METHOD 8085

COMPOUND-INDEPENDENT ELEMENTAL QUANTITATION OF PESTICIDES BY GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTION (GC/AED)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the quantitation of semivolatile organohalide, organophosphorus, organonitrogen, and organosulfur pesticides that are amenable to gas chromatography (see Refs. 1 and 2). The following RCRA compounds have been determined by this method (this method may be useful for the analysis of other compounds):

Analyte	CAS No.[1]
Abate (Temephos)	3383-96-13
Acifluorfen	62476-59-9
Alachlor	15972-60-8
Aldrin	309-00-2
Ametryn	834-12-8
Atraton	1610-17-9
Atrazine	1912-24-9
Azinphos ethyl (Ethyl guthion)	642-71-9
Azinphos methyl (Guthion)	86-50-0
Benfluralin	1861-40-1
α-BHC	319-84-6
β-BHC	319-85-7
δ-BHC	319-86-8
γ-BHC (Lindane)	58-89-9
Bromacil	314-40-9
Bromoxynil (Brominal)	1689-84-5
Butachlor	23184-66-9
Butylate	2008-41-5
Captafol	2425-06-1
Captan	133-06-2
Carbophenothion	786-19-6
Carboxin	5234-68-5

Analyte	CAS No.[1]
trans-Chlordane	5103-74-2
Chlorpropham	101-21-3
Chlorpyrifos	5598-13-0
Chlorthalonil (Daconil)	1897-45-6
Coumaphos	56-72-4
Cyanazine	21725-46-2
Cycloate	1134-23-2
2,4-D acid	94-75-7
2,4-DB acid	94-82-6
DCPA (Dacthal)	2136-79-0
2,4'-DDD	53-19-0
4,4'-DDD	72-54-8
2,4'-DDE	3424-82-6
4,4'-DDE	72-55-9
2,4'-DDT	789-02-6
4,4'-DDT	50-29-3
DEF (Butifos)	78-48-8
Demeton-O	298-02-3
Demeton-S	126-75-0
Diallate	2303-16-4
Diazinon	333-41-5
Dicamba	1918-00-9
Dichlobenil (Casoron)	1194-65-6
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dichlorvos (DDVP)	62-73-7
Diclofol (Kelthane)	115-32-2
Diclofop-methyl	51338-27-3
Dieldrin	60-57-1
Dimethoate	60-51-5
Dinoseb	88-85-7
Dioxathion	78-34-2
Diphenamid	957-51-7
Disulfoton (Disyston)	298-04-4
Diuron**	330-54-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
EPN	2104-64-5
Eptam (EPTC)	759-94-4
Ethalfluralin (Sonalan)	55283-68-6
Ethion	563-12-2

Analyte	CAS No.[1]
Ethoprop	13194-48-4
Fenamiphos*	22224-92-6
Fenarimol	60168-88-9
Fenitrothion	122-14-5
Fensulfothion	115-90-2
Fenthion	55-38-9
Fluridone	59756-60-4
Fonofos	944-22-9
Gardona (Tetrachlovinphos)	961-11-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Hexazinone	51235-04-2
Imidan (Phosmet)	732-11-6
Ioxynil	1689-83-4
Malathion	121-75-5
MCPA acid	94-74-6
MCPP acid	7085-19-0
Merphos	150-50-5
Metalaxyl	57837-19-1
Methoxychlor	72-43-5
Methyl chlorpyrifos	5598-13-0
Methyl paraoxon	311-45-5
Methyl parathion	298-00-0
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Mevinphos	7786-34-7
MGK-264	113-48-4
Mirex	2385-85-5
Molinate	2212-67-1
Napropamide	15299-99-7
Norflurazon	27314-13-2
4-Nitrophenol	100-02-7
Oxyfluorfen	42874-03-3
Parathion	56-38-2
Pebulate	1114-71-2
Pendimethalin	40487-42-1
Pentachlorophenol (PCP)	87-86-5
Phorate	298-02-2
Phosphamidon*	297-99-4
Picloram	1918-02-1
Profluralin	26399-36-0
Prometon (Pramitol 5p)	1610-18-0
Prometryn	7287-19-6

Analyte	CAS No.[1]
Pronamide (Kerb)	23950-58-5
Propachlor (Ramrod)	1918-16-7
Propargite (S-181)	2312-35-8
Propazine	139-40-2
Propetamidophos	31218-83-4
Ronnel	299-84-3
Silvex (2,4,5-TP)	93-76-5
Simazine	122-34-9
Sulfotepp	3689-24-5
Sulprofos (Bolstar)	35400-43-2
2,4,5-T acid	94-82-6
2,4,5-TB	93-80-1
Tebuthiuron**	34014-18-1
Terbacil	5902-51-2
Terbutryn (Igran)	886-50-0
2,3,4,5-Tetrachlorophenol	4901-51-3
2,3,4,6-Tetrachlorophenol	58-90-2
Triademefon	43121-43-3
Triallate	2303-17-5
Triclopyr (Garlon)	55335-06-3
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2
Trifluralin (Treflan)	1582-09-8
Vernolate	1929-77-7

[1] Chemical Abstract Service Registry Number
* These analytes were not recovered from water during low-level detection studies.
** These analytes were quantitated from their breakdown products.

1.2 This method employs an atomic emission detector (AED) which is used for the detection of organic compounds containing heteroatoms. Heteroatoms, in this case, are defined as those elements other than carbon, hydrogen, and oxygen.

1.3 Quantitations are made from a compound-independent calibration (CIC) utilizing an AED elemental response that is not compound specific. A calibration and response check standard is used to validate the quantitation of a target analyte by CIC and to generate its quantitation limit.

1.4 Analytes that are detected in a sample must have their identifications confirmed by evidence that the ratios of their component elements agree with the empirical formulae of the analytes, based on their retention times on a dissimilar column, or by gas chromatography/mass spectrometry (GC/MS). The techniques of confirmation by element ratios are addressed in this procedure. Other confirmation techniques are described in Method 8000.

1.5 This method may be used for screening samples for the presence of organic compounds containing heteroatoms. Unknown elemental responses should be investigated further. Elemental ratios, relative retention time matching, and GC/MS spectral information provide tentative identification. Element responses and element fractions from tentative identifications are used to estimate the concentration of the analyte in the sample.

1.6 This method also may be used for screening samples to determine that target analytes are not present. When the response criteria have been met using the calibration and response check standards, then the target analytes can be reported as non-detects at the calculated quantitation limits.

1.7 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 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.

1.8 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use of GC/AED and the interpretation of the resulting data. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (liquid, solid, or other) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Liquid samples may be extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), or other appropriate technique. Acid herbicides should be extracted and processed by Method 8151 or other appropriate technique.

2.3 Solid samples to be analyzed for neutral compounds may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), or other appropriate technique. Acid herbicides should be extracted and processed by Method 8151 or other appropriate technique.

2.4 If the sample is to be screened for both neutral pesticides and herbicide acids, the extracts may be combined following methyl ester/ether derivatization and solvent exchange of the herbicide fraction.

NOTE: Combining the acid herbicide and neutral pesticide fractions is not generally recommended.

2.5 The extract is analyzed by injecting a measured aliquot into a gas chromatograph equipped with a fused-silica capillary column and an atomic emission detector (GC/AED). The AED uses a microwave-induced helium plasma to generate temperatures in the detector that are high enough to break the molecular bonds of the compounds that elute from the GC. The resulting free atoms undergo electron excitation, followed by relaxation and photo emission. These atomic emissions occur at frequencies that are characteristic of the element. The intensity of the atomic emission is proportional to the concentration of the element in the detector. In this method, the emission frequencies and intensities are monitored for seven elements. The results are used for detecting and quantitating the eluting pesticides. If multiple heteroatoms are present, the ratio of the heteroatoms of the eluting pesticides can be determined as an aid to identification.

2.6 Two types of instrumental calibration are available with this method.

2.6.1 Compound-independent calibration (CIC) -- The AED response to each element is independent of compound structure, thus compound-independent calibration, or elemental calibration, is possible. The heteroatoms sulfur, nitrogen, chlorine, bromine, iodine, phosphorous, and fluorine (if needed) are calibrated using a compound-independent calibration mixture (CIC mix). The elemental response factors obtained from the CIC are used to quantitate individual heteroatoms contained in any or all compounds eluting from the column. The results of the heteroatom quantitation are then translated into the concentrations of the target compounds and/or to tentatively identified unknown compounds (TICs).

2.6.2 Compound-dependent calibration -- If the presence of a target analyte is confirmed in the sample, but the calibration and response check criteria fail for that analyte, then a compound-dependent multi-level calibration for that analyte must be performed. See Method 8000 or other appropriate 8000 series methods for details on compound-dependent multi-level calibration and the associated quality assurance and control.

3.0 DEFINITIONS

3.1 Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure. Method 8000 also contains detailed descriptions for some terms used in this method.

3.2 Heteroatoms -- This method considers all elements other than carbon, hydrogen and oxygen to be heteroatoms. In this method, bromine, chlorine, fluorine, iodine, nitrogen, phosphorous, and sulfur are heteroatoms of interest.

3.3 Compound-dependent calibration -- An instrument calibration model that relates the response of the detector to a standard of the actual target compound, such that standards for each analyte of interest are necessary. This approach historically has been used in methods for organic compounds.

3.4 Compound-independent calibration (CIC) -- An instrument calibration model where the compound used to calibrate the instrument is not necessarily the analyte of interest. For the atomic emission detector described in this method, the intensity of the spectral emission line of an element is calibrated to the concentration of that element. The analyte of interest must contain the element for which the instrument is to be calibrated, but it need not be the compound with which the instrument is calibrated. The source of the element for calibration is thus independent of the analyte of interest.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. Due to the unique selectivity of AED, if these interferences do not contain the heteroatom(s) of interest, they will not likely pose a problem for the analysis. All reagents and equipment routinely must be demonstrated to be free from problem interferences under the conditions of the analysis by running laboratory reagent blanks as described. Refer to Method 8000 and each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware.

4.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in a muffle furnace at from 420 °C to 430 °C for a minimum of one-half hour. Thorough rinsing with acetone may be substituted for the heating process. After drying and cooling, seal and store glassware in a clean environment to prevent accumulation of dust or other contaminants.

CAUTION: Thermally stable compounds such as PCBs may need longer heating times. However, oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses of other compounds.

