Validation Analysis of EPA CLP Target Organochlorine Pesticides with the Agilent 6890 Series GC and Micro-ECD

Application

Gas Chromatography

February 1998

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Abstract

Generating environmental data for organochlorine pesticides in various matrices can be time-consuming for laboratories and engineering firms. To keep a gas chromatograph/electron capture detector (GC/ECD) system operating within control limits, precious analytical time must be spent on tasks such as recalibration, reinjection of samples, detector cleaning, and reintegration of chromatographic peaks. These tasks take time away from running billable samples and adversely affect laboratory throughput.

The Agilent 6890 Series Micro-ECD used in this study shows improved performance in several key areas: increased linear working range (greater than 4 orders of magnitude for some components), increased sensitivity (organochlorine pesticides at sub-ppb levels), increased stability, and increased resistance to contamination.

Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are found worldwide in the environment. Because many of these pesticides are suspected to be carcinogenic and/or endocrine hormone disrupters[1,2], determination of their presence in water, air, soil, and food is required by governmental agencies such as the U.S. EPA, the FDA, and the World Health Organization.

The U.S. EPA provides several comprehensive guidelines[3,4] and regulations[5,6] for analysis of OCPs and PCBs by gas chromatography with electron capture detectors (GC/ECD). These include EPA method 8081 for wastewater/solid wastes, EPA methods 505 and 508 for drinking water/water supplies, EPA method 608 for municipal and industrial discharges, and the Contract Laboratory Program (CLP) method for waste/clean-up sites. Most contract laboratories competing for the large number of potential CLP samples find that competition is strong and profit margins very low compared with other environmental methods.

CLP methods have very specific performance criteria that can be very time-consuming for laboratories to meet consistently. To keep a GC/ECD system operating within control limits, precious analytical time must be spent on tasks such as recalibration, reinjection of samples, detector cleaning, reintegration of chromatographic peaks, etc. Spending too much time with any of these tasks takes time away from running billable samples, and adversely affects the throughput and profitability of the laboratory.

In this study, the 6890 Series Micro-ECD greatly reduced the time required to meet CLP quality control criteria for CLP analysis of OCPs and PCBs. Validated results show four key improvements: increased linear working range (greater than 4 orders of magnitude), increased sensitivity (detecting OCPs at sub-ppb level), more stable calibration, and increased resistance to contamination (more robust, fast detector recovery and reduced maintenance).

Experimental

Water and soil samples were extracted after spiking with surrogates tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DBC). Extracts of OCPs were analyzed in accordance with EPA CLP method OLM03.1[6]. Typically, a 1-L volume of water sample was extracted with methylene chloride by liquid-liquid extraction or a 30-g aliquot of soil/sediment sample extracted with 1:1 acetone/methylene chloride by sonication. These extracts were concentrated and solvent-exchanged into a 10-mL volume of hexane.

Working standards for checking linearity and CLP QA/QC criteria were prepared from certified standards (available commercially) in hexane, as described in the CLP method[5].

All analyses were performed using a 6890 Series GC with an automatic liquid sampler, a single split/splitless inlet, a pair of primary and confirmatory columns, and two 6890 Micro-ECDs. Instrument conditions are listed in table 1.

A sample extract or working standard (1 µL) was injected into the 6890 Series GC in the splitless mode. A guard column (equivalent to a 5-m retention gap, part no. 19095-60610) was used. It was connected to a "Y" glass butt connector that split the sample equally between the pair of columns.

Column A (an equivalent of the Agilent HP-608 column) was used as the primary analytical column, and column B (an equivalent of the Agilent HP-1701 column) was used as the confirmatory column, in accordance with the CLP method.

In the case of poor chromatography or a failing control limit for inlet degradation, routine maintenance was performed. This involved changing the inlet septum, installing a new inlet liner, and clipping a short piece of the retention gap. Columns were routinely conditioned to remove late-eluting column contaminants. When CLP criteria could not be met after routine maintenance, columns were replaced with new columns of the same type.

