



## Project Summary

# Development of Methods for Pesticides in Wastewaters

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The project covered by the full report involved the development of monitoring procedures for the analysis of 33 pesticides in relevant industrial wastewaters. The procedures were modeled after existing 304(h) procedures, specific yet as simplified as possible. Common techniques such as packed column gas chromatography (GC) and high performance liquid chromatography (HPLC) with specific detection systems were used in conjunction with standard work-up procedures based on separatory funnel-methylene chloride extraction, Kuderna-Danish (K-D) concentration, and silica gel or Florisil cleanup whenever possible. Method detection limit (MDL) and the applicable analytical range were determined from spiked reagent water samples. Precision and accuracy of the methods were determined in relevant industrial wastewaters where possible.

*This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The methods described in the full report were developed to meet USEPA's responsibility to promulgate multi-residue test procedures for the analysis of pesticides in industrial wastewaters. This protocol was modeled after the form and philosophy of existing and proposed 304(h) methods. Common techniques and equipment were employed and although specificity was required, the procedures were kept as simple as possible with a minimum

number of steps. The preferred determinative step was gas chromatography; high pressure liquid chromatography was the second choice.

The compounds investigated were categorized according to:

- Similarities in structure
- Similarities in determinative step
- Co-occurrence in relevant industrial wastewater

The protocol had the following goals:

- 1  $\mu\text{g}/\text{L}$  gas chromatographic detection limit or 10  $\mu\text{g}/\text{L}$  HPLC detection limit, and
- 85 percent recovery of analytes from reagent water.

### Chromatography

The first step in development of each test procedure was the experimental determination of a detection system that met the sensitivity requirement for each one of the compounds to be analyzed in a given group. Chromatographic columns and operating parameters were selected that would separate the compounds expected to co-occur in a given industrial waste sample. The separation had to be sufficient for quantitation while keeping the analysis time under 1 hr. In some cases, more than one system was required for a given wastewater. This occurred when a single industrial facility manufactured either structurally very similar or very dissimilar compounds. Problems requiring the development of a second chromatographic system were coelution, retention times of more than 1 hr, and inadequate sensitivity for one or more compounds produced at a single site.

## Model Verification or Modification

After chromatographic conditions were selected, the applicability of the model procedure suggested by existing 304(h) methods was tested for each compound. The model utilized 1-liter sample volumes extracted with three aliquots of methylene chloride followed by K-D concentration and standard column cleanup techniques, if required.

## Extraction and Concentration

The percent recovery of each compound from deionized water at neutral pH was determined, and adjustments in the pH of the water or the volume of the extraction solvent were used to maximize the percent recovery value of this step.

## Cleanup

The appropriate solvent fortified with each compound was applied to a standard adsorbent column and the column eluted with various solvent mixtures. The elution pattern and percent recovery value for this procedural step were determined for each compound. Variations from the cleanup step of the model procedure included changes in the composition of elution mixture, water deactivation of the sorbent, and use of various sorbents. Often, further method modifications were required to separate the compounds of interest from interferences found in the relevant wastewater. The systems developed and described in each report must be considered only as a starting point in effecting an adequate cleanup.

## Application to Relevant Industrial Wastewater

After extraction and cleanup procedures were developed using fortified reagent water, industrial wastewaters, which reflected the matrices in which the studied compounds were likely to be present, were analyzed. Further modifications were made as necessary. Selected compound groups were then fortified at detectable levels into relevant industrial wastewater samples and percent recovery values from this matrix were determined.

Precision and accuracy were determined from the analysis of seven replicates of fortified relevant industrial wastewaters. Method detection limits were determined in fortified reagent water samples. Analytical curves were generated to determine and demonstrate the linearity of recovery of the compounds from reagent water.

Table 1 lists the methods developed and the compounds within each method. The compounds within a method designation are grouped according to similar analytical characteristics.

