

METHOD 8540

PENTACHLOROPHENOL BY UV-INDUCED COLORIMETRY

1.0 SCOPE AND APPLICATION

1.1 This method may be used for field-testing of soil samples for pentachlorophenol (PCP). This method was designed for use at sites where PCP is the principal contaminant. Wood treatment sites are the primary application for this test, and it has been designed around the presence of other wood treatment-related compounds such as fuel oil and creosote. Testing products are commercially available for this method.

Compound	Abbreviation	CAS Number*
Pentachlorophenol	PCP	87-86-5

* Chemical Abstracts Service Registry number

1.2 Method 8540 is recommended for analyzing soil samples to determine whether PCP is present at concentrations above 1.5 mg/kg. Method 8540 provides for the quantitation of PCP relative to a three-point standard curve over a calibration range of 2-90 ppm.

1.3 Using the testing products from which this method was developed, 0% of spiked sand samples containing 0.75 mg/kg PCP produced a false positive result, and 0% of spiked sand samples containing 3.0 mg/kg PCP produced a false negative result. Tables 1 and 2 contain the results of the false positive and false negative analyses, respectively.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two, Sec. 2.1, for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

2.0 SUMMARY OF METHOD

2.1 PCP is extracted from soil using methanol. The mixture is shaken manually, allowed to settle, and filtered.

2.2 An aliquot of the filtered methanol extract is added to acidified (pH=2) HPLC-grade water and the mixture is loaded onto a solid-phase extraction (SPE) column. The PCP is eluted from the column with hexane. The hexane eluate is mixed with basic (pH=12) water and is shaken. The PCP is now in the aqueous phase and the hexane is decanted off.

2.3 The aqueous solution containing the PCP is poured into a vial containing acidic water, octane, and cobalt chloride to facilitate separation. The mixture is shaken and allowed to separate. The PCP is now in the octane. Approximately half of the octane is removed and added to a vial containing approximately 50 mg of sodium sulfate.

2.4 An aliquot of the octane is taken from the vial containing the octane/sodium sulfate and is added to the vial containing the Quick Test[®] Reagent in an isopropyl alcohol solution. The mixture is placed in a plastic cuvette, mixed, and capped. The concentration of the PCP is determined using a dedicated colorimeter with UV light exposure set at 260 nm.

3.0 DEFINITIONS

Refer to Chapter One, Method 8000, and the manufacturer's instructions for definitions associated with this analytical technique.

4.0 INTERFERENCES

4.1 The use of this field-testing product should be limited to determination of pentachlorophenol in soil. It is not intended for use in other media or for other contaminants. The color producing reaction used in this test method is not specific to pentachlorophenol. In general, the reagent will react with halogenated aliphatics and PCBs. Sensitivity increases with the number of halogens. For example, a dichlorophenol does not react as strongly as a trichlorophenol. The solid-phase extraction and acid-base cleanup steps remove almost all of the listed interferents with the exception of chlorophenol.

4.1.1 The presence of compounds that are chemically similar may cause positive test results (false positives) for PCP. The testing product used in preparation of this method was evaluated for interferences. Table 3 provides the concentrations of various compounds found to yield a false positive result when PCP was present in the sample at 5 mg/kg (ppm).

4.1.2 Other compounds have been tested for cross-reactivity with PCP, and have been demonstrated to not interfere with this method. Table 4 provides a list of compounds that do not interfere with the determination of 5 mg/kg of PCP using this method

4.2 Follow the manufacturer's recommendations regarding storage of testing products.

4.3 Due to the presence of reagents that are highly sensitive to UV light, it is recommended that the testing product be protected from direct sunlight or indirect sunlight during storage and use. Quality assurance and calibration check samples are included with every kit and allow the operator to verify reagent and system integrity.

4.4 The photochemical reaction (which produces the color used for quantitation) is carried out inside the instrument automatically. The color that is produced from the reaction of PCP with the reagent is not stable and begins to decay shortly after exposure. The rate of decoloration is

dependent on the temperature and PCP concentration. Table 8 illustrates the reaction stability observed. The relative instability of the reaction is not of concern since the instrument measures the color automatically and immediately after exposure. Using the instrument design that was evaluated by EPA, it is not possible to remeasure the color, and therefore the PCP concentration; because the final product is not stable.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The Quick Test[®] for PCP in Soil Testing product contains the following hazardous materials and it is recommended that proper precautions be taken during their use: pentachlorophenol (2, 20, 90 ppm solutions in octane) standards and calibration checks, Quick Test[®] reagent, methanol, isopropyl alcohol, and octane. Material safety data sheets for all solvents and reagents should be reviewed prior to use of this kit.

