Organohalide Pesticides in Water by GC/μECD with Agilent J&W DB-CLP1 and DB-CLP2

Application Note

Environmental

Authors

Doris Smith and Ken Lynam
Agilent Technologies, Inc.

Abstract

Organohalide pesticides were successfully extracted from water samples using liquid-liquid extraction and analyzed by a dual column GC/μECD method. An Agilent J&W DB-CLP1 and DB-CLP2 column set provided suitable separation of the targeted analytes, while enabling reliable detection at and below established maximum contaminant level concentrations. The method was calibrated over a range of 0.02-1.0 μg/L, demonstrating the effectiveness of this application.

Introduction

The widespread agricultural application of organohalide pesticides and herbicides has led to their detection in many environmental ground and surface waters. Pesticide residues can enter water supplies through runoff from direct applications and by leaching through the soil into groundwater. Because of their toxicity and potential health risks, monitoring pesticides in water for human consumption is of particular concern. The European Union (EU) and United States Environmental Protection Agency (EPA) have established regulations for maximum pesticide levels in drinking waters [1,2,3].

One of the most common analytical techniques for the determination of pesticides in water is gas chromatography. Many of the EPA methods established for the analysis of pesticides in water are determined by gas chromatography with electron capture detection (ECD), which provides excellent sensitivity and selectivity for trace organohalide pesticides. These methods also recommend the use of 2 GC columns; a primary analytical column along with a second column having a different selectivity for confirmatory analysis.

Agilent Technologies

This application note uses an Agilent pesticide column set for pesticide analysis using EPA Method 505 [4]. The Agilent J&W DB-CLP1 column is employed for primary analysis, while an Agilent J&W DB-CLP2 column provides confirmatory analysis with a less polar stationary phase and different selectivity to help verify the analyte's identity.

Several of the targeted analytes of EPA Method 505 present separation problems on some manufacturers' pesticide column sets. Difficulties in separation have been noted based on published competitor chromatograms between trans-nonachlor/α-chlordane, simazine/atrazine/γ-BHC, and alachlor/aldrin. The Agilent J&W DB-CLP1 column offers resolution of all 16 pesticides, allowing for more accurate determination.

The procedural standard calibration technique is employed by EPA Method 505 to establish the calibration curves. This technique requires that the calibration standards be treated as samples and processed in the same manner as a sample prior to analysis. This method is used to compensate for inefficiencies in the sample preparation procedure.

Experimental

An Agilent 7890A GC equipped with dual µECD detection and an Agilent 7683B Automatic Liquid Sampler was used for this study. An inert tee was used to split the effluent 1:1 to the primary and confirmation columns. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow path consumable supplies.

Table 1. Chromatographic conditions

Column 1:	Agilent DB-CLP1 30 m x 0.32 mm, 0.25 µm (p/n 123-8232)
Column 2:	Agilent DB-CLP2 30 m x 0.32 mm, 0.5 µm (p/n 123-8336)
Carrier:	Helium, constant flow 2.5 mL/min
Oven:	90 °C (0.5 min), 35 °C/min to 175 °C, 12 °C/min to 300 °C (1.75 min)
CFT device:	Inert tee (p/n G3184-60065), split ratio 1:1
Retention gap:	5 m x 0.32 mm id deactivated fused silica tubing
Inlet:	2 µL splitless 250 °C, purge flow 60 mL/min at 0.5 min
GC/µECD:	Agilent 7890A GC
Sampler:	Agilent 7683B Automatic Liquid Sampler, 5.0 µL tapered syringe (p/n 5181-1273)
µECD:	325 °C, constant column + makeup (N_2) = 30 mL/min

Table 2. Flow path supplies

Vials and caps:	MS certified amber crimp top glass vials and caps kit (p/n 5190-2283)
Vial inserts:	250 µL glass/polymer feet (p/n 5181-8872)
Syringe:	5 µL tapered (p/n 5181-1273)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Ultra inert double tapered liner (p/n 5190-3983)
Ferrules:	0.5 mm id short; 85/15 Vespel/graphite (p/n 5062-3514)
CFT fittings:	Internal nut (p/n G2855-20530)
CFT ferrules:	SilTite ferrules, 0.32 mm id (p/n 5188-5362)
20x magnifier:	20x magnifier loop (p/n 430-1020)

Reagents and chemicals

All reagents and solvents were ACS or Ultra Resi grade. Methanol (MeOH) and hexane from JT Baker were purchased through VWR International (West Chester, PA). Sodium sulfite (Na_2SO_3) and sodium chloride (NaCl) were purchased from Sigma-Aldrich (St. Louis, MO). The EPA 505 analyte standard was purchased from Ultra Scientific (North Kingston, RI, USA).