Table 1. Experimental Conditions

Sampler	Agilent 7673, 10-µL syringe, 1-µL injection
Inlet	Split/splitless; 200 °C, pulsed splitless mode (28 psi for 1 min)
Carrier	Helium, 16.8 psi (150 °C); 3.5 mL/min constant flow (each column)
Column	(1) 30 m, 0.53 mm id, 0.8-µm film DB-608, an equivalent of Agilent HP-608 (part no. 19095S-023)
	(2) 30 m, 0.53 mm id, 1.0-µm film RTX-1701, an equivalent of Agilent HP PAS-1701 (part no. 19095S-123)
Oven	150 °C (0.5 min); 5 °C/min to 280 °C (5–15 min).
Detector	330 °C; makeup gas: nitrogen, constant column and makeup flow (60 mL/min)

Results and Discussion

Sensitivity

Figures 1 and 2 show chromatograms of CLP target organochlorine pesticides on column A using the GC conditions listed in table 1. All 20 OCPs in the midpoint calibration standards (mix A and mix B) were baseline resolved with both the primary analytical column (column A) and the confirmation column (column B, shown in figure 3). The amount of individual OCPs in the midpoint calibration standard was 20–40 pg on-column (methoxychlor was 200 pg). Table 2 lists the concentration of midpoint calibration standards, peak identification, and the Contract Required Quantitation Limits (CRQLs)[6] for all CLP target OCPs.

Figures 1 and 2 also show good responses for dilute OCPs (0.25–0.5 pg on-column, 1/20th of the concentration of those for CRQLs). Quantitation at this level was easy with the micro-ECD; most OCPs exhibited a signal-to-noise ratio greater than 10 (see the lower chromatograms in figures 1 and 2). These results, confirmed by column B and the second micro-ECD (see figure 3), show that the 6890 Series Micro-ECD can easily detect low levels of OCPs (lower than 1/20 of those required by CLP). This is in good agreement with Channel and Chang[7], who reported detection of OCPs as low as 0.050 pg on-column. However, detection of this low level is not necessary because the CRQLs[5] range from 5 to 10 pg (methoxychlor at 50 pg) on-column (see table 2).

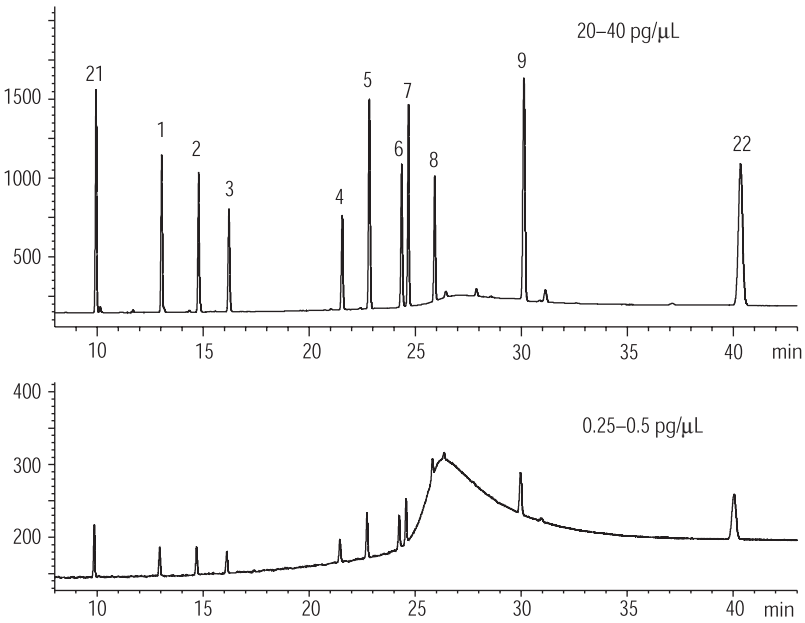

Figure 1. Pesticides in CLP calibration mix A on the primary column (A). 20 pg/µL (upper chromatogram) and 0.25 ng/µL (lower chromatogram) for methoxychlor (peak 9).