6.0 EQUIPMENT AND SUPPLIES

6.1 The Quick Test[®] for PCP in Soil Testing product (Envirol, Inc.) or equivalent. Each commercially-available testing product will supply the reagents and materials necessary for completion of five tests as well as solutions for calibration verification.

6.2 A portable instrument (the Envirometer) is required for use of this method. The Envirometer serves two functions. First, it exposes each sample to a controlled amount of UV light. Second, the Envirometer functions as a colorimeter to quantify absorbance. The Envirometer also performs the necessary calculations to convert the sample absorbance into a concentration that is displayed in mg/kg of PCP.

6.3 A portable balance (Acculab PP-150-B, Davis Instruments or equivalent) is necessary to weigh the soil samples.

6.4 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample and sample container.

6.5 An adjustable pipette (200-1000- μ L) (Wheaton, 851268 or equivalent) is necessary to measure and transfer solutions.

7.0 REAGENTS AND STANDARDS

7.1 Each commercially-available testing product will supply or specify the reagents necessary for successful completion of the test. Reagents should be labeled with appropriate expiration dates.

NOTE: The Quick Test[®] reagent is very sensitive to UV light and is compromised when exposed to strong UV sources such as sunlight. The thermal and reactive stability (aside from photoreactivity) of the reagent was tested over a period of 6 months at 40°C and over a period of 3 months at 60°C. The Quick Test[®] reagent was observed to deteriorate slowly (based on post-exposure absorbance) remaining useful at 40°C for up to 50 days. Deterioration at 60°C occurred almost immediately, and post-exposure absorbance was significantly lower after 7 days. The reagent has been tested at 25°C and remained stable for 4 months at that temperature. Notably, even after deterioration due to thermal extremes, the Quick Test[®] reagent may still be used, provided that the field instrument is standardized using deteriorated reagent, although this is not a recommended practice.

NOTE: PCP is relatively stable thermally and reactively, except when exposed to UV light. The thermal and reactive stability of PCP was tested over a period of four weeks at 45°C and was found acceptable, although loss of solvent limited the period of the experiment (See Ref. 3). Based on these data, it has been determined that the thermal and reactive stability of key components (reagent and PCP) will not be important factors in determining the shelf life of the testing products.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

8.2 The soil samples being analyzed may be contaminated with PCP or other compounds, and should be handled accordingly.

8.3 The balance should be calibrated according to the manufacturer's instructions. To help assure accurate quantitation, large pebbles, roots, twigs, or any foreign material should be removed from the soil sample prior to weighing.

8.4 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for quality control procedures specific to use of the testing product. Additionally, follow the guidance in Chapter One.

9.2 Procedures to verify the testing product performance.

This method is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.2.1 The standard curve should be run at the beginning of each analysis period, when large ambient temperature variations occur (greater than 30°F or 15°C) during the course of the testing, or when the calibration verification results fall outside of the acceptance limit (see Sec. 9.2.2).

9.2.2 The calibration verification samples provided with each kit contain 20 mg/L (ppm) of PCP and are analyzed periodically to verify Envirometer calibration. In order to be

acceptable, the results for the calibration verification sample must be within $\pm 20\%$ of the true value (i.e., 16 to 24 mg/L).

9.3 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the testing product.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The Envirometer is calibrated by analyzing three standard solutions (2, 20, 90 mg/kg); provided in each kit, after which the results are stored in the memory of the Envirometer. These three points make up the standard curve that is used for quantitation.

10.2 Consult the manufacturer's instructions regarding the details of generating the calibration curve and the calculations performed by the Envirometer.

11.0 PROCEDURE

Follow the manufacturer's instructions for the use of the testing product. The sections below summarize the procedure. If this summary conflicts with the manufacturer's instructions, follow the manufacturer's instructions.

11.1 Extraction

A 5.0-g soil sample is weighed and transferred to the container supplied with the testing product. PCP is extracted from the soil sample using 5 mL of methanol. The mixture is shaken manually for 3 minutes and then allowed to settle for approximately 10 minutes. The soil extract is filtered using a 0.45- μm filter provided with the testing product.

11.2 Cleanup

11.2.1 1.0 mL of the filtered methanol extract is added to 1.5 mL of acidified (pH=2) HPLC-grade water. This mixture is then passed through an SPE column. The PCP is eluted from the SPE column using 7 mL of hexane.

11.2.2 The hexane eluate is mixed with 2.0 mL of basic water (pH=12), shaken for 3 minutes, and allowed to separate. The PCP is in the aqueous phase and the hexane is decanted off.