Solutions and standards

An aqueous sodium sulfite solution was prepared at 5 mg/mL. This solution was added to the sample during collection to reduce any residual chlorine.

The analyte primary dilution standard (PDS) was prepared by diluting the commercially prepared pesticide stock solution with methanol to yield the analytes at a varied concentration of 0.05-12.5 µg/mL. Individual analyte concentrations in the PDS can be found in Table 3. This solution was used to fortify reagent water for method calibration.

Table 3. Individual analyte concentrations for the primary dilution standard based on the commercially prepared neat standard concentrations.

Compound	Commercial standard µg/mL	Primary dilution std (PDS) µg/mL
Alachlor	10.00	10.50
Aldrin	1.00	0.05
Atrazine	250.00	12.50
γ-BHC	1.00	0.05
α-Chlordane	1.00	0.05
γ-Chlordane	1.00	0.05
Dieldrin	1.00	0.05
Endrin	1.00	0.05
Heptachlor	1.00	0.05
Heptachlor epoxide	1.00	0.05
Hexachllorocyclopentadiene	1.00	0.05
Methoxychlor	5.01	0.25
cis-Nonachlor	1.00	0.05
trans-Nonachlor	1.00	0.05
Simazine	251.00	12.55

Sample preparation

A 35 mL water sample was extracted using liquid-liquid extraction with hexane, and the top hexane layer used for GC analysis. Figure 1 illustrates the sample extraction procedure graphically.

A 35 mL aliquot of water was collected in a 40 mL vial and 0.35 mL of 5 mg/mL aqueous Na_2SO_3 was added to convert any residual free chlorine. The calibration standards were prepared by adding the appropriate amount of primary dilution standard to yield the desired analyte concentrations.

Six grams of NaCl were added to the sample, followed by 2 mL hexane. The sample was sealed and shaken vigorously by hand for 1 minute. The organic and aqueous layers were allowed to separate, and the hexane layer transferred to GC vials for analysis.

Results and Discussion

The 16 targeted organohalide pesticides were resolved on the DB-CLP1 primary analysis column and DB-CLP2 confirmation column in less than 14 minutes. Figure 2 depicts the dual column GC/μECD chromatograms of a 1.0 μg/L extracted standard. Atrazine and simazine co-elute on the DB-CLP2, but are resolved on the primary analysis column. The DB-CLP1 was able to sufficiently separate *trans*-nonachlor from the chlordane isomers, and atrazine from simazine. The resolution, as calculated by the half width method, for *trans*-nonachlor relative to *gamma*-chlordane, was 1.03 and 2.91 relative to *alpha*-chlordane. The resolution between atrazine and simazine was determined to be 2.12.