4.1.2 The use of high purity reagents and solvents helps to minimize interferences. Purification of solvents by distillation in all-glass systems may be necessary.

CAUTION: Solvents may contain stabilizers that have been added by the manufacturer but that may be removed by redistillation, thus potentially reducing the shelf-life and safety of the solvents.

4.2 Although phthalate esters do not contain heteroatoms within their molecular structure and thus will not be seen on the heteroatom channels, these compounds can still pose a problem in the analysis. These compounds generally appear as large peaks on the carbon channel chromatogram. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached during laboratory operations. Cross-contamination of glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of the reagents (especially sodium sulfate, sodium chloride, cellulose thimbles and glass wool, which usually come packed in plastic) and glassware may be necessary to eliminate background phthalate contamination.

4.3 Cross-contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the syringe and associated equipment with an appropriate solvent(s) can minimize sample cross-contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of solvent should be made to ensure that accurate values are obtained for the next sample.

4.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. Also, note that all the analytes listed may not be totally resolved from each other on any column, i.e., one analyte of interest may interfere with another. The extent of matrix interferences will vary considerably from source to source, and is dependent on the matrix type (i.e., soil/sediment and water matrices with high percent solids are more likely to have higher interferences than a well water matrix, etc.). Sulfur is a common matrix contaminant, especially in marine sediments, and may render the sulfur channel partially, or totally, useless. Cleanup of sample extracts may be necessary for some target compounds. See the 3600 series of methods for different cleanups.

CAUTION: This method may be used for screening samples for any compound containing nitrogen, sulfur, iodine, bromine, chlorine, or phosphorus that can be chromatographed by GC. However, it has been observed that cleanup of any sort may remove certain compounds, thereby preventing them from being detected by this method. Therefore, when this method is used in a screening mode, extract cleanup should be avoided until all samples have been screened. Alternatively, standards containing the analytes of interest should be processed through all cleanup steps to determine the losses during cleanup.

4.5 A dirty septum or the GC inlet can be a potential source of contamination, especially if high analyte concentrations were present in a previous sample. If several blank or solvent injections display a contaminant present at about the same concentration, then the septum should be changed. In addition, dirty injector liners may cause degradation of some analytes or a loss of late-eluting compounds.

4.6 Iodine will respond on the sulfur 181 nm channel as a negative deflection. In addition, iodine and very large amounts of sulfur will respond as a positive deflection on the phosphorous 178 nm channel. It is recommended that the phosphorous 186 nm channel, which does not respond to these elements, be simultaneously monitored with the phosphorous 178 nm channel.

4.7 Analytical difficulties encountered for target analytes include, but are not limited to:

4.7.1 Demeton (Systox) is a mixture of two compounds; O,O-diethyl-O-[2-(ethylthio)ethyl]phosphorothioate (demeton-O) and O,O-diethyl-S-[2-(ethylthio)ethyl]phosphorothioate (demeton-S). Two peaks are observed in the chromatograms corresponding to these isomers. Thus, any new standard of demeton may need to have an elemental calibration performed to assess the concentrations of the individual isomers. These compounds have also exhibited poor method performance.

4.7.2 Merphos (tributyl phosphorotrithioite) is a single-component pesticide that is readily oxidized to phosphorotrithioate (merphos oxone) under aqueous conditions. This oxidation product happens to be the organophosphorous pesticide tribufos (DEF). If tribufos is detected in a sample, further investigation would be needed to determine which of the two pesticides was initially present.

4.7.3 Chlorpyrifos and parathion co-elute on the DB-5 column and both contain the elements sulfur, nitrogen and phosphorous. Furthermore, the elemental ratios of these heteroatoms for both pesticides are very similar. However, chlorpyrifos contains chlorine, whereas parathion does not. Especially in this situation, it is recommended that a sample be analyzed for all of the heteroatoms in the target compound (in this case, sulfur, phosphorus, nitrogen and chlorine). This is also the case when dealing with the methyl analogues of these compounds, i.e., methyl chlorpyrifos and methyl parathion.

4.7.4 The retention times of some analytes, particularly terbacil and bromacil, may increase with increasing concentrations injected. Analysts should check for retention time shifts in highly contaminated samples.

4.7.5 Tebuthiuron shown in the tables and figures is actually a breakdown product of this pesticide. Tebuthiuron quantitatively degrades in the hot split/splitless injector liberating methyl-isocyanate which elutes with the solvent.

4.7.6 MGK-264 and diallate each produce two peaks.

4.7.7 The benzonitrile compounds such as dichlobenil have a tendency to hydrolyze under alkaline conditions. Therefore it may be desirable to monitor for the benzamide and benzoic acid derivatives as well as the benzonitrile. Under certain conditions, the compound chlorthalonil may be hydrolyzed to its di-acid derivative, thus being detected as dacthal. Bromoxynil and ioxynil are easily hydrolyzed, therefore, because the herbicide extraction procedure entails a hydrolysis step, the derivatives should be the target analytes.

4.7.8 Some compounds, such as 4,4'-DDE and dieldrin, may co-elute on both of the suggested columns using the gas chromatographic programs described. To achieve compound confirmation, an altered gas chromatographic program may be necessary. Alternatively, GC/MS may be used for compound identification/ confirmation.

4.7.9 Cleanliness of the inlet liner and column have various affects on the analytes. Some analytes are affected by active sites found in clean systems and some are affected by actives site created by injecting dirty samples. Often the matrix of the sample may influence the activity of the GC system, causing enhancement of some analytes and degradation of others. Experience of the analyst with the various conditions of a GC system is invaluable.

5.0 SAFETY

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 listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph -- An analytical system complete with gas chromatograph suitable for on-column and/or split-splitless injection and all necessary accessories including syringes, analytical columns, gases, and recorder/integrator or data system.

6.2 GC columns -- The columns listed in this section were the columns used to develop the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other capillary columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.2.1 Column 1 -- 30 m x 0.32-mm ID, DB-5 bonded fused-silica column, 0.25-mm film thickness (J&W Scientific) or equivalent.

6.2.2 Column 2 -- 30 m x 0.32-mm ID, DB-17 bonded fused-silica column, 0.25-mm film thickness (J&W Scientific) or equivalent.

6.3 Detector -- Atomic emission detector (AED) capable of monitoring the following elements:

1st injection	2nd injection	3rd injection
193 - Carbon	478 - Bromine	186 - Phosphorous
181 - Sulfur	479 - Chlorine	178 - Phosphorous
174 - Nitrogen		
206 - Iodine		

The elemental emission wavelengths (in nm) and injection groups shown above are only recommendations. Other wavelengths for these elements and other injection groups may be utilized, provided that the analyst can document acceptable performance for the intended application. It may also be useful to be able to monitor the emission wavelength for fluorine.

6.4 Autosampler vials -- 2-mL, crimp-top type (micro-volume inserts recommended).

6.5 Volumetric syringes -- 10.0-µL to 2.5-mL.

6.6 Borosilicate or Pyrex® vials -- 10-mL to 100-mL.

6.7 Graduated concentrator tubes -- various sizes.

6.8 Graduated centrifuge tubes.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade or pesticide-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at ≤6 °C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When standards are prepared, it is recommended that aliquots of each lot be stored in individual small vials. All stock standard solutions must be replaced if routine QC tests indicate a problem (see Sec. 11.5.12).

7.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include *n*-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and should be exchanged to isooctane prior to analysis.

Isooctane is suggested for standards and samples in this procedure. Acetone, methylene chloride, methanol and/or MTBE may be necessary for the preparation of some stock standard solutions due to better analyte solubility (see Sec. 7.4).

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be interference free. Solvents may be degassed prior to use.

7.3 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water as defined in Chapter One.

7.4 Compound-independent calibration (CIC) standard solution

Tables 17 and 18 describe a suggested CIC mixture, but alternative CIC mixtures may be used. Isooctane is commonly used as the solvent system, but solvent choice is dependent on the final solvent system used by the extraction and cleanup methods employed, as well as the solubility of the analytes. When producing a CIC mixture, consideration should be given to the stability of the compounds used, their retention times, the number of elements calibrated, and the range of elemental response. The CIC mixture described in this method contains compounds that are relatively stable in solution and less sensitive to chromatographic conditions. Furthermore, consideration is given to retention times, ensuring that compounds with the same elements do not co-elute, all the major elements of concern are included, and much of the linear range of each element is applied.

7.5 Calibration and response check standard solutions

Since the number of analytes calibrated in this method exceeds that which can be practically diluted into a single working standard, multiple working standard mixtures should be prepared. Tables 6 through 9 present a list of suggested mixtures of standards showing the analytes contained and their appropriate concentrations. Each mixture is designed to yield the quantitation limits of the compounds contained when diluted by a factor of 10.

7.6 Surrogate standards

The following are suggested surrogate compounds for use in this method: 1,3-dimethyl-2-nitrobenzene, dibromo-octafluorobiphenyl (DBOB), tetrachloro-*m*-xylene, decachlorobiphenyl, and triphenylphosphate. The surrogate compounds are prepared in acetone and the appropriate relative final concentrations can be found in Tables 12 and 13. Surrogate compounds used in other pesticide methods may also be employed in this method, provided that they contain a heteroatom and the analyst can demonstrate appropriate performance.

7.7 Matrix spike and laboratory control sample (LCS) standard solutions

These standard solutions should be made up of those analytes that are of concern at the time of analysis. They can be prepared in acetone and their final concentrations should be in a range between two and four times the quantitation limit as established by the calibration and response check analyses (see Sec. 11.6).

7.8 Gas-oil spiking mixture

For this method application, a gas-oil mixture is considered to be an oil formed through distillation of petroleum of intermediate boiling range and viscosity. More specifically it is a light fuel oil consisting of a type 2 classification that is used mostly for the production of heat in domestic and small commercial liquid-fuel burning equipment. It is light in color and has on average a specific gravity in the range of 0.82 to 0.86 and should be available from most home heating oil vendors. An appropriate portion of this material can be added to both the sample extracts and calibration standards in order to enhance the linearity of the phosphorus response. See Sec. 11.5.8 for further details.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Extracts should be stored under refrigeration in the dark and analyzed within 40 days after they are extracted.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, information on retention time checks, GC system degradation monitoring, CIC calibration, and calibration and response checking can be found in Sec. 11.0 of this method.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

NOTE: Given the large number of compounds that may be analyzed using this procedure, it is highly unlikely that all of the compounds could be included in a single spiking solution, or successfully spiked into a single set of four reagent water aliquots. As a result, successful completion of the initial demonstration of proficiency may need the analyst to consider one of the following approaches: preparing mixtures of target compounds and spiking the mixtures into different sets of reagent water aliquots, identifying the actual target compounds of interest for a given project and demonstrating the performance for only those compounds, or demonstrating the performance for some subset of all the analytes and only using the method as a screening tool for any other analytes. Other approaches may also be developed by the analyst.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

The laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Secs. 11.5 through 11.8 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample extraction

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples for neutral compounds may be extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510) a continuous liquid-

liquid extractor (Method 3520), solid-phase extraction (Method 3535), or other appropriate technique. Solid samples for neutral compounds may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550) procedures, or other appropriate technique. Acid herbicides should be extracted and processed according to Method 8151, or other appropriate technique.

Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample type should be spiked with the analytes of interest to determine the percent recovery. See Method 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

11.2 Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. A cleanup procedure that works for one pesticide may be removing another pesticide of concern. If extract cleanup is desired, then the specific cleanup procedure used will depend on the target compounds, the nature of the sample to be analyzed, and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section, and in Methods 3600 and 8151.

CAUTION: Cleanup procedures should be avoided if this method is used for general screening of samples.

11.2.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup -- pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or Florisil®) may also be necessary following the GPC cleanup.

11.2.2 Method 3610 (alumina) may be used to remove phthalate esters.

11.2.3 Method 3620 (Florisil®) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

11.2.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

11.2.5 Elemental sulfur, present in certain sediments and industrial wastes, interferes with the sulfur channel response. Sulfur should be removed by the technique described in Method 3660.

11.3 Suggested GC operating conditions

The following operating conditions were used for the generation of the data found in Tables 1 and 2. These GC conditions serve as guidance.

11.3.1 GC oven program for Column 1 (Sec. 6.2.1)

Initial temperature	75 °C for 0.67 min,
Ramp 1	10 °C/min to 140 °C
Ramp 2	5 °C/min to 250 °C, hold for 1.0 min,
Ramp 3	20 °C/min to 320 °C, hold for 5.0 min.

Injector settings for Column 1

Temperature	250 °C
Splitless injection	15 PSI helium with 3-μL injection volumes, vent closed for 0.67 min

11.3.2 GC oven program for Column 2 (Sec. 6.2.2)

Initial temperature	75 °C hold for 0.67 min,
Ramp 1	10 °C/min to 140 °C
Ramp 2	5 °C/min to 250 °C, hold for 1.0 min,
Ramp 3	20 °C/min to 300 °C, hold for 10.0 min.

Injector settings for Column 2

Temperature	250 °C
Splitless injection	3-μL injection volumes, vent closed for 0.67 min.

Programmable pressure control with the following conditions

40 psi initial for 0.2 min,
then 99 psi/min to 15 psi, followed by the constant-flow mode.

11.4 Suggested AED operating conditions

11.4.1 Establish the detector operating conditions using the manufacturer's specifications for reagent gas types along with pressure and flow settings for all reagent and make-up gases. Temperatures of the transfer line and cavity should be at 280 °C and 300 °C, respectively, if the analytical columns listed in Secs. 6.2.1 or 6.2.2 are used. Detector solvent vent should be on from 0 - 3.5 mins.

11.4.2 Background correction -- Element background settings need calibration prior to analysis. Follow manufacturer's instructions regarding background corrections.

NOTE: The injection of a 50 ng/μL diethyl phthalate (retention time about 10 - 15 mins) solution may be helpful in determining background suppression settings.

11.5 Compound-independent calibration (CIC)

The AED responds to the various elements, such as carbon, nitrogen and chlorine, within a given compound. The AED's response is independent of the compound's structure and is proportional to the concentration of the elements contained in the compound (see Refs. 1 and 2). Since the elemental response is independent of the compound, any compound that can be chromatographed by GC and contains the desired element may be used to calibrate the instrument for that element. The resulting elemental calibration can be used to quantitate other compounds.

11.5.1 Bracket all sample analyses by analyses of a CIC mixture. It is recommended that the CIC mixture be analyzed at least after every 10 samples or less. A more frequent rate may be necessary if the samples affect the stability of the GC system. Tables 17 and 18 describe a suggested CIC mix, but alternative CIC mixtures may be used. The average elemental response factors (AERFs) for the elements to be scanned are determined with this mixture.

11.5.2 Determining elemental response factors (ERFs)

$$ERF_k = \frac{A_{ck}}{(C_c)(ef_k)(V_{inj})}$$

where:

ERF_k = Elemental response factor (area/ng) for element k
A_{ck} = Peak area of compound c from the element k AED channel
C_c = Concentration (ng/µL) of compound c in the CIC mix
ef_k = Element fraction of element k (% element in compound, see Tables 6 through 11)
V_{inj} = Volume (µL) of CIC mix injected

11.5.3 Calculating the average elemental response factors (AERF)

For any mixture of compounds containing heteroatoms, calculate the average elemental response factor for each element by the following formula:

$$AERF_k = \frac{\sum_{c=1}^{n} (ERF_k)_c}{n_k}$$

where:

$AERF_k$ = Average elemental response factor (area/ng) for element k
$(ERF_k)_c$ = Elemental response factor (area/ng) for element k of compound c
n_k = Number of compounds in the standard mixture containing the element k from which the AERF is calculated

11.5.4 AERF validation

The suggested CIC mixture contains 15 compounds that provide elemental calibrations for nitrogen (5 points), sulfur (5-6 points), iodine (1 point), bromine (2 points), chlorine (5-6 points) and phosphorus (5-6 points). Determine the validity of the AERFs for the CIC mix through a calculation of the relative standard deviation (RSD) of the contributing individual elemental response factors.

$$SD_k = \frac{\sqrt{\sum_{c=1}^{n} [(ERF_k)_c - AERF_k]^2}}{n_k - 1}$$

and

$$RSD_k = \frac{SD_k}{AERF_k} \times 100$$

where:

SD_k	=	Standard deviation of the AERF for element k
$(ERF_k)_c$	=	Elemental response factor (area/ng) for element k of compound c
$AERF_k$	=	Average elemental response factor (area/ng) for element k
n_k	=	Number of compounds in the standard mixture containing the element k from which the AERF is calculated
RSD_k	=	Relative standard deviation for the response factors of element k

The RSDs of the AERFs for all elements except phosphorous should be less than or equal to 10%. RSDs for the AERF for phosphorous should be less than or equal to 20%. If the standard is spiked to yield a 0.1% gas oil mixture (See Sec. 7.8) to enhance the response of low phosphorous concentrations (see Sec. 11.5.8), then the RSD of the AERF for phosphorous should also be less than or equal to 10%. Bromine and iodine ERFs are calculated using a two-point and single-point calibration, respectively, so the RSDs cannot be calculated for these elements. At times, chromatographic conditions may cause a compound to become an outlier. It is up to the experienced analyst to determine when and why a compound is designated as an outlier and thus is not included in the AERF calculation.

11.5.5 CIC mixture validation

After the CIC mix has been analyzed, compare the AERFs to a known standard that contains stable compounds with the desired elements, such as a certified standard or standard reference material, to minimize bias. Ongoing checks of the CIC mix against known standards may be necessary to ensure continued minimum bias. The recommended precision for the check standard analysis is 25% RPD.

11.5.6 Use of the AERF for target analyte quantitation

If the compound in question demonstrates adequate chromatographic performance and does not degrade in the GC inlet, then calibration via AERFs should produce the same results as a compound-dependent calibration. When a target analyte is confirmed to be present in the sample, then AERFs are used for quantitation when all of the following criteria are met:

11.5.6.1 The AERFs meet the criteria outlined in Sec. 11.5.4.

11.5.6.2 The AERFs before and after sample analyses have a relative percent difference (RPD) of less than or equal to 20%. The following equation is used to calculate RPD:

$$RPD_k = \frac{\left| AERF_{k1} - AERF_{k2} \right|}{\left(\dfrac{AERF_{k1} + AERF_{k2}}{2} \right)} \times 100$$

where:

RPD_k = Relative percent difference for element k
$AERF_{k1}$ = Average elemental response factor for k before sample analyses
$AERF_{k2}$ = Average elemental response for k after sample analyses

11.5.6.3 The calibration check produces an elemental response factor (ERF) within 20% of the AERF both before and after the injection of samples (see Sec. 11.6).

11.5.6.4 A minimum of five points is used for the calculation of the AERF.

11.5.6.5 The quantitated target analyte elemental concentration must fall within the elemental calibration range.

11.5.7 AERF for tentatively identified compound (TIC) quantitation

The AED's unique selectivity reduces the effort needed for detection of non-target compounds that contain heteroatoms. However, identification needs additional efforts, the most common of which is GC/MS. After the tentative identity is established, quantitation by AERF follows as described in Sec. 11.11. TIC results calculated using AERF quantitation are considered estimates.

NOTE: GC/MS analysis is usually necessary to provide better identification of TICs. The GC/AED screening of TICs can facilitate GC/MS analysis. The extent of background matrix interference can be assessed by examining the carbon channel. Estimations of retention times, types of heteroatoms present, and the ratios of heteroatoms if more than one is present, also help in the GC/MS analysis. Often standards for TICs may not be readily accessible. In those instances, AERF quantitation may be the least biased method of quantitation available.

11.5.8 Calibration of phosphorus-containing compounds

Interaction of phosphorus in the discharge tube (Ref. 1) may affect the quantitation accuracy. This effect is quenched when a high level of organic material co-elutes with the analytes. This may occur with highly contaminated samples. Therefore, some additional steps may be necessary for proper quantitation of a compound containing phosphorus.

NOTE: There are at least three different methods that could facilitate phosphorus quantitation. One method is to spike a gas-oil mixture (See Sec. 7.8), to yield a concentration of approximately 0.1%, into both the sample extracts and standards to insure relative homogeneity of matrix. This addition of the gas-oil mixture will also enhance the linearity of the phosphorus response. A second method is to use a phosphorus-containing internal standard that will compensate for the different matrices. The third method is to use a heteroatom other than phosphorus to quantitate the compound. Most organophosphorus pesticides contain a heteroatom in addition to phosphorus. None of these methods is necessary for screening pesticides, since the matrix generally tends to increase the sensitivity for phosphorus. Thus, though biased high, phosphorous compounds, if present, can still be detected at or above their QLs in a high background matrix.

