S-CUBED
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# NARRATIVE ON THE DEVELOPMENT AND VALIDATION OF THE "CONSOLIDATED GC METHOD FOR THE DETERMINATION OF ITD/RCRA ANALYTES USING SELECTIVE GC DETECTORS"

## Under SAS 107

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# 1.0 INTRODUCTION

Several very similar packed column GC methods have been developed for the analysis of hazardous chemicals and water. These include Methods 608, 608.1, and 617 for halogenated organics and Methods 614, 622 and 701 for organophosphates. In order to allow quality environmental data to be collected in the most cost effective manner, S-CUBED has developed a consolidated method for the determination of all of the parameters of Methods 608, 608.1, 614, 617, 622 and 701. This method requires a single extraction followed by two separate capillary GC analyses using the electron capture detector (ECD) or the flame photometric detector (FPD). While it was not possible to develop a method that could be used to quantitate simultaneously appear organochlorine, organophosphate, and phenoxyacid herbicides (Method 615), S-CUBED presents an improved and safer procedure for the analysis of phenoxyacid herbicides than the present Method 615.

The two methods have bee consolidated into a single analytical scheme that can be used for the quantitative determination of the ITD/RCRA analytes listed in Tables 1 and 3. A flow scheme for the analysis of samples is pictures in Figure 1.

## 2.0 CATALOG OF METHODS

A comparison of Methods 608, 608.1, 614, 615, 617, 622, and 701 is presented in Table 4. Each of the methods is a water method that specifies in initial sample size of 800 to 1,000 mL. Adjustment of the pH of the sample is required in only two of the methods (615 and 617). The extraction solvents that are required are methylene chloride, 15 percent methylene chloride in hexane, or diethyl ether. The required volume of extracting solvents is less than 200 mL for each of the methods. The final volume of the extract used for GC analysis ranges between 1 and 10 mL. Several GC columns are required at GC oven temperatures ranging from 100°C to 215°C. The primary column for most methods is a 1.5 percent SP2250/1.9 percent SP2401 mixed phase column that was specifically developed for pesticide analysis. Seven other coatings are required by different methods including SP2401, DC-200, OV-1 Ultrabond 20M, OV-210, and QF-1. The QA/QC requirements for all of the methods are the same. They require that (1) the individual laboratory demonstrate the precision and accuracy of the method using standards in the laboratory prior to analyzing samples, (2) the laboratory demonstrate adequate recovery of the analytes of interest, and (3) the laboratory spike at least ten percent of the samples to demonstrate method performance on actual samples. Several cleanup options are also allowed by these various methods. They include shaking the sample with mercury to remove sulfur contaminants, and the use of absorbent columns to remove polar contaminants, (the absorbent generally specified is Florisil but alumina is specified in the case of Method 701).

The one method that is quite different from all the others presented in Table 4 is Method 615. It is used for the analysis of phenoxyacid herbicides and requires three different extractions during sample preparation. In addition, a base hydrolysis must be done so that

any herbicide esters are converted to the free acids prior to derivatization. The fact that this method requires partitions between different acid/base solutions, as well as hydrolysis and derivatization means that the modified Method 615 was included in the consolidated pesticide method as a separate procedure.

## 3.0 DEVELOPMENT OF THE PROCEDURE FOR APOLAR ANALYTES

Each of the 600 series method was published for the analysis of water samples only. While in actual practice these methods have been used for a variety of environmental matrices including solids, sludges, and even tissue, the methods work best for determining analytes in clean water. It was the purpose of this study to develop a method that could be used to analyze the full list of parameters in Table 1 from complex multimedia environmental samples.

### 3.1 SAMPLE EXTRACTION FOR APOLAR ANALYTES

One liter water samples are required and are adjusted in pH between 5 and 9 using either one-to-one sulfuric acid in water or six normal sodium hydroxide. Once the pH of the samples has been adjusted the water is extracted using methylene chloride in a continuous liquid-liquid extractor for a 18-hour period. The continuous liquid extractor is specified as the extraction method of choice because it is less prone to forming emulsions than the separatory funnel extraction and it provides the most reproducible extraction of the combined parameters from water.

Soil samples are extracted using an ultrasonic horn (Heat Systems Ultrasonics or equivalent). Thirty grams of the solid sample is mixed with 60 g of sodium sulfate and extracted using one-to-one acetone/methylene chloride. It is critical that the sodium sulfate adsorb all of the water in the solid sample since there is a significant loss in extraction efficiency using the ultrasonic horn when water is present. It was decided that solid samples should not have the pH adjusted because such pH changes could cause the evolution of toxic gases such as $H_2S$ or could change the surface chemistry of the solids and thus affect the extraction efficiency unpredictably.