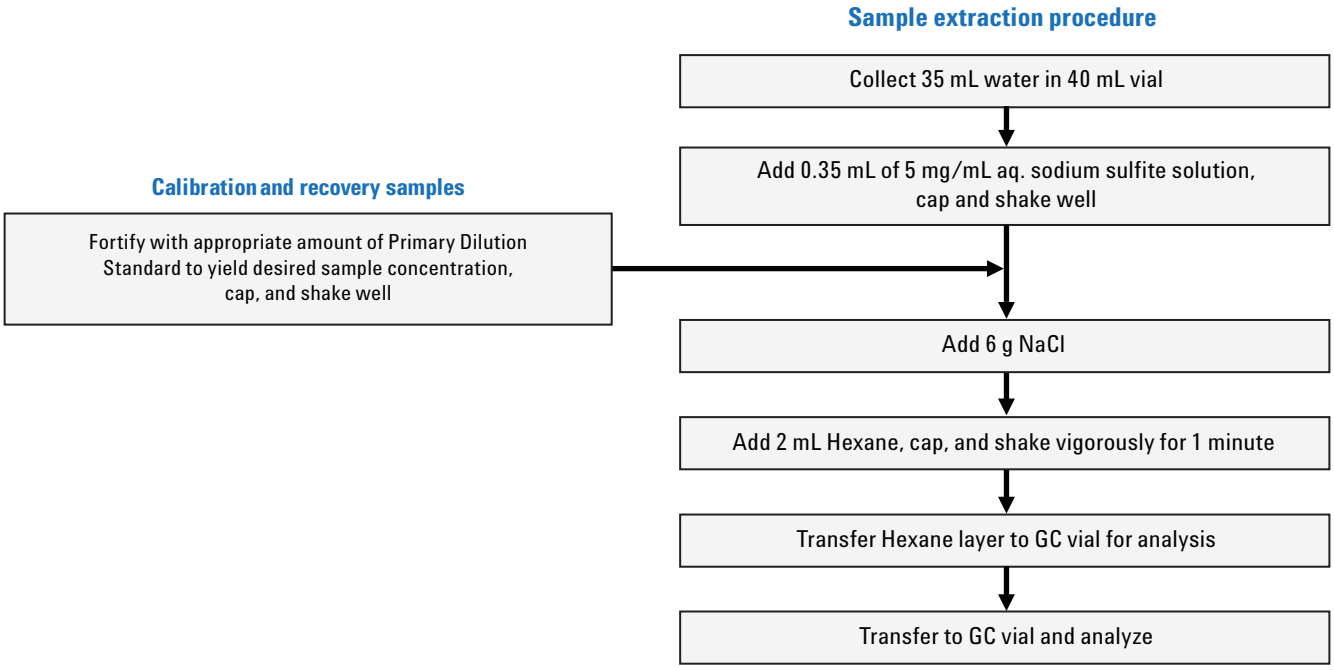

Figure 1. Flow chart for the extraction of organohalide pesticides in water.