11.5.9 Use of the AERF for dilution factor determination

If a target compound is detected during the AED scan, then the AERF may be used to determine what dilution of the extract is needed to bring the detected compound into the calibration range prior to running the quantitative analysis.

11.5.10 Use of the AERF for the demonstration of detector linearity

The AERF calculation needs validation through the calculation of RSDs. The CIC utilizes multi-level elemental calibrations for the determination of AERFs. If the RSD for an element shows linearity, then it follows that the detector will also show linearity for a given compound utilizing that same element, provided that the conditions in Sec. 11.5.6 are met.

11.5.11 Use of the AERF for the demonstration of system stability

The AERFs calculated prior to the screening or quantitative analysis of samples should not substantially differ from the AERFs calculated following the analyses. If the AERFs differ by more than 20% for all elements, then explore and correct the cause of the deviation.

11.5.12 Use of the AERF for validation of a standard

If a standard's accuracy or integrity is in question, it can be compared to the CIC mix. If the compounds in question do not degrade on-column or in the inlet, then the concentration calculated via the AERF should agree with the stated concentration of the standard within ± 15%.

<u>CAUTION</u>: A compound having negative ERF deviations from CIC-generated AERFs may be displaying degradation or be a result of an improperly prepared standard. Positive deviations of compound ERFs from CIC-generated AERFs can only result from an improperly prepared standard (unless the compound is a degradation product of another compound in a standard mixture). If all compounds in a standard mixture display deviations from the AERFs, then a dilution error is probably the cause.

11.5.13 Use of the AERF for compound confirmation -- See Sec. 11.10.

11.6 Calibration and response check

Analyze a calibration and response check standard(s) before and after the injection of samples. This is done at the same frequency as the CIC mixture (see Sec 11.5). The check standard should contain all the analytes of interest for the analysis. Multiple standards may be necessary when analytes have overlapping retention times. The concentration of the analytes in the check standard should correspond to the level needed to calculate their respective minimum quantitation limits (QL). In general this concentration reflects the lowest concentration from a multi-level compound-dependent calibration. Only one heteroatom needs to be monitored for each analyte for this check standard.

The purpose of the calibration and response check is to show that all reported compounds can be detected at or above their minimum quantitation limits, and that the compounds can be successfully chromatographed. It is a check to validate the use of CIC quantitation when a target analyte is present in the sample and it serves as a justification for reporting a QL when a target analyte is considered not detected.

NOTE: By utilizing a low-level standard mix, the time needed for determining that target compounds are not present is reduced without diminishing the validity of the reporting limits.

11.6.1 The calibration and response check for CIC validation

The calibration and response check is a comparison between the elemental response (ERF) for each analyte from the calibration and response check standard and the average elemental response (AERF) from the CIC. This comparison is expressed as a percent difference (%D) from the AERF, as determined from the CIC. If the %D is less than or equal to 20% both before and after the injection of samples, then the compound-independent calibration is considered valid for that analyte for quantitation. Use the following equation to calculate %D:

$$\%D_c = \frac{\left| ERF_{ck} - AERF_k \right|}{AERF_k} * 100$$

where:

$\%D_c$ = Percent difference for compound c
ERF_{ck} = Elemental response factor (area/ng) for compound c using element k from the calibration and response check standard
$AERF_k$ = Average elemental response factor (area/ng) for element k derived from the CIC

11.6.2 If a target compound is detected above the QL and the use of CIC has been determined to be invalid for this target compound (see Sec. 11.5.6), then the sample should be reanalyzed using an alternative determinative method for the target compound. This may entail a multi-level calibration for the analyte detected with the associated quality control procedures described in Method 8000. The reanalysis may utilize the GC/AED or another instrument, if appropriate. The concentrations of the target compounds detected below their respective QLs can only be considered estimated values.

11.6.3 The calibration and response check for reporting minimum quantitation limits

The QL is dependent on the sample size and extract dilution. Its calculation can be found in Sec. 11.12. A valid response check that is used as the basis for reporting a QL for a target analyte must satisfy the following conditions:

11.6.3.1 The calibration and response check standard must be analyzed before and after the analyses of samples.

11.6.3.2 The same element used to calculate the ERF for the check standard is used to monitor the target analyte in the sample.

11.6.3.3 An elemental response for a target analyte in the check standard that is at least five times above the mean chromatographic noise level is considered a valid response. (Conventional instrument detection is determined at a 2.5:1 signal-to-noise ratio (S/N) in a single channel system. Ref. 1 uses 3:1 S/N, based on peak-to-peak noise or 6σ for 99% confidence for detection.)

11.7 Retention times

The retention times of target analytes should be determined from calibration and response check standard mix before and confirmed after samples are injected. The professional judgment of the experienced analyst should be used to determine the appropriate windows for target compound identifications. See Tables 8 through 11 and Table 13 for example retention times on the DB-5 and DB-17 columns. These retention times are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

11.8 Degradation checks

Endrin and 4,4'-DDT are used to determine the degradation potential of the GC system. Both compounds should have a percent difference (%D), as determined in Sec. 11.6, of less than or equal to 20%. If these values are exceeded, GC maintenance is needed before continuing. Other compounds, such as dimethoate or captan, which display column degradation/absorption properties that are different from DDT and endrin, may also be helpful in determining the condition of the system.

11.9 Sample extract injection

Inject an aliquot of the concentrated sample extract into the GC/AED. The injection volume and operating conditions should be the same as those used for the calibration standards, unless the analyst can demonstrate acceptable performance using different volumes or conditions. (The use of different injection volumes for samples versus standards need special attention paid to the equations in Secs. 11.5 and 11.11). Record the AED response for each GC peak, for all the elements that are monitored.

11.10 Qualitative analysis

11.10.1 Appropriate elemental ratios may be used to confirm the identification of pesticides. In addition, identification may be confirmed by GC with a dissimilar column, specific element detector, or mass spectrometer, as described in Method 8000.

11.10.2 Appropriate elemental ratios -- If an analyte contains two or more heteroatoms, its identification can be confirmed by elemental ratios. This is done by calculating the analyte concentration (see Sec. 11.11) in the extract using each of the heteroatoms and comparing them. All concentrations must be calculated from the AERFs. If the relative percent difference (RPD) of the concentration ratio is less than or equal to 20% and there is an acceptable primary column retention time match, then the identification of the compound is considered confirmed.

$$RPD_c = \frac{\left| Conc_{ck} - Conc_{cm} \right|}{\left(\frac{Conc_{ck} + Conc_{cm}}{2} \right)} \times 100$$

where:

RPD_c = Relative percent difference for compound c,
$Conc_{ck}$ = Concentration of compound c in the extract using element k,
$Conc_{cm}$ = Concentration of compound c in the extract using element m,

<u>NOTE</u>: An equivalent technique is to calculate the elemental molar amounts and compare the results to the empirical formula of the compound. Equivalent acceptance criteria should be applied to the molar ratios.

11.10.3 If a compound contains three or more heteroatoms, then detection of at least three heteroatoms along with an acceptable primary column retention time match is considered acceptable for compound confirmation, although elemental ratios of all elements present should still be examined.

11.11 Quantitative analysis

The quality control conditions found in Secs. 11.5 and 11.6 need to be met in order to reduce bias when quantitating compounds using AERFs from the CIC mix. If no standard of the analyte is available, then the estimations made from the CIC AERFs should be considered minimum concentrations.

11.11.1 Concentration calculations for water samples

$$Concentration_c\ (\mu g/L) = \frac{(A_c)(V_f)(DF)}{(AERF_k)(V_s)(ef_{ck})(V_{inj})}$$

where:

A_c = Area of compound c on the k element AED channel
V_f = Final volume (mL) of the sample extract
DF = Dilution factor
$AERF_k$ = Average elemental response factor (area/ng) for element k
V_s = Volume (L) of sample extracted
ef_{ck} = Elemental fraction of element k (% of element in compound c)
V_{inj} = Volume (µL) of extract injected

11.11.2 Concentration calculations for soil/sediment samples

$$\text{Concentration}_c \ (\mu g/kg) = \frac{(A_c)(V_f)(DF)}{(AERF_k)(M_s)(ef_{ck})(S)(V_{inj})}$$

where:

A_c = Area of compound c on the k element AED channel
V_f = Final volume (mL) of the sample extract
DF = Dilution factor
$AERF_k$ = Average elemental response factor (area/ng) for element k
M_s = Mass (kg) of sample extracted
ef_{ck} = Elemental fraction of element k (% of element in compound c)
S = Percent solids expressed as a decimal fraction
V_{inj} = Volume (µL) of extract injected

NOTE: Quantitative results derived from AERFs should be equal to or less than those derived from compound-dependent calibrations. Compound-dependent calibrations tend to compensate for losses that occur during gas chromatography. If a compound behaves well chromatographically, nearly one hundred percent of the injected compound reaches the detector. If there are losses due to compound degradation or absorption in the GC system, the quantity of the analyte reaching the detector is reduced and the concentrations of those compounds calculated from AERFs will be less than concentrations calculated from a compound-dependent calibration.

11.12 Quantitation limits

The minimum quantitation limits (QLs) may only be used if the response check is valid for the target analyte of concern (see Sec. 11.6.2) and the compound is considered not detected. It is dependent upon sample size and extract dilution.

11.12.1 Quantitation limit calculations for liquid samples

$$\text{Quantiation limit}_c \ (\mu g/L) = \frac{(Conc_c)(V_{STDinj})(V_f)(DF)}{(V_s)(V_{inj})}$$

where:

$Conc_c$ = Concentration (µg/mL) of compound c in the calibration and response check standard mix
V_{STDinj} = Volume (µL) of standard mix injected
V_f = Final volume (mL) of the sample extract
DF = Dilution factor
V_s = Volume (L) of sample extracted
V_{inj} = Volume (µL) of sample extract injected

11.12.2 Quantitation limit calculations for solid samples:

$$\text{Quantitation limit}_c\ (\mu g/kg) = \frac{(\text{Conc}_c)(V_{STDinj})(V_f)(DF)}{(M_s)(S)(V_{inj})}$$

where:

Conc_c	=	Concentration (µg/mL) of compound c in the calibration and response check standard mix
V_{STDinj}	=	Volume (µL) of standard mix injected
V_f	=	Final volume (mL) of the sample extract
DF	=	Dilution factor
M_s	=	Mass (kg) of sample extracted
S	=	Percent solids expressed as a decimal fraction
V_{inj}	=	Volume (µL) of sample extract injected

12.0 DATA ANALYSIS AND CALCULATIONS

See Secs. 11.10 through 11.12 and Method 8000 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2 The data presented in Tables 8 through 11 and Table 13 provide example retention times for the target compounds on a DB-5 column and a DB-17 column. The elemental percentages of target compounds also are provided in these tables. These data are provided for guidance purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

13.3 The surrogates used for neutral pesticides and for the acid herbicides and related compounds are provided in Tables 14 and 15. The elemental percentages of the surrogates are shown in Table 16. These data are provided for guidance purposes only.