Selecting the technique for extracting sludge samples is typically difficult for the analysis laboratory. The proposed combined method states the most sludges should be diluted with water and extracted with a continuous liquid-liquid extractor, but does allows the option of extracting them by sonication after sufficient sodium sulfate is added to adsorb all water. Since sludges vary greatly in their water content, it was felt that flexibility in the choice of sample preparation be allowed. While it may be possible to use total moisture content or percent suspended solids as more rigid criteria for making this decision, the time required to perform those procedures does not seem cost effective and would delay analyses. Organophosphate pesticides should be extracted as soon as possible after sampling in order to reduce potential analyte hydrolysis which occurs rapidly for this class of compounds.

### 3.2 SAMPLE CLEANUP FOR APOLAR ANALYTES

Because each of the 600 series method was originally developed as a water method, they do not contain sufficient cleanup steps to ensure adequate chromatography of complex samples. These deficiencies in cleanup are addressed in this consolidated method. All solid and sludge samples must be cleaned up using gel permeation chromatography (GPC) to remove high molecular weight molecular that degrade chromatographic columns (GPC is an option for water samples). It is requires that each sample be cleaned up using adsorption chromatography on Diol cartridges (supplied by a number of manufacturers including Analytichem, J.T. Baker, or Supelco) to remove polar interferents that could co-chromatograph with method parameters and/or cause poor chromatography. It is felt that both of these cleanup steps are needed to remove all of the potential interfering compounds that might be extracted from samples.

## 3.3 GC ANALYSIS OF APOLAR

In order to achieve analytical separation of the large number of analytes included in the ITD/RCRA list, it is required that temperature programmed capillary GC be used. Megabore capillary (ID 0.53 mm) is a superior alternative to regular (narrow bore) capillary analysis in this application because (1) megabore capillary columns can be placed into normal one-quarter inch packed column injector and detector ports with only a minimal amount of modification, and (2) megabore capillary columns can handle a larger injection, which means that highly complex sample extracts are less likely to overload the column. We chose to use the DB-5 and the SPB-608 megabore columns for this analysis.

The retention time of the apolar parameters of the consolidated method are given in Tables 1 and 2 (different temperature programs were used for organochlorine and organophosphates). As can be seen from the table, these large lists of analytes are resolved very well on each of the columns with a <40 min run time. Using the megabore capillary columns, there is only a minimum number of analytes that co-elute.

## 3.4 MODIFIED HERBICIDE METHOD

Method 615 presents great difficulties in the normal analytical lab because of its requirement of the use of ethyl ether as an extraction solvent. S-CUBED replaced Method 615 with a modification of the Method 8150 validated at EMSL-LV. The modified method requires methylene chloride as an extraction solvent rather than ether and requires the use of Florisil cartridge cleanup of the derivatized phenoxyacid herbicides prior to GC analysis. We have found that this additional cleanup greatly improves the chromatography of the derivatized herbicides by removing the large tail on the solvent peak that is observed whenever environmental samples have been derivatized using dioazomethane.

Retention times for the derivatized herbicides on the DB-5 and the SPB-608 columns are reported in Table 8. We found that it was not possible to combine the neutral organochlorine pesticides with the derivatized herbicides because it caused too much co-elution of analytes, for this reason separate GC analysis of the derivatized herbicides must be performed. The retention times of the derivatized herbicides will be reported by the end of August.

## 4.0 METHOD VALIDATION

Validation of the consolidated method is underway. This is being done by determining the recovery of method parameters spiked into water. Recovery values for the high concentration organochlorine experiment are reported in Table 50. The recoveries generally fall between 80% and 120% except where poor chromatography caused poor quantitative results.

Work is in progress to determine the recovery of the apolar organochlorine parameters when they are spiked at 5 and 50 ng/L, as well as the recoveries of the organophosphate and the phenoxyacid parameters. Work that has been completed at S-CUBED on organophosphates or by LEMSCO on the phenoxyacids demonstrate >70% recovery of these parameters using this method.

## 5.0 METHOD DETECTION LIMITS

The method detection limits reported in the protocol are 50 ng/L for apolar organochlorine pesticides, 500 ng/L for organophosphate pesticides and 5 ng/L for phenoxyacids. The limits for the apolar compounds can be reduced by a factor of 10 by passing all of the hexane extract through the Diol column (Section 4.3.4) prior to GC analysis. This modification in the protocol results in a detection limit of <5 ng/L for apolar organochlorines and <50 ng/L for organophosphates.

