisole	10
2,4-D methyl ester	100	picloram methyl ester	50
2,4-DB methyl ester	100	quinclorac methyl ester	50
DCPA methyl ester (Dacthal [™])	100	2,4,5-T methyl ester	25
dicamba methyl ester	50	2,4,5-TP (Silvex) methyl ester	25

In methyl *tert*-butyl ether, 1mL/ampul

cat. # 32444 (ea.)

515.4 Internal Standard

4,4-dibromooctafluorobiphenyl

2,000μg/mL in methyl *tert*-butyl ether, 1mL/ampul

2,000 cat. # 31856 (ea.)

515.4 Surrogate Mix

2,4-dichlorophenylacetic acid

1,000μg/mL in acetone, 1mL/ampul

1,000 cat. # 32439 (ea.)