13.4 Table 19 summarizes the results of a four-laboratory round robin study that evaluated the performance of the determinative method using two spiked sample extracts. These data are provided for guidance purposes only.

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 operations. 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., N.W. Washington, D.C. 20036, http://www.acs.org.

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. N. Olson, R. Carrell, R. Cummings and R. Rieck, "Gas Chromatography/Atomic Emission Detection For Pesticide Screening and Confirmation," *LC-GC* 12, 142, 1994.

2. N. L. Olson, R. L. Carrell, R. K. Cummings, and R. H. Rieck, and S. Reimer, "Atomic Emission Detection for Gas Chromatographic Analysis of Nitrogen-Containing Herbicides in Water," *J. Assoc. Off. Anal. Chem*. 78, No. 6, 1464-1473, 1995.

3. N. Olson, R. Cummings, and R. Araki, "SW-846 Method 8085 Pesticide Screening and Compound Independent Quantification by Gas Chromatography with Atomic Emission Detection (A Round Robin Study)," USEPA Manchester Environmental Laboratory, Port Orchard, WA, September 18, 1997.

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

The following pages contain the tables referenced by this method.

TABLE 1

SINGLE-LABORATORY PERFORMANCE DATA FOR NITROGEN-CONTAINING HERBICIDES[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Alachlor	0.500	100	0.033	6.6
Ametryn	0.209	99	0.013	6.4
Atraton	0.625	88	0.040	7.2
Atrazine	0.208	97	0.015	7.0
Benfluralin	0.313	50	0.047	30
Bromacil	1.25	74	0.087	9.4
Butachlor	0.729	101	0.051	6.8
Butylate	0.313	50	0.046	29
Carboxin	2.29	82	0.13	6.7
Chlorpropham	1.04	93	0.083	8.6
Chlorthalonil	0.500	87	0.057	13
Cyanazine	0.313	94	0.020	6.8
Cycloate	0.313	76	0.062	26
Diallate	0.792	71	0.053	9.5
Dichlobenil	0.25	59	0.020	13
Diphenamid	0.625	112	0.043	6.0
Diuron[2]	1.25	97	0.067	5.5
Eptam (EPTC)	0.313	70	0.070	32
Ethalfluralin	0.313	55	0.024	14
Fenarimol	0.625	79	0.074	15
Fluridone	1.67	91	0.21	14
Hexazinone	0.313	51	0.017	11
Metalaxyl	1.42	91	0.11	8.4
Metolachlor	0.625	105	0.046	7.0
Metribuzin	0.209	91	0.006	3.3
MGK-264	1.46	90	0.084	6.4
Molinate	0.542	89	0.053	11
Napropamide	0.625	111	0.034	4.9
Norflurazon	0.313	101	0.022	6.9
Oxyfluorfen	0.542	100	0.030	5.6
Pebulate	0.500	83	0.036	8.5
Pendimethalin	0.313	99	0.019	6.0
Profluralin	0.500	46	0.021	8.9
Prometon	0.209	89	0.013	7.0
Prometryn	0.208	101	0.013	6.2

TABLE 1
(continued)

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Pronamide	0.625	100	0.041	6.6
Propachlor	0.417	84	0.039	11
Propargite (S-181)	0.458	117	0.043	8.1
Propazine	0.209	98	0.017	8.1
Simazine	0.208	103	0.014	6.9
Tebuthiuron[2]	0.209	86	0.0095	5.4
Terbacil	1.04	100	0.041	3.9
Terbutryn	0.209	101	0.016	7.5
Triademefon	0.542	95	0.040	7.8
Triallate	0.542	72	0.082	21
Trifluralin	0.313	54	0.030	18
Vernolate	0.313	67	0.069	33

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.5-mL extract volume and a 3-µL injection.

[2] Recovery based upon breakdown product.
These data are provided for guidance purposes only.

TABLE 2

SINGLE-LABORATORY PERFORMANCE DATA FOR ORGANOPHOSPHORUS PESTICIDES
Medium Spiking Level, No Gas Oils Spiked[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Abate	1.88	84	0.32	20.4
Azinphos methyl	0.334	103	0.024	7.1
Azinphos ethyl	0.334	78	0.026	10.1
Carbophenothion	0.209	83	0.0091	5.3
Chlorpyrifos	0.167	77	0.0091	7.1
Coumaphos	0.250	98	0.014	5.8
DEF	0.292	94	0.015	5.5
Demeton-O	0.146	73	0.017	15.9
Diazinon	0.167	95	0.010	6.4
Dichlorvos	0.167	95	0.014	8.7
Dioxathion	0.355	103	0.017	4.6
Disulfoton	0.125	61	0.0076	10.1
EPN	0.209	79	0.011	6.8
Ethion	0.146	83	0.0064	5.3
Ethoprop	0.167	93	0.018	11.5
Fenitrothion	0.146	89	0.0089	6.9
Fenthion	0.146	80	0.011	9.7
Fonofos	0.125	90	0.0074	6.6
Gardona	0.418	97	0.030	7.5
Imidan	0.230	94	0.011	5.2
Malathion	0.167	82	0.016	11.9
Merphos[b]	0.250	63	0.026	16.3
Methyl chlorpyrifos	0.167	78	0.0069	5.3
Methyl parathion	0.146	102	0.0074	5.0
Parathion	0.167	95	0.010	6.6
Phorate	0.146	83	0.011	9.1
Propetamidophos	0.418	101	0.023	5.4
Ronnel	0.146	99	0.0065	4.5
Sulfotepp	0.125	85	0.0061	5.8
Sulprofos	0.146	87	0.013	9.9
Poor Performing Analytes				
Demeton - S	0.146	12	0.021	120
Dimethoate	0.209	20	0.016	37.1
Fenamiphos	0.313	0	--	--
Fensulfothion	0.334	14	0.024	52.0
Methyl paraoxon	0.376	47	0.051	29.1
Mevinphos	0.209	33	0.018	25.5
Phosphamidon	0.501	0	--	--

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.5-mL extract volume and a 3-µL injection. These data are provided for guidance purposes only.

TABLE 3

SINGLE-LABORATORY PERFORMANCE DATA FOR ORGANOPHOSPHORUS PESTICIDES
Medium Spiking Level, 0.1% Gas Oil Spiked in All Extracts[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Abate	1.88	83	0.22	14.4
Azinphos ethyl	0.334	92	0.018	5.8
Azinphos methyl	0.334	84	0.015	5.3
Carbophenothion	0.209	92	0.0052	2.7
Chlorpyrifos	0.167	95	0.0055	3.4
Coumaphos	0.250	92	0.0086	3.8
DEF	0.292	95	0.0086	3.1
Demeton-O	0.146	80	0.016	13.9
Diazinon	0.167	92	0.0065	4.3
Dichlorvos	0.167	95	0.0094	5.9
Dioxathion	0.355	99	0.011	3.3
Disulfoton	0.125	65	0.0060	7.4
EPN	0.209	100	0.0047	2.2
Ethion	0.146	92	0.0036	2.7
Ethoprop	0.167	87	0.015	10.6
Fenitrothion	0.146	94	0.0040	2.9
Fenthion	0.146	79	0.0086	7.4
Fonofos	0.125	91	0.0047	4.2
Gardona	0.418	94	0.0079	2.0
Imidan	0.230	87	0.0084	4.2
Malathion	0.167	91	0.013	8.8
Merphosb	0.250	105	0.018	6.7
Methyl parathion	0.146	90	0.0042	3.2
Methyl paraoxon	0.376	66	0.032	13.0
Methyl chlorpyrifos	0.167	93	0.0054	3.5
Parathion	0.167	91	0.0059	3.9
Phorate	0.146	79	0.0088	7.6
Propetamidophos	0.418	92	0.015	3.9
Ronnel	0.146	90	0.0068	5.1
Sulfotepp	0.125	94	0.0043	3.7
Sulprofos	0.146	80	0.0070	5.9
Poor Performing Analytes				
Demeton-S	0.146	17	0.025	102.0
Dimethoate	0.209	35	0.016	21.9
Fenamiphos	0.313	0	--	--
Fensulfothion	0.334	28	0.037	39.9
Mevinphos	0.209	44	0.015	16.9
Phosphamidon	0.501	1	--	--

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.5-mL extract volume and a 3-µL injection. These data are provided for guidance purposes only.

TABLE 4

SINGLE-LABORATORY PERFORMANCE DATA FOR ORGANOPHOSPHORUS PESTICIDES
Low Spiking Level, 0.1% Gas Oil Spiked in All Extracts[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Azinphos ethyl	0.10	89	0.0079	8.9
Azinphos methyl	0.10	85	0.0065	7.7
Carbophenothion	0.063	89	0.0029	5.1
Chlorpyrifos methyl	0.050	88	0.0027	6.2
Chlorpyrifos	0.050	92	0.0013	2.8
Coumaphos	0.075	89	0.0032	4.8
Demeton-O	0.044	53	0.0068	29
Diazinon	0.050	89	0.0044	9.8
Disulfoton	0.038	59	0.0052	23
EPN	0.063	93	0.0025	4.2
Ethion	0.044	95	0.0018	4.2
Ethoprop	0.050	84	0.0039	9.3
Fenitrothion	0.044	102	0.0014	3.1
Fenthion	0.044	54	0.0036	15
Fonofos	0.038	90	0.0013	3.8
Imidan	0.069	88	0.0022	3.7
Malathion	0.050	85	0.0032	7.5
Methyl parathion	0.044	91	0.0017	4.2
Parathion	0.050	85	0.0030	7.1
Phorate	0.044	67	0.0021	7.2
Ronnel	0.044	90	0.0016	4.0
Sulfotepp	0.038	89	0.0018	5.3
Sulprofos	0.044	58	0.0036	14

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.5-mL extract volume and a 3-µL injection.
These data are provided for guidance purposes only.