It has been our experience that this sample concentration is not required for the samples that we have received thus far on this project. In fact, samples often require further dilution in order to bring chromatograms on scale.

TABLE 1 APOLAR ORGANOCHLORINE
PARAMETERS OF THE CONSOLIDATED METHOD

| COMPOUND | METHOD | RETENTION TIME DB-5 | SPB-608 |
|---|---|---|---|
| Aldrin | 608,617 | 19.77 | 18.33 |
| Aroclor 1016 | 608,617 | multiple | multiple |
| Aroclor 1221 | 608,617 | multiple | multiple |
| Aroclor 1232 | 608,617 | multiple | multiple |
| Aroclor 1242 | 608,617 | multiple | multiple |
| Aroclor 1248 | 608,617 | multiple | multiple |
| Aroclor 1254 | 608,617 | multiple | multiple |
| Aroclor 1260 | 608,617 | multiple | multiple |
| BHC,alpha | 608,617 | 13.77 | 13.70 |
| BHC,beta | 608,617 | 14.74 | 15.62 |
| BHC,gamma | 608,617 | 15.01 | 15.22 |
| BHC,delta | 608,617 | 15.93 | 17.15 |
| Captan | 617 | 22.03 | 24.24 |
| Carbophenthion | 617,622 | 28.44 | 28.69 |
| Chlordane | 608,617 | multiple | multiple |
| Chlorobenzylate | 608.1 | 26.49 | 26.03 |
| DDD | 608,617 | 26.99 | 27.10 |
| DDE | 608,617 | 24.70 | 24.16 |
| DDT | 608,617 | 29.01 | 28.75 |
| Diallate(cis,trans) | no | 13.57,13.91 | 12.89,13.20 |
| Dichloran | 617 | 14.31 | 14.80 |
| Dieldrin | 608,617 | 24.88 | 24.35 |
| Endosulfan I | 608,617 | 23.54 | 22.81 |
| Endosulfan II | 608,617 | 26.49 | 27.15 |
| Endosulfan sulfate | 608,617 | 28.77 | 29.71 |
| Endrin | 608,617 | 26.02 | 26.11 |
| Endrin Aldehyde | 608,617 | 27.48 | 28.82 |
| Endrin ketone | no | 31.25 | 33.27 |
| Heptachlor | 608,617 | 16.14 | 16.87 |
| Heptachlor epoxide | 608,617 | 21.69 | 21.01 |
| Hexachlorobenzene | no | 14.24 | 13.37 |
| Isodrin | 617 | 21.19 | 20.33 |
| Methoxychlor | 617 | 32.17 | 33.37 |
| Mirex | no | 34.49 | 33.59 |
| Nitrofen | 608.1,617 | 25.99 | 26.35 |
| PCNB | 617 | 15.24 | 14.78 |
| Toxaphene | | multiple | multiple |
| Trifluralin | | 12.95 | 11.01 |

| COMPOUND | RELATED COMPOUNDS METHOD | DB-5 | SPB-608 |
|---|---|---|---|
| Captofol | no | 31.26 | 26.83 |
| Chloroneb | 608.1 | 10.46 | 10.67 |
| Chloropropylate | 608.1 | nd | nd |
| DBCP | 608.1 | 5.91 | 5.96 |
| Dicofol | 617 | 32.35 | 32.76 |
| Etridazole | 608.1 | 9.82 | 9.76 |
| Kepone | no | 28.04 | 26.28 |
| Perthane (Ethylan) | no | 26.23 | 26.09 |
| Propachlor | 617 | nd | nd |
| Vinclozolin | 608,617 | multiple | multiple |