Separation of EPA 505 organohalide pesticides

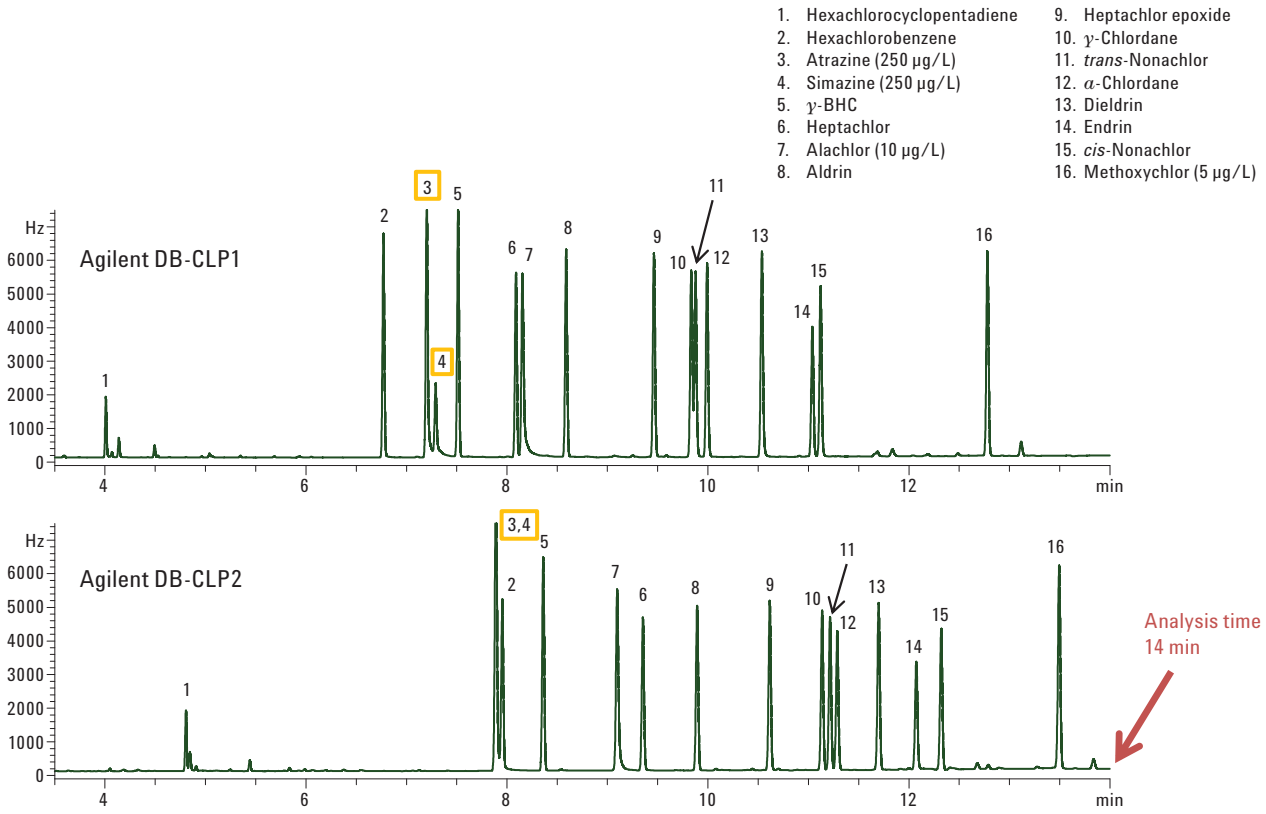

Figure 2. GC/µECD chromatogram of a 1 µg/L fortified standard analyzed on an Agilent J&W DB-CLP1 30 m × 0.32 mm, 0.25 µm column (part number 123-8232) and DB-CLP2 30 m × 0.32 mm, 0.5 µm column (part number 123-8336). This sample was prepared and extracted according to the sample preparation procedure detailed in Figure 1. Chromatographic conditions are listed in Table 1.

A 6 point calibration curve was generated to test the linearity of the method. Linearity as defined by the correlation coefficient (r^2) of the calibration curve can be used to evaluate the performance of a gas chromatographic column. The calibration standards were fortified at 0.02, 0.05, 0.1, 0.2, 0.5, and 1 µg/L. These standards were processed and extracted in the same manner as samples to account for any deficiencies in the sample preparation procedure.

A nonlinear response can be indicative of breakdown or adsorption of the compound in the inlet or column. The performance of the DB-CLP1 and DB-CLP2 columns yielded correlation coefficient (r^2) values ≥ 0.998 over the calibration range of this study, with the exception of simazine which was slightly lower. The individual pesticide analyte values are shown in Table 4.

Figure 3 depicts the GC/µECD chromatogram for a 0.1 µg/L fortified sample. This level is at the maximum contaminant level (MCL) set by current EU regulations, and below MCLs established by the EPA. The chromatogram shows excellent response and separation at this level which enables the accurate quantification needed for reliable pesticide monitoring.

Table 4. Correlation coefficients (r^2) for EPA 505 organohalide pesticides calibration standards determined by GC/µECD.

Linearity results

	r^2 values	
Analyte	**DB-CLP1**	**DB-CIP2**
Hexachlorocyclopentadiene	1.0000	0.9999
Hexachlorobenzene	1.0000	0.9983
Atrazine	0.9997	0.9998
Simazine	0.9911	*
γ-BHC	0.9998	0.9998
Heptachlor	0.9996	0.9999
Alachlor	0.9996	0.9993
Aldrin	0.9995	0.9998
Heptachlor epoxide	0.9999	1.0000
γ-Chlordane	0.9997	1.0000
trans-Nonachlor	0.9999	0.9999
α-Chlordane	0.9999	1.0000
Dieldrin	0.9998	1.0000
Endrin	0.9998	0.9998
cis-Nonachlor	0.9999	0.9999
Methoxychlor	0.9999	0.9998