TABLE 5

SINGLE-LABORATORY PERFORMANCE DATA FOR CHLORINATED PESTICIDES[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)
Aldrin	0.17	32	0.0020	3.6
α-BHC	0.17	102	0.0089	5.1
β-BHC	0.17	104	0.0093	5.2
δ-BHC	0.17	104	0.0093	5.2
γ-BHC (lindane)	0.17	104	0.0098	5.5
Captafol[4]	0.84	139	0.11	6.9
Captan, captafol breakdown[2&3]	NA	98	0.034	7.3
Captan[4]	0.50	140	0.081	8.2
trans-Chlordane	0.17	82	0.0090	6.5
Diclofol[4]	0.67	124	0.012	13
Dicofol breakdown[4]	NA	100		5.1
Dieldrin[3]	0.17	94	0.0055	3.4
2,4'-DDD	0.17	91	0.0070	4.5
4,4'-DDD	0.17	101	0.0072	4.2
2,4'-DDE	0.17	49	0.0069	4.8
4,4'-DDE[2]	0.17	94	0.0055	3.4
2,4'-DDT	0.17	78	0.088	5.3
4,4'-DDT	0.17	116	0.0046	5.2
Endosulfan I	0.17	100	0.0000	0
Endosulfan II	0.17	110	0.0000	0
Endosulfan sulfate	0.17	114	0.010	5.2
Endrin	0.17	103	0.0083	4.8
Endrin aldehyde	0.17	111	0.0070	3.7
Endrin ketone	0.085	113	0.011	4.8
Heptachlor	0.17	47	0.0032	4.0
Heptachlor epoxide	0.17	99	0.0026	1.5
Hexachlorbenzene (HCB)[3]	0.25	55	0.024	8.9
Methoxychlor	0.17	124	0.012	5.2
Mirex	0.17	77	0.0040	9.4
Pentachlorocyclopentadiene[3]	1.00	37	0.057	6.7

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.5-mL extract volume and a 3-µL injection.
[2]Quantitated together from one peak.
[3]Data based on 1-L sample size with 0.5-mL extract volume.
[4]Subject to GC breakdown, breakdown products where monitored; recoveries were captan 50%, captafol 40%, diclofol 3% when compared to ClC; 55% recovery of dicofol breakdown product, captan breakdown monitored on the carbon channel.
These data are provided for guidance purposes only.

TABLE 6

SINGLE-LABORATORY PERFORMANCE DATA FOR ACIDIC HERBICIDES[1]
Medium Spiking Level

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)	Alternative quantitation element[2]
Acifluorfen	1.67	79	0.24	17.9	
Bromoxynil	0.421	104	0.080	18.3	Br
2,4-D	0.421	96	0.046	11.5	
2,4-DB	0.503	68	0.036	10.6	
Dacthal	0.334	64	0.021	10.0	
Dicamba	0.416	91	0.047	12.5	
3,5-Dichlorobenzoic acid	0.414	82	0.053	15.8	
Dichlorprop	0.457	90	0.061	14.8	
Diclofop-methyl	0.624	85	0.058	10.9	
Dinoseb	0.625	79	0.10	20.2	N
Ioxynil	0.424	109	0.051	11.1	N, I
MCPA	0.833	77	0.12	20.2	
MCPP	0.850	71	0.12	20.3	
4-Nitrophenol	0.721	28	0.031	15.6	N
PCP	0.208	102	0.037	17.1	
Picloram	0.421	40	0.029	17.0	
Silvex	0.328	96	0.051	16.3	
2,4,5-T	0.331	101	0.044	13.2	
2,4,5-TB	0.376	59	0.041	18.3	
2,4,5-TCP	0.245	48	0.029	24.5	
2,4,6-TCP	0.248	72	0.033	18.7	
2,3,4,5-TCP	0.229	65	0.031	20.8	
2,3,4,6-TCP	0.229	98	0.038	17.1	
Triclopyr	0.333	100	0.044	13.1	

[1]Data based on 8 replicate spikes utilizing a 3-L sample with 0.25-mL extract volume and a 3-µL injection.

[2]For all other analytes, the quantitation element was chlorine.
These data are provided for guidance purposes only.

TABLE 7

SINGLE-LABORATORY PERFORMANCE DATA FOR ACIDIC HERBICIDES
Low Spiking Level[1]

Analyte	Spiking Level (µg/L)	Average Recovery (%)	Std. Dev.	RSD (%)	Alternative quantitation element[3]
Acifluorfen	0.17	107	0.048	27	
Bentazon	0.063	92	0.0020	3.5	N
Bromoxynil	0.042	110	0.0069	15	Br
2,4-D[2]	0.042	91	0.0061	16	
2,4-DB	0.050	118	0.0071	12	
Dacthal	0.033	71	0.0026	11	
Dicamba	0.042	79	0.0072	22	
3,5-Dichlorobenzoic acid	0.042	100	0.0054	13	
Dichlorprop	0.046	100	0.0043	9.4	
Diclofop-methyl	0.063	117	0.0042	5.8	
Dinoseb	0.063	44	0.0052	19	N
Ioxynil	0.042	98	0.0020	4.9	I
MCPA	0.083	97	0.0072	8.9	
MCPP	0.083	100	0.0092	11	
4-Nitrophenol	0.073	58	0.0072	17	N
PCP[2]	0.021	112	0.0022	9.6	
Picloram	0.042	22	0.0013	14	
Silvex	0.033	95	0.0032	10	
2,4,5-T	0.033	115	0.0058	15	
2,4,5-TB	0.038	111	0.0022	5.3	
2,4,5-TCP	0.025	106	0.0064	24	
2,4,6-TCP	0.025	112	0.0062	22	
2,3,4,5-TCP	0.023	113	0.0069	26	
2,3,4,6-TCP	0.023	118	0.0058	21	
Triclopyr[2]	0.035	94	0.0029	8.9	

[1]Data based on 7 replicate spikes utilizing a 3-L sample with 0.25-mL extract volume and a 3-µL injection.
[2]Recoveries for these compounds are based upon CIC calculations using seven compounds for the AERF: 2,5-Dichlorobenzonate, MCPP, MCPA, dichlorprop, silvex, 2,4,5-T and diclofop-methyl in the initial calibration standard.
[3]For all other analytes the quantitation element was chlorine.
These data are provided for guidance purposes only.

TABLE 8

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR ORGANONITROGEN PESTICIDES

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages							
				C	S	N	Cl	P	O	F	Other
Nitrogen-containing mix #1											
Dichlobenil	8.19	9.44	10.0	48.8		8.15	41.2				
Tebuthiuron	10.93	13.00	7.5	47.3	18.7	24.6					
Propachlor	12.72	13.96	12.0	62.4		6.62	16.7		7.56		
Ethalfluralin	13.75	12.19	7.50	46.8		12.6			19.2	17.1	
Trifluralin	14.09	12.24	7.50	46.5		12.5			19.1	17.0	
Simazine	15.11	17.06	5.00	41.6		34.7	17.6				
Atrazine	15.34	16.79	5.00	44.5		32.5	16.4				
Pronamide	16.04	15.97	20.0	56.2		5.47	24.7		6.25		
Terbacil	16.62	19.10	15.0	49.8		12.9	16.4		14.8		
Metribuzin	17.82	20.23	5.00	44.8	15.0	26.2			7.47		
Alachlor	18.45	19.06	18.0	62.3		5.19	13.1		11.9		
Prometryn	18.64	19.78	5.00	49.7	13.3	29.0					
Bromacil	19.31	22.39	20.0	41.3		10.7			12.3		30.6 Br
Metolachlor	19.83	20.22	20.0	63.4		4.94	12.5		11.3		
Diphenamid	20.68	23.30	15.0	80.2		5.85			6.69		
Pendimethalin	21.25	21.48	7.50	55.4		14.9			22.7		
Napropamide	23.04	24.42	15.0	75.2		5.16			11.8		
Oxyfluorfen	24.01	23.83	20.0	49.8		3.87	9.8		17.7	15.8	
Norflurazon	26.34	28.40	10.0	47.4		13.8	11.7		5.27	18.8	
Fluridone	33.61	35.05	30.0	69.2		4.25			4.86	17.3	

TABLE 8
(continued)

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	C	S	N	Cl	P	O	F	Other
				Elemental Percentages							
Nitrogen-containing mix #2											
EPTC	8.37	8.22	10.0	57.0	16.9	7.40			8.45		
Butylate	9.53	8.76	10.0	60.7	14.8	6.44			7.36		
Vernolate	9.79	9.42	10.0	59.0	15.8	6.89			7.87		
Pebulate	10.03	9.73	10.0	59.0	15.8	6.89	--	--	7.87		
Molinate	11.31	12.38	10.0	57.7	17.1	7.48	--	--	8.54		
Cycloate	13.14	13.32	10.0	61.3	14.9	6.50			7.43		
Chlorpropham	13.46	13.90	20.0	56.2		6.56	16.6	--	15.0		
Prometon	15.2	16.33	5.00	53.2		31.1			7.10		
Propazine	15.52	16.51	5.00	47.0		30.5	15.4				
Profluralin	16.14	14.25	12.0	48.4	--	12.1	--	--	18.4		
Chlorothalonil	16.68	18.33	12.0	36.1		10.5	53.3				
Triallate	16.87	16.76	13.0	39.4	10.5	4.60	34.9		5.25		
Ametryn	18.46	20.06	5.00	47.5	14.1	30.8					
Terbutryn	19.1	20.32	5.00	49.7	13.3	29.0					
Cyanazine	19.98	22.96	7.50	44.4	--	34.9	14.7	--	--		
Hexazinone	26.82	30.09	7.50	57.1		22.2			12.7		
Propargite	27.25	27.33	10.0	65.0	9.15	--	--	--	18.3		
Nitrogen-containing mix #3											
Linuron/Diuron Breakdown	7.52	11.20	NA	44.7	--	7.45	37.7		8.51		
Diallate	14.24/14.59	14.36/14.65	35.0	44.4	11.9	5.19	26.2		5.92		
Atraton	14.94	16.47	7.5	51.1	--	33.2	--		7.57		
Triallate	16.87	16.76	15.0	34.4	10.5	4.60	34.9		5.25		
Metalaxyl	18.64	20.25	30.0	64.5	--	5.02	--		22.9		
Triadimefon	20.4	20.41	13.0	51.1	--	14.9	12.6		11.4		
MGK 264	20.62/21.03	20.44/21.38	40.0	74.1	--	5.09	--		11.6		

TABLE 8
(continued)

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/μL)	Elemental Percentages C	S	N	Cl	P	O	F	Other
Diuron	21.45	16.63	30.0	46.6	--	12.1	30.6		6.90		
Butachlor	22.82	22.39	30.0	65.4	--	4.49	11.4		10.3		
Carboxin	23.76	26.39	30.0	61.2	13.6	5.95	--		13.6		
Hexazinone	26.82	30.09	7.50	57.1	--	22.2	--		12.7		
Fenarimol	30.74	31.76	15.0	61.6	--	8.47	21.4		4.83		
Carbon quantitated analytes											
Resmethrin	27.55	27.49	10.0	78.0	--	--	--		14.2		
Phenothrin	29.57	29.45	10.0	76.9	--	--	--		15.4		
cis-Permethrin	31.82	31.89	10.0	64.4	--	--	18.1		12.3		
Fenvalerate* (*cis-trans*)	33.82/34.09	33.82/34.07	20.0	71.4	--	3.33	8.44		11.4		

*The analyst may want to include these isomers in Chlorinated mix #3 (see Table 9).