nd = not determined

TABLE 2 APOLAR ORGANOPHOSPHOROUS PARAMETERS OF THE CONSOLIDATED METHOD

| COMPOUND | METHOD | RETENTION TIME DB-5 | SPB-608 |
|---|---|---|---|
| Azinphos ethyl | no | 39.04 | 38.49 |
| Azinphos methyl | 614,622 | 38.34 | 38.04 |
| Carbophenthion | 617,622 | 25.25 | 35.10 |
| Chlorfenvinphos | no | 33.57 | 31.86 |
| Chlorpyrophos | 622 | 31.17 | 26.88 |
| Coumophos | 622 | 39.83 | 38.87 |
| Demeton(mixed) | 614,622 | 18.31,20.96 | 15.90,18.84 |
| Diazinon | 614,622,7 | 24.27 | 20.00 |
| Dichlovos | 622 | 9.63 | 7.91 |
| Dicrotophos | | 15.23 | 19.12 |
| Dimethoate | | 20.64 | 20.18 |
| Dioxathion | | 39.93 | 33.17 |
| Disulfoton | 614,622 | 23.71 | 19.96 |
| EPN | | 37.80 | 36.71 |
| Ethion | 614,701 | 36.17 | 34.79 |
| Famphur | | 36.43 | 35.93 |
| Fensulfothion | 622 | 35.83 | 35.20 |
| Fenthion | 622 | 31.83 | 29.45 |
| HMPA | | 10.69 | 9.23 |
| Leptophos | | 38.47 | 37.25 |
| Malathion | 614,701 | 34.72 | 28.78 |
| Mevinphos | 622 | 14.18 | 12.88 |
| Monocrotophos | | 20.04 | 20.11 |
| Naled | 622 | 19.01 | 17.40 |
| Parathion, ethyl | 614,701 | 31.85 | 27.62 |
| Parathion, methyl | 614,622,7 | 31.83 | 23.71 |
| Phorate | 622 | 19.94 | 17.52 |
| Phosmet | | 37.56 | 37.20 |
| Phosphamidon | | 27.05 | 24.46 |
| Sulfotepp | | 20.11 | 18.02 |
| TEPP | | 6.44 | 5.12 |
| Terbuphos | | 22.63 | 18.81 |
| Tetrachlorovinphos | | 34.65 | 32.99 |
| TOCP | | 38.79 | 37.71 |
| Trichlorofon | | 11.91 | nd |
| Trimethyl phosphate | | 2.35 | nd |

| COMPOUND | RELATED COMPOUNDS METHOD | DB-5 | SPB-608 |
|---|---|---|---|
| Bolstar | 622 | 36.34 | nd |
| Chlorpyrophos,me | 622 | nd | nd |
| Crotoxyphos | no | 34.06 | 33.07 |
| Dichlorfenthion | 701 | 9.63 | 7.91 |
| Ethoprop | 622 | 18.62 | 16.48 |
| Merphos | 622 | nd | 26.82 |
| Methyl trithion | 701 | nd | nd |
| Ronnel | no | 29.23 | 22.98 |
| Tokuthion | no | 34.67 | nd |
| Trichloronate | no | 32.19 | nd |

nd = not determined
Oxydemeton methyl no signal, not a method parameter

TABLE 3 PHENOXYACID
ANALYTES OF CONSOLIDATED METHOD

| COMPOUND | METHOD | DB-5 | SPB-608 |
|---|---|---|---|
| Dinoseb | 615 | | |
| 2,4-D | 615 | | |
| 2,4,5-T | 615 | | |
| 2,4,5-TP | 615 | | |
| RELATED COMPOUNDS | | | |
| Dalapon | 615 | | |
| 2,4-DB | 615 | | |
| Dicamba | 615 | | |
| Dichlorprop | 615 | | |
| MCPA | 615 | | |
| MCPP | 615 | | |

## *TABLE 4 Consolidation of Methods*

| Method Number | Sample Volume | pH Adjust | Extraction Solvent | Extraction Volume (mL) | Final Volume (mL) |
|---|---|---|---|---|---|
| | | | **Organochlorines** | | |
| 608 | 1 L | No | Methylene Chloride | 3 x 60 | 10 |
| 608.1 | 1 L | No | Methylene Chloride | 3 x 60 | 10 |
| 617 | 1 L | 6 to 8 | 15% $CH_2Cl_2$/Hexane | 3 x 60 | 10 |
| | | | **Organophosphates** | | |
| 614 | 1 L | No | 15% $CH_2Cl_2$/Hexane | 3 x 60 | 10 |
| 622 | 1 L | No | 15% $CH_2Cl_2$/Hexane | 3 x 60 | 10 |
| 701 | 800-900 mL | No | 15% $CH_2Cl_2$/Hexane | 3 x 25 | 1 |
| | | | **Phenoxyacid Herbicides** | | |
| 615 | 1 L | pH 2 | Ethyl Ether | 150, 50, 50 | NA |
| | | pH 10 | Water | 10 | NA |
| | | pH 2 | Ethyl Ether | 20, 10, 10 | 1 |