11.2.3 The aqueous solution containing the PCP is then poured into a vial that contains 0.5 mL of acidified water, 0.1 g of cobalt chloride, and 1.0 mL of octane. The mixture is shaken for 2 minutes and allowed to separate. The PCP is now in the octane layer.

11.3 Drying the extract

Approximately 0.6 mL of the octane (containing the PCP) is removed and added to a vial containing approximately 50 mg of sodium sulfate. Let the solution stand about 30 seconds.

11.4 Reagent addition

A 0.4-mL aliquot of the octane solution is taken from the vial containing the octane/sodium sulfate and is added to a vial containing 1.0 mL of the Quick Test[®] reagent (QT reagent) in an isopropyl alcohol solution. This mixture is poured into a plastic cuvette, mixed gently, and capped.

11.5 Reaction/readout

11.5.1 The cuvette is placed in the Envirometer. The Envirometer performs the following steps automatically:

- Reading the initial absorbance of the eluate/QT reagent solution.
- Exposing the eluate/QT reagent solution to UV light (7-8 minutes).
- Reading the final absorbance of the eluate/QT reagent solution.
- Subtracting the initial absorbance from the final absorbance.
- Using a standard curve stored in the calibration mode, converting the difference, and displaying the concentration of PCP in mg/kg.

11.5.2 The Envirometer displays the results as the PCP concentration in mg/kg.

12.0 DATA ANALYSIS AND CALCULATIONS

Consult the manufacturer's instructions for details on how to generate concentration readings from the Quick Test[®] Envirometer. The Quick Test[®] Envirometer, an integral part of this method, performs all the necessary calculations.

13.0 METHOD PERFORMANCE

13.1 Table 5 provides data on the long-term stability of the Envirometer. These data are based on a single operator and represent 32 measurements of the calibration verification sample over a period of six weeks.

13.2 Table 6 provides data on method accuracy and precision for sand samples spiked with two different concentrations of PCP, 3 mg/kg and 75 mg/kg. The user should be able to obtain accuracy and precision similar to those given in Table 6.

13.3 This method was applied to soils from a former wood-treating site and the results were compared with GC/MS determinations of PCP using Method 8270 in a single laboratory. These results are presented in Table 7.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, D.C. 20036, (202) 872-4477.

14.3 This method does not use any halogenated solvents and may be used to help reduce the number of samples sent to the laboratory under certain project scenarios. Traditional laboratory extraction methods (e.g. Soxhlet or ultrasonic extraction) would generally require much larger volumes of solvents to extract the sample.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Dong Chen, David Shattuck, Mark Hines, and Joan McLean, "Performance Evaluations of the Quick Test[®], a Colorimetric Field Method for the Determination of Pentachlorophenol in Soil," *Field Analytical Chemistry and Technology*, 2(1):29-37, 1998.
2. Quick Test[®] for PCP in Soil Instruction Booklet, Envirol, Inc.
3. Validation Study for Quick Test[®] Soil Analysis Procedure for Pentachlorophenol (PCP), Envirol, Inc., Logan, UT 84321.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages that follow contain Tables 1 through 8. Since this procedure is based on a commercially-available testing product, there is no flow chart for this method.

TABLE 1

FALSE POSITIVE ANALYSIS FOR SAND SPIKED WITH PCP AT 0.75 PPM

Matrix	Number of samples analyzed	Number of samples greater than the detection limit	Number of samples less than the detection limit	Semi-quantitative results: Mean, (s) (mg/kg)	% False Positive
Sand	20	0	20	0.56 (0.16)	0%

Data taken from Reference 3.

TABLE 2

FALSE NEGATIVE ANALYSIS FOR SAND SPIKED WITH PCP AT 3.0 PPM

Matrix	Number of samples analyzed	Number of samples greater than the detection limit	Number of samples less than the detection limit	Semi-quantitative results: Mean, (s) (mg/kg)	% False Negative
Sand	20	20	0	2.6 (0.4)	0%

Data taken from Reference 3.

TABLE 3

COMPOUNDS THAT DEMONSTRATED A POSITIVE INTERFERENCE
WITH THE DETERMINATION OF PCP AT 5 PPM

Compound	Concentration Resulting in Detectable Interference (ppm)
4-Chlorophenol	500
2,4-Dichlorophenol	50
2,4,6-Trichlorophenol	5
2,3,4,6-Tetrachlorophenol	5
Pentachloroanisole	500
Aroclor 1262	500

Data taken from Reference 3.