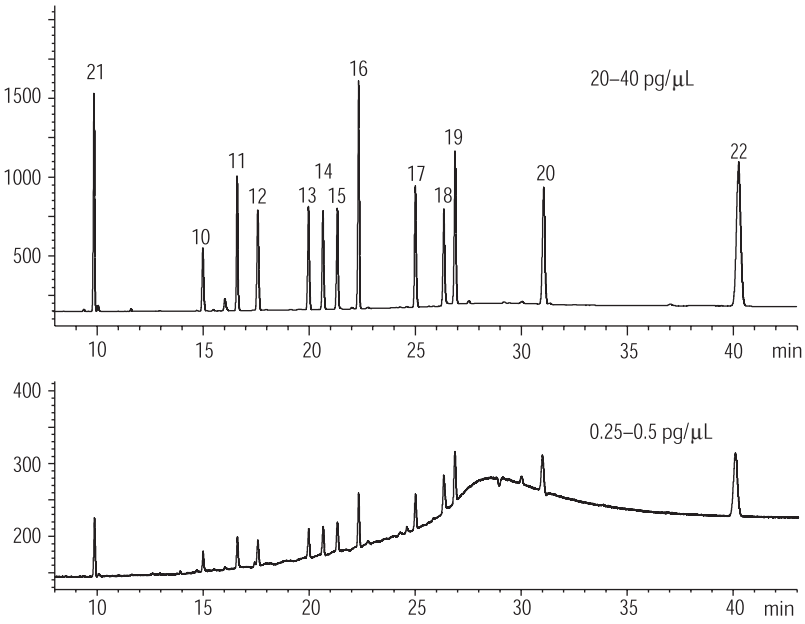

Figure 2. Pesticides in CLP calibration mix B on the primary column (A).

To ensure reliable results, three-point initial calibrations were routinely performed in accordance with CLP requirements using standards of 5, 20, and 80 pg/µL for lindane. Table 2 lists typical response factors and percent relative standard deviation (% RSD) for all CLP target OCPs. Typical % RSDs ranged from 2 percent for beta-BHC to 14 percent for endrin aldehyde, easily meeting the CLP criterion of 20.0 percent or less over the CLP calibration range.

Micro-ECD Linearity

Although classical electron capture detectors can provide sensitive detection, they are notorious for nonlinear response toward OCPs. For example, linearity is problematic for isomers of BHCs, particularly at the high concentration level. On the other hand, linearity as well as low response is problematic for methoxychlor, particularly at the low concentration level. These problems were not encountered using the 6890 Series GC system with micro-ECDs.

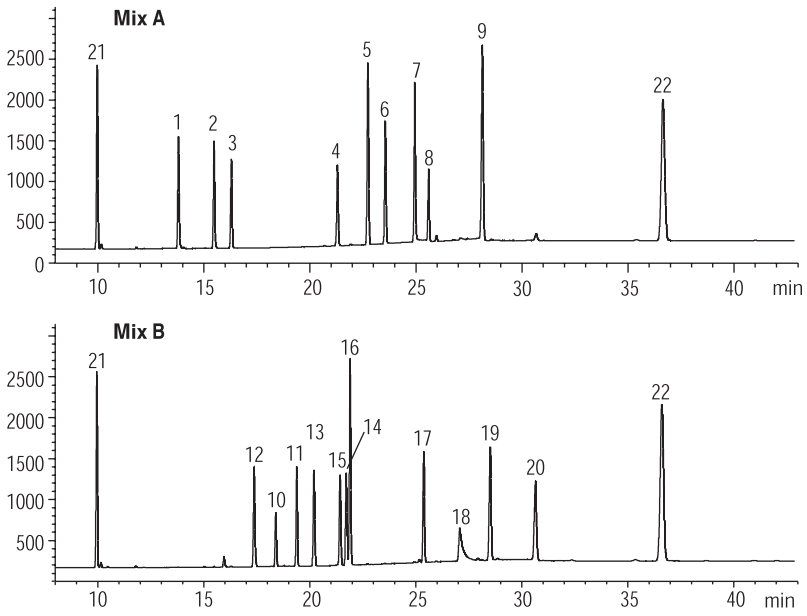

Figure 3. Pesticides on the confirmatory column (B). 20 to 40 pg/µL each, 200 pg/µL for methoxychlor.