**Table 1. Pesticides Grouped by EPA Method Numbers**

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604.1	<i>Phenolic Pesticides</i>
	<i>Dichlorophen</i>
	<i>Hexachlorophen</i>
616	<i>Neutral C, H &amp; O Pesticides</i>
	<i>Cycloprate</i>
	<i>Kinoprene</i>
	<i>Methoprene</i>
	<i>Resmethrin</i>
618	<i>Volatile Pesticides</i>
	<i>Chloropicrin</i>
	<i>Ethylene dibromide</i>
620	<i>Diphenylamine</i>
622.1	<i>Thiophosphates</i>
	<i>Dichlorofenthion</i>
	<i>Famphur</i>
	<i>Fenitrothion</i>
	<i>Fonofos</i>
	<i>Phosmet</i>
	<i>Thionazin</i>
633.1	<i>Neutral Nitrogen Containing Pesticides</i>
	<i>Fenarimol</i>
	<i>MGK - 264</i>
	<i>MGK - 326</i>
	<i>Pronamide</i>
634	<i>Thiocarbamate Pesticides</i>
	<i>Butylate</i>
	<i>Cycloate</i>
	<i>EPTC</i>
	<i>Moilnate</i>
	<i>Pebulate</i>
	<i>Vernolate</i>
	<i>Giv Gard</i>
635	<i>Rotenone</i>
636	<i>Bensulide</i>
637	<i>MBTS and TCMTB</i>
638	<i>Oryzalin</i>
639	<i>Bendiocarb</i>
640	<i>Mercaptobenzothiazole</i>

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Table 2 lists some chromatographic systems and parameters utilized in the methods. Stability studies (holding times, etc.) were not specified in this contract.

**Table 2. Chromatographic Systems and Parameters Developed for Methods**

Method	Compound	MDL ( $\mu\text{g/L}$ )	Detector	Chromatographic Column	Operating Parameters	Retention Time (min.)
604.1	Dichlorophen	1.0	UV/254	5 $\mu$ Spherisorb-ODS, 250 x 4.6 mm	65/35 acetonitrile/water .05% $\text{H}_3\text{PO}_4$ at 1 mL/min	4.2
	Hexachlorophen	1.2				9.7
616	Cycloprate	21	FID	3% SP-2250 on 100/120 mesh Supelcoport	Programmed from 180° to 240° at 8°/min, Injector = 280 Det. = 300°	3.6
	Kinoprene	18	FID			4.4
	Methoprene	22	FID			5.5
	Resmethrin	36	FID			8.4
618	Chloropicrin	0.8	ECD	1% SP-1000 on Carboapak B (60/80 mesh), 1.8 m x 2 mm ID, glass column	135° Isothermal	5.6
	Ethylene Dibromide	0.2	ECD			9.9
620	Diphenylamine	1.6	NPD	3% SP-2250 on Supelcoport (100/120 mesh), 180 cm x 2 mm ID, glass column	Column temp. held at 80° for 4 min programmed to 300°C at 8°/min and held at 300° for 4 min	18.1
622.1	Aspon	0.6	NPD	3% SP-2250 on Supelcoport (100/200 mesh) 1.8 m x 2 mm ID, glass column	Column temp. held at 80°C for 4 min and programmed to 300°C at 8°/min and held at 300° for 4 min	22.6
	Dichlorofenthion	0.7	NPD			21.4
	Famphur	19	NPD			28.1
	Fenitrothion	2	NPD			23.1
	Fonofos	0.7	NPD			20.5
	Phosmet	1	NPD			30.0
	Thionazin	1	NPD			18.3
633.1	Fenarimol	4	NPD	3% SP-2250 on Supelcoport (100/200 mesh) 1.8 m x 2 mm ID, glass column	Column temp. at 80° for 4 min and programmed to 300° at 8°/min and held for 4 min	30.6
	MGK-264	2	NPD			23.0
	MGK-326	6	NPD			21.9
	Pronamide	4	NPD			19.9
634	Butylate	0.6	NPD	3% SP-2100 on Supelcoport (100/120 mesh) 1.8 m x 2 mm ID, glass column	Column temp. at 80°C for 4 min programmed to 300° at 8°/min and held for 4 min	18.2
	Cycloate	1.6	NPD			24.2
	EPTC	0.9	NPD			17.9
	Molinate	0.6	NPD			23.8
	Pebulate	0.8	NPD			20.2
	Vernolate	1.1	NPD			19.6
635	Rotenone	1.6	UV/254	5 $\mu$ Zorbax-CN 250 x 4.6 mm	30/70 methylene chloride/hexane, at 1 mL/min	8.6
636	Bensulide	1.6	UV/270	5 $\mu$ Spherisorb-ODS, 250 x 4.6 mm	55/45 acetonitrile/water, 1 mL/min	14.1
637	MBTS	0.5	UV/254	5 $\mu$ Dupont Zorbax-CN, 250 x 4.6 mm	15/85 methylene chloride/hexane, at 1 mL/min	6.6
	TCMTB	1.0				9.3
638	Oryzalin	0.5	UV/254	5 $\mu$ Spherisorb-ODS, 250 x 4.6 mm	40/60 acetonitrile/water at 1 mL/min	6.2
639	Bendiocarb	1.8	UV/254	5 $\mu$ Spherisorb-ODS, 250 x 4.6 mm	40/60 acetonitrile/water at 1 mL/min	9.3
640	Mercaptobenzothiazole	1.7	UV/254	5 $\mu$ Spherisorb-ODS, 250 x 4.6 mm	50/50 acetonitrile/water at 1 mL/min	8.4