TABLE 4

COMPOUNDS THAT DEMONSTRATED NO INTERFERENCE
WITH THE DETERMINATION OF PCP AT 5 PPM

Compound	Concentration Resulting in No Detectable Interference (ppm)
Phenol	> 500
Anthracene	> 500
Anthraquinone	> 500
Benzophenone	> 500
9-Fluorenone	> 500
Diesel fuel	> 5000
Creosote	> 5000

Data taken from Reference 3.

TABLE 5

SINGLE-OPERATOR PERFORMANCE FOR A CALIBRATION VERIFICATION STANDARD

Test Conc. (mg/L)	Number of Measurements	Std. Dev. (mg/kg)	Recovery Range (%)	Range of Conc. (mg/kg)
20	32	1.6	85 - 120	17 - 24

Data taken from Reference 3.

Results were generated by a single operator over a period of 6 weeks

TABLE 6

METHOD ACCURACY AND PRECISION FOR SPIKED SAND SAMPLES

Test Conc. (mg/kg)	Number of Measurements	Mean Conc. Found (mg/kg)	Precision, as Std. Dev. (mg/kg)	Observed Range (mg/kg)
3	20	2.6	0.4	1.8 - 3.2
75	10	71	5.6	62 - 80

Data taken from Reference 3.

TABLE 7

COMPARISON OF QUICK TEST® FOR PCP WITH GC/MS IN A SOIL MATRIX

Sample ID	Concentration as Determined by Method 8270 (mg/kg PCP)	Concentration as Determined by Quick Test® (mg/kg PCP)	% Difference
S009	48	81	69
S0014	116	48	-59
S0015	576	>900	NA
S0016	<1.7	<2.0	NA
S0017	109	59	-46
S0018	90	48	-47
S0019	<1.7	<2.0	NA
S0020	<1.7	<2.0	NA
S0021	<1.7	<2.0	NA
S0022	8.7	7.4	-15
S0023	<1.7	<2.0	NA
S0023D	<1.7	ND	NA
S0024	39	42	8
S0025	<1.7	<2.0	NA
S0026	<1.7	2.2	NA
S0027	<1.7	<2.0	NA
S0028	<1.7	<2.0	NA
S0028D	<1.7	ND	NA
S0029	14	17.7	26
S0030	<1.7	3.3	NA
S0031	4.4	3.9	-11
S0032	18	17.5	-3
S0032Q	15	14.5	-3
S0033	31	36	16
S0034	2.0	<2.0	NA
S0035Q	<1.7	<2.0	NA
S0036Q	24	4.7	-80
S0045	127	100	-21
S0048	2.5	2.3	-8
S0050	376	250	-34
S0051	20	15	-25
S0052	<1.7	3.2	NA
S0053	4.7	6.2	32

TABLE 7
(continued)

Sample ID	Concentration as Determined by Method 8270 (mg/kg PCP)	Concentration as Determined by Quick Test® (mg/kg PCP)	% Difference
S0056	42	55	31
S0058	<1.7	<2.0	NA
S0058Q	NA	<2.0	NA
S0060	38	51	34
S0067	40	46	15
S0068	58	64	10
S0084	79	51	-35
S0089	1.7	<2.0	NA
S0090	5.2	5.3	2
S0091	<1.7	<2.0	NA
S0092	494	430	-13
S0093	639	690	8
S0094	99	78	-21
S0097	3	105	3400
S0098	<1.7	<2.0	NA
S0098Q	<1.7	<2.0	NA
S0111	4.6	4.6	0
S0111Q	4.6	3.8	-17
S0116	4.3	5.0	16
S0136	<1.7	<2.0	NA
S0137	<1.7	<2.0	NA
S0138	<1.7	<2.0	NA
S0139	196	122	-38

Data taken from Reference 3.

ND = Not determined

NA = Not applicable

TABLE 8
STABILITY OF COLORED SOLUTION

Time After Exposure (minutes)	PCP Concentration with Time (mg/L)		
	1 mg/L PCP Solution	30 mg/L PCP Solution	90 mg/L PCP Solution
0	0.95	30.7	91.8
1	0.76	30.3	91.5
2	0.62	30.3	90.6
3	0.43	29.5	59.1
4	0.33	29.1	87.9
6	0.29	28.3	84.4
8	0.24	27.5	80.9
10	0.10	26.9	77.1
12	0.10	26.1	73.6
14	0.05	25.6	69.9
16	0.00	25.3	66.1
18	0.00	24.9	62.7
20	0.00	24.4	58.9
22	0.00	24.0	56.3
24	0.00	23.7	56.5
27	0.00	23.1	49.6
30	0.00	22.3	46.8

Data taken from Reference 3.