Table 2. CLP Target Organochlorine Pesticides and Responses

	Peak	Pesticides	Mid-Level Standard pg/µL (4X)	CRQLs (on column) pg	Response Factors*	
					Average (peak height)	% Relative Standard Deviation
Mix A	1	alpha-BHC	20	5	23052	10.90
	2	gamma-BHC(lindane)	20	5	21729	6.51
	3	Heptachlor	20	5	17661	3.40
	4	Endosulfan I	20	5	15536	2.68
	5	Dieldrin	40	10	16204	4.83
	6	Endrin	40	10	10515	4.54
	7	4,4'-DDD	40	10	14334	5.06
	8	4,4'-DDT	40	10	12418	7.65
	9	Methoxychlor	200	50	4652	5.55
	21	TCX	20	50	16567	2.13
	22	DCB	40	10	5752	14.73
Mix B	10	beta-BHC	20	5	16190	2.40
	11	delta-BHC	20	5	10586	5.40
	12	Aldrin	20	5	20609	11.58
	13	Heptachlor epoxide	20	5	16482	7.01
	14	alpha-Chlordane	20	5	15929	5.20
	15	gamma-Chlordane	20	5	16527	5.69
	16	4,4'-DDE	40	10	15913	5.29
	17	Endosulfan II	40	10	16791	9.52
	18	Endrin aldehyde	40	10	8453	14.20
	19	Endosulfan sulfate	40	10	8926	5.59
	20	Endrin ketone	40	10	2144	3.39
	21	TCX	20	5	10114	3.01
	22	DCB	40	10	5667	14.97

* Typical three-point calibration from column A (concentrations: 1X, 4X, and 16X)

Linearity of the micro-ECD was determined by analyzing a series of dilutions of OCPs at concentrations ranging from 0.1 pg/µL to 3.2 ng/µL for lindane (see the 15-level calibration in table 3). For most OCPs, correlation coefficients were better than 0.99 over a concentration range greater than 5 orders of magnitude (0.1 to 3.2 pg/µL for lindane).

Table 3. Linearity Study

Pesticides		15-Point Calibration		10-Point Calibration			
		Concentration pg/µL	Correlation Coefficients	Concentration pg/µL	Response Factors		Correlation Coefficients
					Average	% Relative Standard Deviation	
Mix A	alpha-BHC	0.1 to 32,000	0.995	1 to 1,600	52,557	19.3	0.998
	Lindane	0.1 to 32,000	0.997	1 to 1,600	46,635	17.3	0.997
	Heptachlor	0.1 to 32,000	0.997	1 to 1,600	35,712	18.0	0.997
	Endosulfanl	0.1 to 32,000	0.997	1 to 1,600	31,858	13.9	0.998
	Dieldrin	0.2 to 64,000	0.995	2 to 3,200	35,718	19.0	0.995
	Endrin	0.2 to 64,000	0.992	2 to 3,200	24,849	19.5	0.996
	4,4'-DDD	0.2 to 64,000	0.995	2 to 3,200	33,903	17.3	0.996
	4,4'-DDT	0.2 to 64,000	0.992	2 to 1,600	20,618	18.2	0.993
	Methoxychlor	1 to 320,000	0.990	10 to 4,000	8,199	16.1	0.998
	TCX	0.1 to 32,000	0.997	1 to 1,600	72,423	10.8	0.998
	DCB	0.2 to 64,000	0.996	2 to 3,200	23,956	17.2	0.998
Mix B	beta-BHC	0.1 to 32,000	0.995	1 to 1,600	21,388	11.6	0.998
	delta-BHC	0.1 to 32,000	0.993	1 to 1,600	47,532	17.0	0.997
	Aldrin	0.1 to 32,000	0.994	1 to 1,600	35,851	14.3	0.997
	Heptachlor epoxide	0.1 to 32,000	0.994	1 to 1,600	36,234	11.9	0.998
	alpha-Chlordane	0.1 to 32,000	0.995	1 to 1,600	34,958	12.2	0.997
	gamma-Chlordane	0.1 to 32,000	0.995	1 to 1,600	35,250	11.3	0.997
	4,4'-DDE	0.2 to 64,000	0.989	2 to 3,200	40,065	18.6	0.996
	Endosulfan II	0.2 to 64,000	0.991	2 to 1,600	24,212	16.4	0.997
	Endrin aldehyde	0.2 to 64,000	0.990	2 to 3,200	18,628	16.6	0.995
	Endosulfan sulfate	0.2 to 64,000	0.992	2 to 3,200	27,644	14.7	0.996
	Endrin ketone	0.2 to 64,000	0.990	2 to 3,200	20,803	13.6	0.996

For a smaller concentration range (3 orders of magnitude), correlation improved and % RSDs of calibration factors for most OCPs were within 20 percent as required by CLP (see the 10-point calibration in table 3). Figure 4 shows a linear curve for lindane (1 to 1,600 pg/µL), typical of most OCPs in this concentration range. Figure 4 also shows the linear curve for methoxychlor (10 to 4000 pg/µL), a pesticide that typically responds poorly to classical ECD. This concentration range, typically from 1 to 1,600 or from 2 to 3,200 pg/µL for most OCPs, represents a 100-fold improvement over that required by CLP (CLP specifies 5 to 80 pg/µL for lindane). This wider linearity range allows more analyses for samples without requiring rework (dilution/concentration and re-analysis). If dilution of samples is required, the higher linearity of the detector results in more accurate estimations of correct dilution factors to bring sample concentrations within the CLP range.

