

## Environmental Applications Note #59559: Optimizing the Analysis of Chlorophenoxy Herbicides

Chlorine-substituted phenoxyacetic acids, such as 2,4-D, MCPA, and 2,4,5-T [2,4-dichlorophenoxy acetic acid, (4-chloro-2-methylphenoxy) acetic acid, and 2,4,5-trichlorophenoxy acetic acid respectively], were introduced as selective weed killers in the 1940s. Due to their growth-regulating and herbicidal activities against broadleaf weeds, they have been commonly used for weed control on cereal crops, grasslands, and lawns. 2,4-D and 2,4,5-T also were used as the primary defoliant agents in Agent Orange during the Vietnam War. Today, chlorophenoxy herbicides still are used as commercially available lawn weed killers.<sup>1</sup>

Chlorophenoxy herbicides are applied as either esters or salts, which are easily metabolized by plants. The esters are oil soluble, but also can be applied as emulsions in water. The salts typically are highly soluble in water and are used as aqueous concentrates. Because the chlorophenoxy herbicides are spread on top of the soil or grass and then leach into the ground, there is great potential for groundwater contamination. Chlorophenoxy herbicides readily degrade in the environment and for many years were not considered an environmental or public concern. However, potential hazards to public health and environmental quality led to the development of US Environmental Protection Agency (EPA) methods for the analysis of these herbicides. US EPA Methods 615 (municipal/industrial wastewater) and 8151 (solid waste) were developed to monitor chlorophenoxy herbicides in environmental samples.<sup>2,3</sup>

Analysis of chlorophenoxy herbicides using gas chromatography (GC) is difficult. In their free acid form, these herbicides have limited volatility and are prone to irreversible adsorption. To overcome this problem, they are most frequently analyzed as methyl esters. Because these herbicides can be applied as several different types of esters or as a salt, they must first be converted to the free acid form, then derivatized into methyl esters for GC analysis. Methylation increases herbicide volatility and overcomes matrix interferences of herbicides extracted from soil. Despite this derivatization step, analysts still can experience the problems of poor resolution, matrix interference, and peak misidentification.

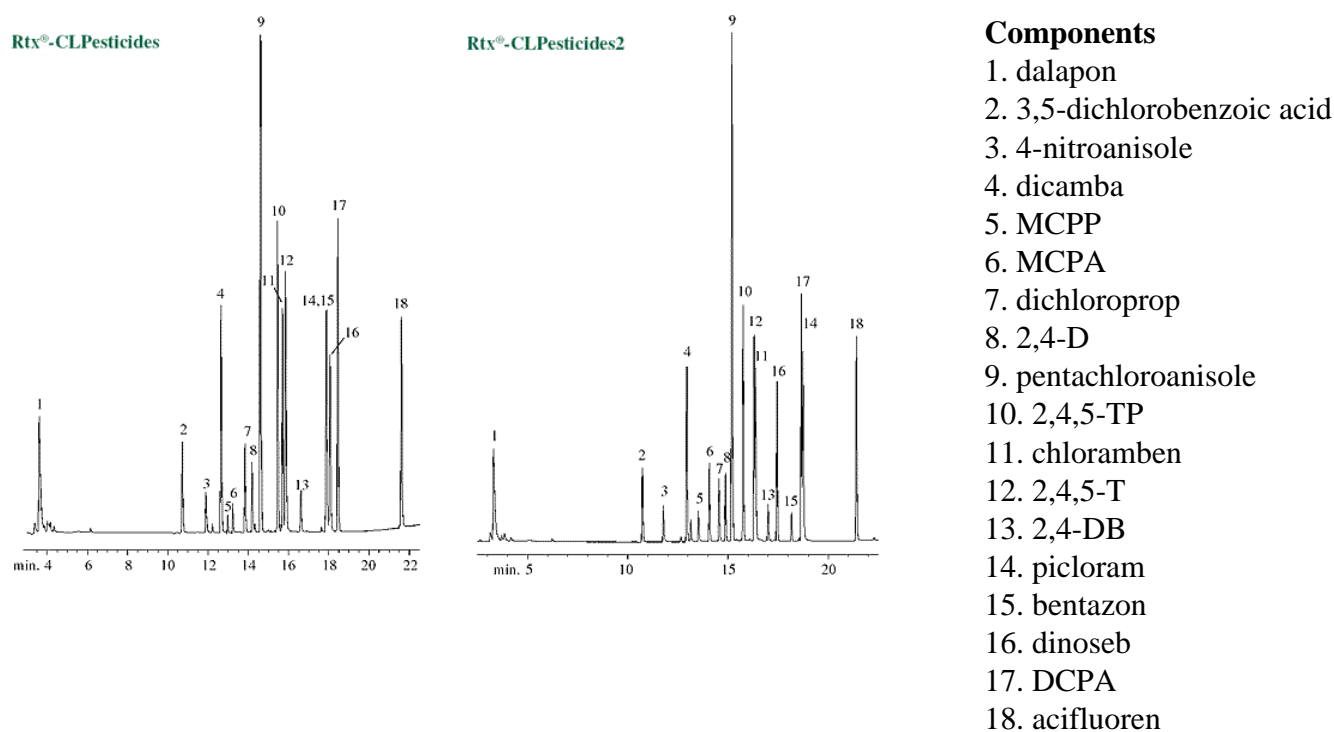
This analysis has been performed on a number of different GC column stationary phases, many of which suffer from slow analysis time, low thermal stability, or coelutions. In addition, many laboratories perform this analysis with the same instrument used for chlorinated pesticide analysis (US EPA 8081). The Rtx®-CLPesticides and Rtx®-CLPesticides2 columns provide unsurpassed separation of pesticides