TABLE 9

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR ORGANONITROGEN PESTICIDES

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/μL)	Elemental Percentages						
				C	S	N	Cl	P	O	F
Chlorinated mix #1										
α-BHC	14.38	15.29	2.5	24.8			73.1			
β-BHC	15.36	17.27	2.5	24.8			73.1			
γ-BHC	15.60	16.83	2.5	24.8			73.1			
δ-BHC	16.47	18.63	2.5	24.8			73.1			
Heptachlor	18.34	17.99	2.5	32.1			66.5			
Aldrin	19.64	19.18	2.5	39.5			58.3			
Heptachlor epoxide	21.17	21.35	2.5	30.8			63.7		4.11	
trans-Chlordane	22.07	21.99	2.5	29.3			69.2			
Endosulfan I	22.52	22.63	2.5	26.5	7.88		52.3		11.8	
4,4'-DDE	23.53	23.75	2.5	52.8			44.6			
Dieldrin	23.54	23.73	2.5	37.8			55.9		4.20	
Endrin	24.30	25.08	2.5	37.8			55.9		4.20	
Endosulfan II	24.65	25.81	2.5	26.5	7.88		52.3		11.8	
4,4'-DDD	25.09	25.76	2.5	52.5			44.3			
Endrin aldehyde	25.36	27.04	2.5	37.7			55.8		4.20	
Endosulfan sulfate	26.25	27.49	2.5	25.5	7.58		50.3		15.1	
4,4'-DDT	26.49	26.85	2.5	47.4			50.0			
Endrin ketone	27.93	30.14	2.5	37.8			55.8		4.20	
Methoxychlor	28.77	30.14	2.5	55.5			30.8		9.26	

Chlorinated mix #2

TABLE 9
(continued)

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages C	S	N	Cl	P	O	F
Pentachloroanisole	14.80	14.85	2.5	30.0			63.2		5.71	
α-Chlordene	18.59	18.51	2.5	35.4			62.8			
γ-Chlordene	18.69	20.09	2.5	35.4			62.8			
4,4'-DDMU	22.17	22.48	2.5	59.2			37.5			
cis-Chlordane	22.66	22.60	2.5	29.3			69.2			
cis-Nonachlor	25.20	25.21	2.5	27.0			71.8			
Chlorinated mix #3										
Hexachlorobenzene	14.68	14.45	2.5	25.3			74.7			
Dicofol breakdown	20.03	21.01	NA	62.1			28.2		6.37	
Captan	21.42	24.25	6.75	35.9	10.7	4.66	35.4		10.6	
2,4'-DDE	22.33	22.85	2.5	52.8			44.6			
trans-Nonachlor	22.86	22.09	2.5	27.0			71.8			
2,4'-DDD	23.84	24.67	2.5	52.5			44.3			
2,4''-DDT	25.21	25.71	2.5	47.4			50.0			
Captafol	27.17	29.69	12.5	34.4	9.18	4.01	40.6		9.17	
Dicofol	28.62	29.34	10	45.3			47.8		4.32	
Mirex	30.05	29.76	2.5	22.0			78.0			

Retention times are for illustrative purposes only.

TABLE 10

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR ORGANOCHLORINE PESTICIDES

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages C	S	N	Cl	P	O	F
Organophosphorus mix #1										
Demeton-O/S	12.8/14.92	13.33/16.21	7.00	37.2	24.8			12.0	18.6	
Sulfotepp	14.21	15.22	3.00	29.8	19.9			19.2	24.8	
Fonofos	16.02	17.16	3.00	48.7	26.0			12.6	6.50	
Disulfoton	16.55	17.28	3.00	35.0	35.1			11.3	11.7	
Chlorpyrifos methyl	18.15	19.36	4.00	26.0	9.94	4.34	33.0	9.60	14.9	
Fenitrothion	19.21	20.86	3.50	39.0	11.6	5.05		11.2	28.9	
Malathion	19.7	21.04	4.00	36.3	19.4			9.37	29.1	
Chlorpyrifos	20.06	20.60	4.00	30.8	9.14	4.00	30.3	8.83	13.7	
Merphos	21.42	20.23	6.00	48.2	32.2			10.4		
DEF*	23.6	27.19		45.8	30.6			9.85	5.09	
Fenamiphos	23.08	23.45	5.00	51.4	10.6	4.62		10.2	15.8	
Ethion	25.38	26.23	3.50	28.1	33.4			16.1	16.6	
Carbophenothion	26.11	26.96	5.00	38.5	28.0		10.3	9.03	9.33	
EPN	28.44	26.69	5.00	52.0	9.92	4.33		9.58	19.8	
Azinphos ethyl	31.04	32.51	8.00	41.7	18.6	12.2		9.00	13.9	
Organophosphorus mix #2										
Ethoprop	13.17	14.01	4.00	39.6	26.5			12.8	13.2	
Phorate	14.33	15.10	3.50	32.3	36.9			11.9	12.3	
Dimethoate	14.9	18.08	4.00	26.2	28.0	6.11		13.5	20.9	
Diazinon	16.48	16.84	4.00	47.3	10.5	9.2		10.2	15.8	
Methyl parathion	18.12	19.80	3.50	36.5	12.2	5.32		11.8	30.4	

TABLE 10
(continued)

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages C	S	N	Cl	P	O	F
Ronnel	18.72	19.36	3.50	29.9	10.0		33.1	9.63	14.9	
Fenthion	19.96	21.78	3.50	43.1	23.0			11.1	17.2	
Parathion	20.07	20.89	4.00	41.2	11.0	4.81		10.6	27.5	
Fensulfothion	24.93	24.48	5.00	42.8	20.8			10.0	20.8	
Sulprofos	25.79	26.80	3.50	44.7	29.8			9.60	9.92	
Imidan	28.24	31.10	5.50	41.6	20.2	4.42		9.76	20.2	
Azinphos methyl	29.7	32.21	8.00	37.8	20.2	13.2		9.76	15.1	
Coumaphos	32.11	32.61	6.00	46.3	8.84		9.77	8.54	22.1	
Organophosphorus mix #3										
Dichlorvos	6.84	7.62	4.00	21.7	--	--	32.1	14.0	29.0	
Mevinphos	9.53	10.95	5.00	37.5	--	--	--	13.8	42.8	
Monocrotophos	14.06	17.45	5.00	37.6	--	6.28	--	13.9	35.8	
Dimethoate**	14.90	18.08	5.00	26.2	28.0	6.11	--	13.5	20.9	
Dioxathion	15.73	17.70	8.50	31.5	28.1	--	--	13.6	21.0	
Propetamidophos	16.02	16.76	10.0	42.7	11.4	4.98	--	11.0	22.8	
Methyl paraoxon	16.52	18.83	9.00	38.9	--	5.67	--	12.5	38.9	
Phosphamidon	17.83	19.84	12.00	40.0	--	4.67	11.8	10.3	26.7	
Gardona	22.65	24.06	10.0	32.8	--	--	38.7	8.46	17.5	
Fenamiphos**	23.08	23.45	7.50	51.4	10.6	4.62	--	10.2	15.8	
DEF**	23.60	27.19	7.00	45.8	30.6	--	--	9.85	5.09	
Fensulfothion**	24.93	24.48	8.00	42.8	20.8	--	--	10.0	20.8	
Abate/Breakdown product	36.39/32.27	29.69	30.0	41.2	20.6	--	--	13.3	20.6	

*DEF is a breakdown product of merphos. **Also present in another mixture. Retention times are for illustrative purposes only.

TABLE 11

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR DERIVATIZED ORGANIC ACID HERBICIDES

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages C	S	N	Cl	P	O	F	Other
Herbicides mix #1											
2,4,6-Trichlorophenol	7.61	7.95	3.00	39.7			50.3		7.57		
4-Nitrophenol	8.92	10.29	10.0	54.9		9.15			30.4		
2,4,5-Trichlorophenol	9.43	10.44	3.00	39.7			50.3		7.57		
2,3,4,6-Tetrachlorophenol	10.71	11.27	2.75	30.1			57.7		6.51		
MCPP	11.07	12.00	10.0	57.7			15.5		21.0		
MCPA	11.36	12.00	10.0	55.9			16.5		22.4		
Bromoxynil	12.45	14.29	5.00	33.0		4.82			5.50		54.9 (Br)
2,3,4,5-Tetrachlorophenol	13.12	14.40	2.75	30.1			57.7		6.51		
Pentachlorophenol (PCP)	14.26	14.90	2.50	30.0			63.2		5.71		
Chloramben	14.99	17.45	5.00	43.6		6.37	32.2		14.5		
5-Hydroxydicamba	15.26	17.84	5.00	43.0			28.2		25.5		
Dinoseb (DNBP)	16.83	17.85	7.50	51.9		11.0			31.5		
Bentazon	17.38	20.38	7.50	51.9	12.6	11.0			18.9		
Acifluorfen	24.00	24.79	20.00	48.1		3.7	9.5		21.4	15.2	

TABLE 11
(continued)

Analyte	DB-5 RT	DB-17 RT	Conc. (ng/µL)	Elemental Percentages C	S	N	Cl	P	O	F	Other
Herbicides mix #2											
Dalapon		4.30	4.00	30.9			45.2		20.4		
3,5-Dichlorobenzoic acid	8.85	8.77	5.00	46.8			34.6		15.6		
Dicamba*	10.54	12.03	5.00	46.0			30.2		20.4		
Dichlorprop	12.22	13.39	5.50	48.2			28.5		19.3		
2,4-D	12.60	14.40	5.00	46.0			30.2		20.4		
Triclopyr	13.81	15.57	4.00	36.9		5.4	40.8		18.4		
Silvex (2,4,5-TP)	14.92	15.86	4.00	42.3			37.5		16.9		
2,4,5-T	15.46	17.06	4.00	40.1			39.5		17.8		
2,4-DB	16.73	18.05	6.00	50.2			26.9		18.2		
Ioxynil	17.40	20.22	5.00	24.9		3.6			4.16		65.9 (I)
Picloram	18.33	22.07	5.00	32.9		11.0	41.6		12.5		
Dacthal (DCPA)	19.53	20.53	4.00	36.1			42.7		19.3		
Diclofop-methyl	27.16	27.93	7.50	56.3			20.8		18.8		

*Dicamba has more than one isomer. The retention time data provided here are for the predominant isomer.
Retention times are for illustrative purposes only.