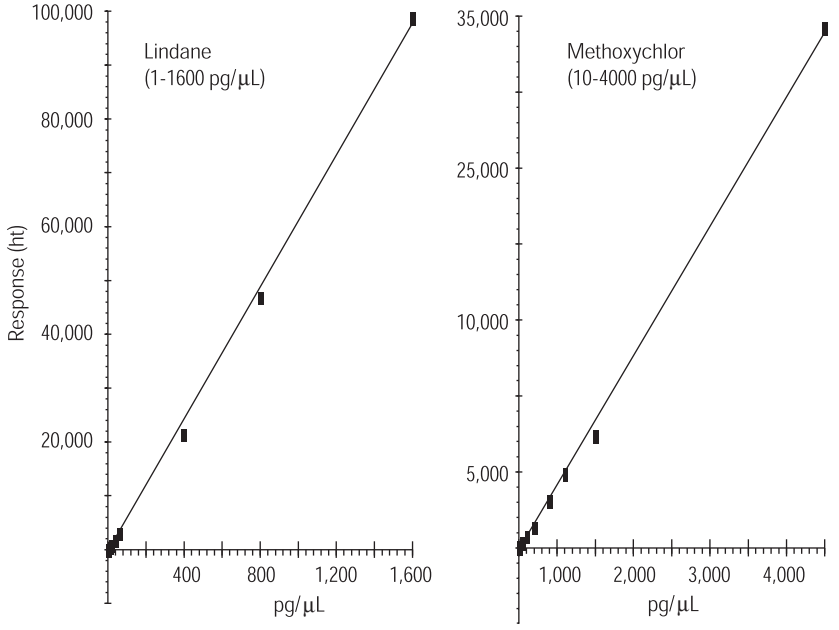

Figure 4. Linear calibration curves for lindane and methoxychlor over extended ranges.

Calibration Stability and System Robustness

The 6890 Series GC system with 6890 Micro-ECDs was regularly calibrated in accordance with CLP requirements. Analyses of blanks, continuous calibration using the midlevel standards, and performance evaluation mix were performed for each 12 hours of operation or every 10 to 20 samples. If results of these analyses failed to meet CLP breakdown, retention time, and response criteria, routine maintenance (such as changing inlet septum and liner or clipping a few inches off the guard column) was performed. If necessary, the instrument was recalibrated (using a three-point initial calibration). No cleaning or baking of the micro-ECD was required, even though a wide variety of samples was analyzed, including some dirty soil extracts[8].

At a minimum, CLP requires that system stability be monitored by analyzing midpoint calibration standards every 12 hours. In this study, system (or calibration) stability was based on verification of the calibration factors and retention times of target OCPs to match those from the initial calibration run within specific limits. The difference in calibration response (RPD—relative percent difference) between the later midpoint calibration run and the initial calibration run must be less than ± 25 percent (upper and lower RPD control limits).

Figure 5 is a continuous calibration verification (CCV) control chart of RPD for lindane and methoxychlor on column A over a 6 month period, typical of most OCPs on both column A and column B.

Throughout this study, the system was within RPD control limits and other calibration verification criteria for several days at a time without performing any re-calibration. When any OCP failed to meet CLP calibration verification criteria (that is, when an OCP was outside the RPD control limits of the CCV), nonintrusive system maintenance was conducted and a new initial calibration was performed. These steps were also done when the instrument was switched for 1 or 2 weeks to analyze a different type of sample, requiring a different GC method. When the instrument was switched back to the original CLP analysis of OCPs and PCBs, the instrument still met calibration verification criteria (within the RPD control limits). This represents a significant improvement over previous designs that usually required full recalibration after switching between methods and indicates that using the micro-ECD saved time and improved laboratory productivity.