and herbicides, while allowing high-temperature operation to facilitate the removal of contaminants from the system by programming to 300°C or higher.

Figure 1 shows the separation of the method 8151 target compounds on the [Rtx®-CLPesticides](#) and the [Rtx®-CLPesticides2](#) columns for simultaneous confirmation. These columns were connected using a glass "Y" connector (cat. # 20403) and a 5m guard column (cat. # 10044) installed into a single injection port. The injection port was configured with a direct injection liner (cat. # 20335), which improves the inertness and sample transfer of a splitless injection.

**Figure 1:** The Rtx®-CLPesticides and Rtx®-CLPesticides2 columns give good resolution for all 18 chlorophenoxy herbicides in a single injection.

[Click chromatograms to enlarge](#)



### Conditions

30m, 0.32mm ID, 0.50µm, Rtx®-CLPesticides column (cat.# 11139) and 30m, 0.32mm ID, 0.25µm Rtx®-CLPesticides2 column (cat.# 11324). 1.0µL direct injection of chlorophenoxy herbicides using a Uniliner® sleeve (cat.# 20335), on-column concentration 200-20,000pg/mL. Oven temp.: 80°C (hold 1 min.) to 300°C @ 10°C/min. (hold 10 min.); Inj. / det. temp.: 200°C/300°C; Carrier gas: helium; Inlet pressure: 12.5psi set @ 80°C; ECD sensitivity: 60kHz.

In summary, by configuring your instrument as described and using the Rtx®-CLPesticides and Rtx®-CLPesticides2 columns, the separation of the chlorophenoxy herbicides can be obtained on both columns simultaneously. The surrogates are not shown in these chromatograms because many laboratories use a variety of compounds as surrogates and internal standards for this analysis. The common compounds (1,4-dichlorobenzene, DCAA, and 4,4'-dibromooctafluorobiphenyl) are baseline resolved on both of these columns, so you may use either of them without compromising the chromatography. This same

instrument configuration is also optimal for the analysis of chlorinated pesticides and PCBs.

## Product Listing

### Rtx®-CLPesticides Column

ID	df (µm)	temp. limits	15-Meter	30-Meter
0.25mm	0.25	-60 to 310/330°C	11120	11123
0.32mm	0.50	-60 to 310/330°C	11136	11139
0.53mm	0.50	-60 to 310/330°C	11137	11140

### Rtx®-CLPesticides2 Column

ID	df (µm)	temp. limits	15-Meter	30-Meter
0.25mm	0.20	-60 to 310/330°C	11320	11323
0.32mm	0.25	-60 to 310/330°C	11321	11337
0.53mm	0.42	-60 to 310/330°C	11324	11340

### Universal Angled "Y" Press-Tight® Connectors

20403 (ea.)      20404 (3-pk.)

### Universal "Y" Press-Tight® Connectors

20405 (ea.)      20406 (3-pk.)

### Phenylmethyl Deactivated Guard Columns

ID	length	cat.#
0.25mm	5m	10043
0.32mm	5m	10044
0.53mm	5m	10045

## References

1. Kaufman, D.D., Kearney, P.C., Herbicides, Vol. 1, *Chemistry, Degradation, and Mode of Action*, 2nd Edition, Marcel Dekker, Inc., New York and Basel.
2. US EPA, *Organic Chemical Analysis of Municipal and Industrial Wastewater*; Method 615, "Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater."
3. US EPA, *SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, Final Update 1*; Method 8150A, "Chlorinated Herbicides by Gas Chromatography."


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