*Co-elution

0.1 µg/L Extracted reagent water sample

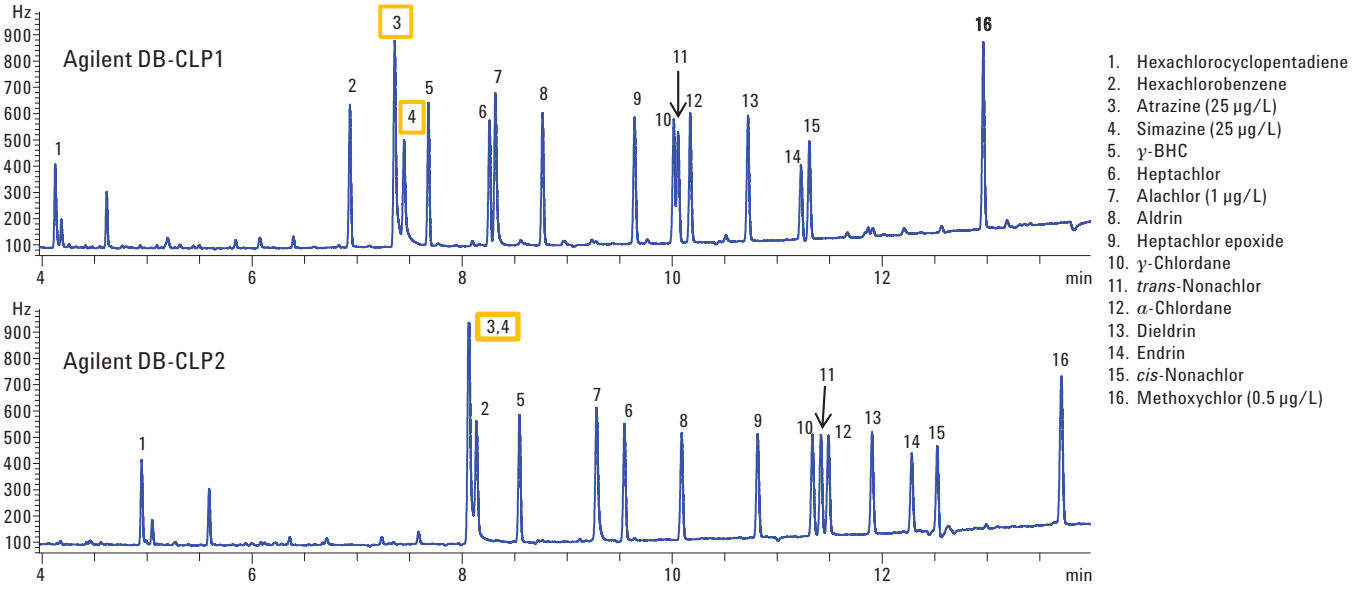

Figure 3. GC/µECD chromatogram for a water sample fortified at the maximum contaminant level of 0.1 µg/L set by current EU and EPA regulations This sample was prepared and extracted according to the sample preparation procedure detailed in Figure 1, and analyzed using an Agilent J&W DB-CLP1 30 m × 0.32 mm, 0.25 µm column (part number 123-8232) and DB-CLP2 30 m × 0.32 mm, 0.5 µm column (part number 123-8336). Chromatographic conditions are listed in Table 1.

The method was able to detect organohalide pesticides with a high level of sensitivity at trace levels. A tap water sample was analyzed for the targeted pesticides to demonstrate the effectiveness of the method. The water sample was collected and prepared according to the sample preparation steps shown in Figure 1 and evaluated under the chromatographic conditions listed in Table 1. Figure 4 shows the tap water sample relative to a reagent blank and an extracted 0.02 µg/L fortified reagent water sample on the DB-CLP1 and DB-CLP2 columns. The 0.02 µg/L sample was fortified at a level well below the established EU and EPA threshold for pesticides in drinking water. The targeted compounds were not detected in the tap water sample at the calibrated range of this study.