Over a period of 6 months, the 6890 Series GC/dual micro-ECD system was in continuous operation

and performed several different methods. For example, the system was used for 2 to 3 weeks to analyze pesticides and aroclors by the CLP method and solid waste method (EPA method 8081). The system was then switched to a drinking water method[8] for a few weeks and later returned to the CLP method for OCPs. In other instances, the system was switched to analyze herbicides (EPA method 8150), then to drinking water (EPA method 504), and back again to the CLP method or method 8081 for OCPs and aroclors. In each case, the stabilization of the micro-ECDs was fast, requiring only a few injections of hexane blanks prior to running the CCV calibration standards.

Throughout this study (which included continuous operations over 6 months), even though routine column and inlet maintenance was needed (columns were replaced once during the course of the study), no micro-ECD maintenance was needed.

Conclusion

The improved performance of the Agilent 6890 Series GC/dual micro-ECD system met all CLP criteria for the analysis of OCPs over a period of 6 months. System validation was performed throughout this period for a wide variety of samples and analyses of different EPA methods. The 6890 Series GC with micro-ECDs easily met and maintained CLP criteria during the study. In addition, the micro-ECD showed improved sensitivity, greater dynamic and linear operating ranges, and more stable response. Moreover, it required minimal maintenance, and showed rapid recovery after switching between methods. Use of the Agilent 6890 Micro-ECD has a high potential to save time, improve quality of data, and increase laboratory productivity.

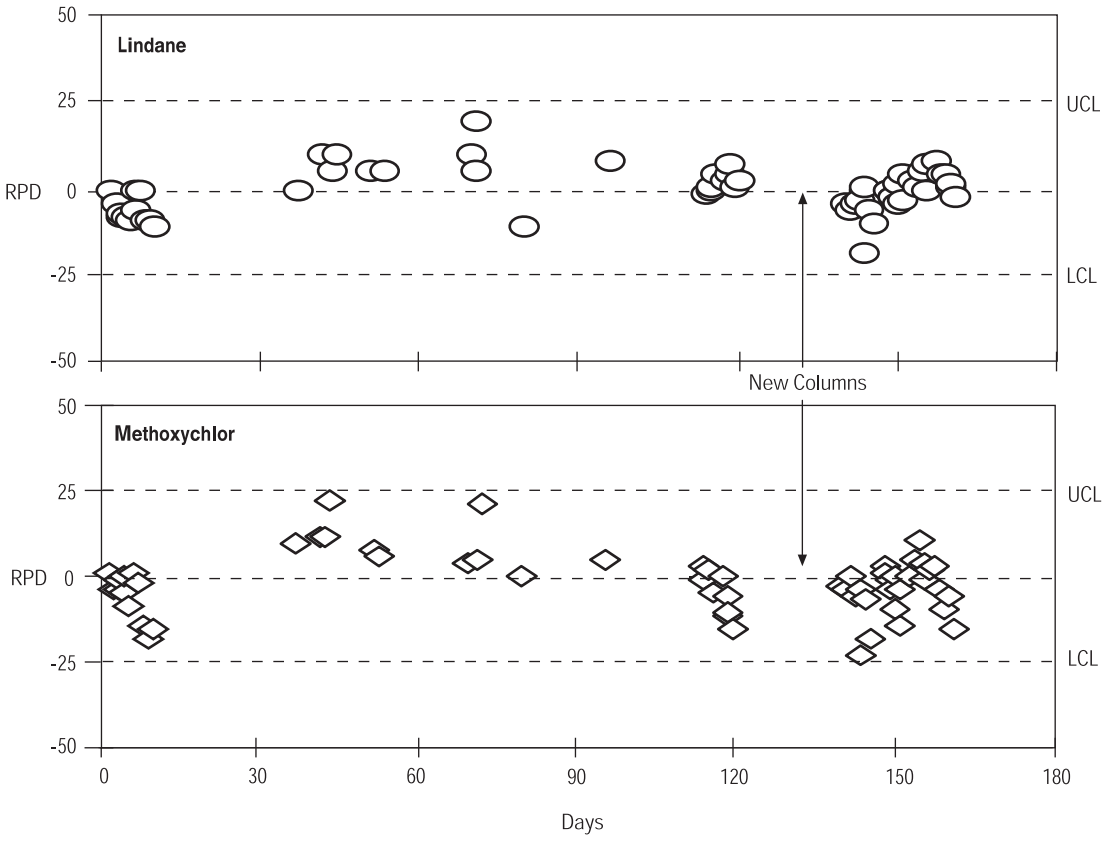

Figure 5. CCV control chart demonstrating stability of response and performance during the study.

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Printed in the USA 4/2000
5966-3742E

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