## *TABLE 4 Consolidation of Methods*

| Method Number | Derivative | GC Column 1 | Temperature | GC Column 2 | Temperature | Detector |
|---|---|---|---|---|---|---|
| 608 | None | 1.5% SP2250/1.95% SP2401 | 200°C | 3% OV-1 | 200°C | ECD |
| 608.1 | None | 1.5% SP2250/1.95% SP2401 | 100-215 (iso) | Ultrabond 20M | 200°C | ECD |
| 617 | None | 1.5% SP2250/1.95% SP2401 | 200°C | 3% OV-1 | 200°C | ECD |
| 614 | None | 1.5% SP2250/1.95% SP2401 | 200°C | 3% OV-1 | 200°C | FPD, NPD |
| 622 | None | 5% SP2401 | 100-215 (prog) | 3% SP2401 | 170-250 (prog) | FPD, NPD |
| 701 | None | 5% DC-200 | 185°C | 5% QF-1 | 185°C | FPD, NPD |
| 615 | Diazomethane | 1.5% SP2250/1.95% SP2401 | 185°C | 5% OV-210 | 185°C | ECD |

## *TABLE 4 Consolidation of Methods*

| Method Number | QA/QC Requirements | Cleanup Options |
|---|---|---|
| 608 | P&A, Recoveries, spike 10% of Samples | Hg for S, Florisil |
| 608.1 | P&A, Recoveries, spike 10% of Samples | Hg for S, Florisil |
| 617 | P&A, Recoveries, spike 10% of Samples | Hg for S, Florisil, Hex/aceto/hex ext. |
| 614 | P&A, Recoveries, spike 10% of Samples | Hg for S, Florisil, Hex/aceto/hex ext. |
| 622 | P&A, Recoveries, spike 10% of Samples | Allowed if recovery > 85% |
| 701 | P&A, Recoveries, spike 10% of Samples | 5% water deactivated alumina, Florisil |
| 615 | P&A, Recoveries, spike 10% of Samples | None specified, allowed if recovery is > 85% |

TABLE 5 RECOVERY OF SINGLE COMPONENT
APOLAR HALOGENATED PESTICIDES (500 ng/L)

| COMPOUND | DB-5 RECOVERY (%) | rsd | SPB-608 RECOVERY (%) | rsd |
|---|---|---|---|---|
| Aldrin | 82.2 | 5.1 | 75.7 | 10.3 |
| BHC,alpha | 105.9 | 7.9 | 108.7 | 5.4 |
| BHC,beta | 94.2 | 9.1 | 99.9 | 6.5 |
| BHC,gamma | 109.9 | 3.8 | 103.3 | 5.7 |
| BHC,delta | * 30.4 | 48 | * 27.0 | 16 |
| Captan | nd | | nd | |
| Carbophenthion | * 185.2 | 8 | * | |
| Chlorobenzylate | 118.2 | 12 | 86.5 | 8.8 |
| DDD | 117.2 | 8.5 | 113.2 | 10.6 |
| DDE | 82.1 | 32 | 89.0 | 25 |
| DDT | 97.3 | 18 | 89.1 | 8.9 |
| Diallate | nd | | nd | |
| Dichloran | 23.4 | 26 | 28.1 | 13 |
| Dieldrin | 93.7 | 16 | 102.8 | 9.3 |
| Endosulfan I | 81.6 | 16 | 83.8 | 13 |
| Endosulfan II | 63.7 | 34 | 74.4 | 24 |
| Endosulfan SO4 | * 38.3 | | * 14.5 | 25 |
| Endrin | 97.2 | 22 | 100.6 | 16 |
| Endrin Aldehyde | * 22.2 | | * | |
| Endrin ketone | * 14.1 | 23 | * | |
| Heptachlor | * 59.1 | 28 | * 60.4 | 28 |
| Heptachlor epoxide | * 468.3 | | 85.1 | 4.6 |
| Hexachlorobenzene | nd | | nd | |
| Isodrin | 54.9 | 21 | 59.2 | 17 |
| Methoxychlor | 104.9 | 12 | 106.6 | 3.9 |
| Mirex | 90.5 | 9.8 | 108.5 | 7.1 |
| Nitrofen | 90.3 | 11 | 115.0 | 6.5 |
| PCNB | 97.5 | 14 | 93.3 | 16 |
| Trifluralin | 111.3 | 5.5 | 123.8 | 2.9 |

Values marked with a (*) had coeluting peaks
nd = not determined