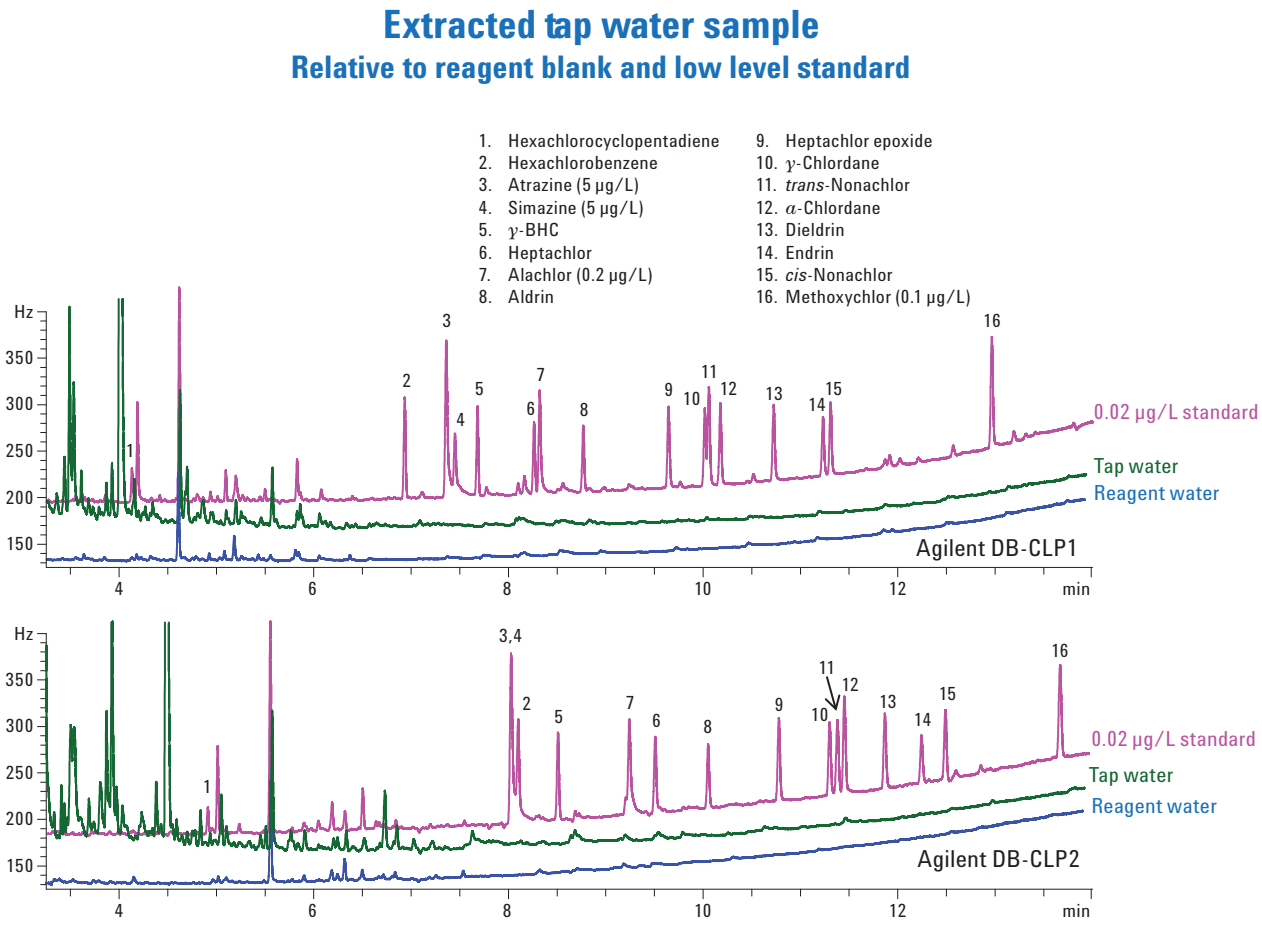

Figure 4. GC/µECD chromatograms for a tap water sample, reagent water blank, and a standard fortified at a level of 0.02 µg/L. The chromatographic traces are same scale, but offset for illustration purposes. These samples were prepared and extracted according to the sample preparation procedure detailed in Figure 1, and analyzed using an Agilent J&W DB-CLP1 30 m × 0.32 mm, 0.25 µm column (part number 123-8232) and Agilent J&W DB-CLP2 30 m × 0.32 mm, 0.5 µm column (part number 123-8336). Chromatographic conditions are listed in Table 1.

Conclusions

This application demonstrates an effective analytical method to extract and detect sub-µg/L level organohalide pesticides in water samples. The Agilent J&W DB-CLP1 and DB-CLP2 column set resolved the 16 targeted analytes, while providing excellent sensitivity and reliable quantitation at sub-µg/L levels. An analysis time just under 14 minutes allows for a higher sample throughput and increased laboratory productivity.

Calibration standards showed good linearity on both columns, yielding regression coefficients $r^2 \geq 0.998$ with the exception of simazine, which was slightly lower at 0.991.

This method was able to detect pesticides at an order of magnitude below the EU and EPA maximum contaminant levels for pesticides in water. A water sample fortified at 0.02 µg/L was prepared and successfully analyzed by this application exhibiting the capability of DB-CLP1 and DB-CLP2 columns for low level pesticide determination. Analysis of a tap water sample did not detect any pesticides at the calibrated levels of this method.

References

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