TABLE 12

DERIVATIZED ORGANIC ACID HERBICIDES[1]

Herbicides	Acid Factor
Dalapon	0.911
2,4-DB	0.947
2,4-D	0.94
Dacthal (DCPA)	0.916
Dicamba	0.94
Dichlorprop	0.944
Dinoseb	0.945
Pentachlorophenol	0.95
Picloram	0.945
2,4,5-TP (Silvex)	0.951
2,4,5-T	0.948
2,4,5-TB	0.953
Bromoxynil	0.952
Ioxynil	0.964
MCPP	0.939
MCPA	0.935
Acifluorfen	0.962
4-Nitrophenol	0.908
Bentazon	0.945
Chloramben	0.936
3,5-Dichlorobenzene	0.931
5-Hydroxydicamba	0.944
2,3,4,5-Tetrachlorophenol	0.943
Diclofop-methyl	1.000
2,4,6-Trichlorophenol	0.934
2,4,5-Trichlorophenol	0.934
Trichlopyr	0.948

[1] The methyl ester/ether derivatives are used for analysis by GC. CIC-derived concentrations are based upon the derivatized compounds. However, many standards for these compounds are based upon the acid species. If the concentration of the acid species is what is needed, then the amount calculated from the AERFs should be multiplied by the respective acid factor.

TABLE 13

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR CHLORINATED HYDROCARBONS

		Elemental Percentages			
Analyte	DB-17 RT	C	S	N	Cl
1,4-Dichlorobenzene	< 4.	49.0			48.2
1,3-Dichlorobenzene	4.02	49.0			48.2
1,2-Dichlorobenzene	4.39	49.0			48.2
Hexachloroethane	4.49	10.1			89.9
1,3,5-Trichlorobenzene	5.13	39.7			58.6
Hexachlorobutadiene	5.98	18.4			81.6
1,2,4-Trichlorobenzene	6.01	39.7			58.6
1,2,3-Trichlorobenzene	6.70	39.7			58.6
Hexachlorocyclopentadiene	7.58	22.0			78.0
1,2,3,5-Tetrachlorobenzene	7.87	33.4			65.7
1,2,4,5-Tetrachlorobenzene	7.93	33.4			65.7
1,2,3,4-Tetrachlorobenzene	8.96	33.4			65.7
β-Chloronaphthalene	9.27	73.8			21.8
Pentachlorobenzene	11.01	28.8			70.8
Hexachlorobenzene (HCB)	14.45	25.3			74.7

Retention times are for illustrative purposes only.

TABLE 14

RECOMMENDED AED SURROGATE SOLUTION FOR NEUTRAL PESTICIDES

Surrogate	CAS No.	Concentration (ng/µL)
4,4'-Dibromo-octafluorobiphenyl (DBOB)	10386-84	20.0
Decachlorobiphenyl (DCB)	2051-24-3	10.0
Triphenyl phosphate (TPP)	115-86-6	20.0
1,3-Dimethyl-2-nitrobenzene (DMNB)	81-20-9	21.0
Alternative surrogates		
Dibutylchlorendate (DBC)	1770-80-5	20.0
2,4,5,6-Tetrachloro-*m*-xylene (TMX)	877-09-8	20.0

TABLE 15

RECOMMENDED AED SURROGATE SOLUTION FOR
ACID HERBICIDES AND RELATED COMPOUNDS

Surrogate	CAS No.	Concentration (ng/µL)
2,4,6-Tribromophenol (TBP)	118-79-6	20.0

TABLE 16

EXAMPLE RETENTION TIMES AND ELEMENTAL PERCENTAGES FOR RECOMMENDED SURROGATES

			Elemental Percentages							
Analyte	DB-5 RT	DB-17 RT	C	S	N	Cl	P	O	F	Other
Neutral surrogates										
1,3-Dimethyl-2-nitrobenzene	6.00	--	63.5		9.27			21.2		
2,4,5,6-Tetrachloro-*m*-xylene	12.89	12.44	39.4			58.1				
Dibromooctafluorobiphenyl	14.15	12.29	31.6						33.3	35.1 Br
Triphenyl phosphate	27.31	29.34	66.2				9.49	19.6		
Dibutylchlorendate	29.32	28.75	40.7			42.5		12.8		
Decachlorobiphenyl	33.51	32.92	18.0			71.1				
Acid herbicide surrogates										
2,4,6-Tribromophenol	12.84	14.00	21.8					4.84		72.5 Br

Retention times are for illustrative purposes only.

TABLE 17

RECOMMENDED COMPOUND-INDEPENDENT CALIBRATION MIXTURES

Analyte	Conc.* (pg/µL)	Elemental Percentages Cl	P	S	N	Br	I	F
Chlorpyrifos	5680	30.3	8.82	9.15	3.99			
Decachlorobiphenyl	492	71.1						
Diazinon	9800		10.2	10.5	9.21			
Dibromooctafluorobiphenyl	1000					35.1		33.3
Dichlobenil	6140	41.3			8.14			
Ethoprop	391		12.8	26.4				
Ioxynil (methyl ether)	500						66.0	
Malathion	1070		9.37	19.4				
Pentachloronitrobenzene	1690	60.1			4.74			
Phorate	2100		11.9	36.9				
Silvex (methyl ester)	400	37.6						
Terbufos	7600		10.8	33.3				
2,4,6-Tribromoanisole	2870					72.5		
1,2,3-Trichlorobenzene	6810	58.7						
Trifluralin	16000				12.5			17.0

*The concentration listed in this column is the total concentration of the analyte. Table 18 contains the concentrations of each element in the analyte.

TABLE 18

RECOMMENDED COMPOUND-INDEPENDENT CALIBRATION MIXTURES

	Elemental Concentration (pg/µL)[1]						
Analyte	S	Cl	N	P	Br	I	F[2]
Chlorpyrifos	520	1720	227	500			
Decachlorobiphenyl		350					
Diazinon	1030		903	1000			
Dibromooctafluorobiphenyl					351		333
Dichlobenil		2540	500				
Ethoprop	103			50			
Ioxynil (methyl ether)						351	
Malathion	208			100			
Pentachloronitrobenzene		1010	80				
Phorate	775			250			
Silvex (methyl ester)		150					
Terbufos	2530			821			
2,4,6-Tribromoanisole					2000		
1,2,3-Trichlorobenzene		4000					
Trifluralin			2000				2720

[1] The elemental concentration is determined from the total concentration of the compound (see Table 17) times the percentage of the element in the compound.

[2] The fluorine channel is not typically used.

TABLE 19

CIC QUANTITATION RESULTS USING AERFs FROM A FOUR-LABORATORY ROUND ROBIN STUDY OF SPIKED MATRIX EXTRACTS[1]

Analyte	Expected Value (ng/µL)	Lab 1[2]	Lab 2	Lab 3	Lab 4	Mean, All Labs	Std. Dev.	RSD	% of Expected Value
Sample #1									
Eptam	8.0	6.2	6.6	6.8	8.3	7.0	0.92	13%	88%
Atrazine	4.5	4.1*	4.1	4.4	4.8	4.4	0.33	8%	98%
Diazinon	3.0	2.6	3.0	3.0	3.0	2.9	0.20	7%	97%
Parathion, methyl	3.8	3.4*	3.7	4.0	2.7	3.5	0.56	16%	92%
Chlorpyrifos	3.5	3.5*	3.6	3.8	3.5	3.6	0.14	4%	102%
Endosulfan I	8.0	8.6*	8.5	8.0	7.9	8.3	0.35	4%	104%
Endosulfan sulfate	5.0	3.9	5.0	4.8	3.9	4.4	0.58	13%	88%
Norflurazon	10.0	9.4	9.2	9.9	7.3*	9.0	1.14	13%	90%
Atrazine desethyl [3]	2.5	2.1*	2.4	2.1	2.4*	2.3	0.17	7%	92%
Sample #2									
Dichlobenil	1.5	1.3	1.4	1.4	1.7*	1.5	0.17	11%	100%
Diallate	4.0	3.6*	3.3	3.1	3.6	3.4	0.24	7%	85%
Atrazine	0.4	0.39	0.26	0.36	0.42	0.34	0.07	20%	85%
Diazinon	0.5	0.32	0.49	0.35	0.43	0.40	0.08	20%	80%
Alachlor	2.0	2.0*	1.9	1.8	2.2	1.8	0.33	18%	90%
Bromacil	3.0	2.7	2.9	3.0	2.8*	2.9	0.13	5%	95%
Ethion	0.4	0.39	0.46	0.46	0.29*	0.40	0.08	20%	100%
4,4'-DDT	0.4	0.08*	0.38	0.20*	0.22*	0.22	0.12	55%	55%
2,6-Dichlorobenzamide [3]	2.5	2.2*	2.5	2.1	2.3*	2.3	0.17	7%	92%

* Results generated using the laboratory's reported AERFs.

[1] The matrix consisted of a soil extract that was diluted to approximate the background level that would be found in a surface water sample extract. Laboratories 1 and 4 used the average of the initial and final AERFs to calculate compound concentrations. Laboratories 2 and 3 used only the initial AERFs to calculate compound concentrations.

[2] Results are averages of all elemental responses reported by this laboratory

[3] Non-target compound

Data are taken from Reference 3.