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This Project Summary covers 13 separate reports, entitled:

"Determination of Thiophosphates in Industrial and Municipal Wastewaters—Aspon, Dichlorofenthion, Famphur, Fenitrothion, Fonofos, Phosmet, and Thionazin," (Order No. PB 85-189 017/AS; Cost: \$10.00)

"Determination of Thiocarbamates in Industrial and Municipal Wastewater—Butylate, Cycloate, EPTC, Molinate, Pebulate, and Vernolate," (Order No. PB 85-189 009/AS; Cost: \$10.00)

"Determination of Neutral Nitrogen-Containing Pesticides in Industrial and Municipal Wastewaters—Fenarimol, MGK 264, MGK 326, and Pronamide," (Order No. PB 85-189 157/AS; Cost: \$10.00)

"C, H, and O Compounds—Cycloprate, Kinoprene, Methoprene, and Resmethrin," (Order No. PB 85-188 951/AS; Cost: \$10.00)

"Determination of Volatile Pesticides in Industrial and Municipal Wastewaters," (Order No. PB 85-189 918/AS; Cost: \$8.50)

"Determination of Bendiocarb in Industrial and Municipal Wastewaters," (Order No. PB 85-188 159/AS; Cost: \$8.50)

"Determination of Bensulide in Industrial and Municipal Wastewaters," (Order No. PB 85-188 977/AS; Cost: \$8.50)

"Determination of Rotenone in Industrial and Municipal Wastewaters," (Order No. PB 85-188 993/AS; Cost: \$8.50)

"Determination of Oryzalin in Industrial and Municipal Wastewaters," (Order No. PB 85-188 985/AS; Cost: \$8.50)

"Determination of Diphenylamine in Industrial and Municipal Wastewaters," (Order No. PB 85-190 874/AS; Cost: \$8.50)

"Determination of Mercaptobenzothiazole in Industrial and Municipal Wastewaters," (Order No. PB 85-191 120/AS; Cost: \$8.50)

"Determination of Hexachlorophene and Dichlorophen in Industrial and Municipal Wastewaters," (Order No. PB 85-188 209/AS; Cost: \$8.50)

"Determination of MBTS and TCMTB in Industrial and Municipal Wastewaters," (Order No. PB 85-189 025/AS; Cost: \$8.50)

The above reports will be available only from: (cost subject to change)

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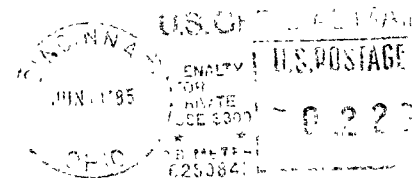
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