

**Affidavit of Michael C. Nichols  
Dated June 23, 2006**



Requirements for the Competence of Calibration and Testing Laboratories” and have been manager of Georgia Power’s Environmental Laboratory since 1992.

3. I have been involved with laboratory work and chemical sampling and analysis since 1983. My job duties include supervision of activities performed by Georgia Power’s Environmental Laboratory. These activities consist of, among others: sample analysis; sampling plans and methods; maintenance and calibration of analysis equipment; and review and approval of laboratory procedures and quality assurance plans for the laboratory’s certification. Georgia Power’s Environmental Laboratory holds current accreditation for analytical chemistry under the National Environmental Laboratory Accreditation Program and for personnel dosimetry under the National Voluntary Laboratory Accreditation Program.
4. I am familiar with the Morgan Falls Project sediment data sampling and analysis performed by the U.S. Fish and Wildlife Service (“USFWS”), Upper Chattahoochee Riverkeeper (“UCR”) and American Rivers (“AR”) on or about March through May, 2006. In preparing this affidavit and my analysis, I reviewed data results, laboratory procedures and methods, standard laboratory methods, and guidance. I was not provided with a sampling plan and was told by representatives of USFWS and UCR that none was prepared for this sampling and analysis event.
5. On March 14, 2006, I was provided with a copy of a permit application submitted by USFWS and UCR to the National Park Service in order to receive authorization to conduct sampling within the Chattahoochee River National Recreation Area. The application provided a list of analytes: total organic carbon (“TOC”), grain size, Polychlorinated Biphenyls (“PCBs”), Pesticides, Metals, and Polycyclic Aromatic

Hydrocarbons (“PAHs”). Other information contained in the application was limited to sampling objectives and reasons cited by USFWS and UCR for the sampling.

6. On March 15, 2006, I observed Elizabeth Nicholas (General Counsel, UCR), Keith Hastie (Contaminants Specialist, USFWS), and Alice Lawrence (Biologist, USFWS) collect a subset of the ten samples in the Morgan Falls impoundment. Also in attendance from Georgia Power were George Martin (Morgan Falls relicensing manager, and Tom Broadwell (Environmental Specialist). The purpose of observing the collection was to familiarize ourselves with the sample collection protocol being used for the study.
7. On May 8, 2006, I received copies of Excel spreadsheets which were represented as the results of the March 15, 2006 sampling. Exhibit A. The spreadsheets contained no analytical methods, no information regarding the laboratory providing the results, and identified no analyst or approval. The values in Exhibit A were filed with the Commission by UCR and AR on May 30, 2006.
8. Upon review of the results I had questions about the methods used and the measurement units. I also noted that several analytes were reported with identical pairwise concentrations and were present at all locations, an unusual pattern for organic contaminants in sediment. On May 10, 2006, I requested information from Alice Lawrence, including information on sample preparation, the analytical methods used, and quality control data.
9. In response to this request, Alice Lawrence provided by email additional information for the trace element analysis on May 19, 2006.
10. Also in response to this request, a meeting was scheduled at the Laboratory for Environmental Analysis, a laboratory affiliated with the University of Georgia

Department of Crop and Soil Sciences, which conducted the analysis. This meeting occurred on June 9, 2006 at 9:30 a.m. Other than myself, in attendance were Dr. Sayed Hassan, Director of the laboratory, Robert Dickerson (Senior Chemist, Georgia Power), Hallie Meushaw (Attorney, Troutman Sanders LLP), Keith Hastie, Alice Lawrence, Elizabeth Nicholas, and an intern (UCR). The purpose of the meeting was to address questions regarding the results and methods used, and develop an understanding of the bases for measurements.

11. During the meeting, UCR, USFWS and I received revised laboratory results for PAHs directly from the Director of the laboratory and were told the May 9, 2006 results should be discarded. Exhibit B. Significantly, the corrected values provided June 9, 2006, are different than the results filed by UCR and AR, and in all cases are lower than the values originally reported.
12. Meeting attendees were also provided with the following handouts, which I have reviewed and are provided in Exhibit C:
  - a. Analysis of Polynuclear Aromatic Hydrocarbons Using Gas Chromatography Mass Spectrometry (dated 6/1/2006);
  - b. Determination of Organochlorine Pesticides by Gas Chromatography Mass Spectrometry (dated 6/1/2006); and
  - c. Analysis of Polychlorinated Biphenyls (PCBs) Using Gas Chromatography Mass Spectrometry (dated 6/1/2006).
13. Based on my observations and discussion with the Director of the laboratory during the meeting, I understand that the laboratory does not participate in a formal program of interlaboratory testing of unknown samples for PAHs, pesticides, or PCBs.

Nor does the laboratory routinely analyze samples to which analytes of interest have been added (matrix spikes) as part of a routine quality control program

14. Based on our inquiries regarding the reported data and discussion during the laboratory tour, the laboratory does not keep regular written records of calibrations, surrogate recoveries, matrix spike recoveries, or method blanks suitable for review and trending. In my experience, calibration, surrogate recovery, matrix spike recovery, method blank records are necessary for evaluating trends and identifying problems with the accuracy and precision of analytical results.
15. Based on my observations and our discussions, the laboratory does not operate under a quality assurance program meeting the requirements of ISO 17025 “General Requirements for the Competence of Calibration and Testing Laboratories.” The absence of performance testing data, routine quality control data from surrogates and matrix spikes, indicates that a formal quality assurance program is not in place. The laboratory does not hold accreditation with a recognized independent review program such as the National Environmental Laboratory Accreditation Program (“NELAP”) or American Association for Laboratory Accreditation (“A2LA”). In my experience, most federal and state regulatory agencies require laboratory accreditation to ensure that results are accurate and reliable and can be used for comparison.
16. The procedures I was provided with do not fully implement Environmental Protection Agency (“EPA”) or other regulatory recognized methods. In specific cases, deviations from prescribed methods were noted; for example, organic extraction procedures do not use prescribed equipment, surrogate and matrix spike data is absent, and limited calibration data is employed for specific methods.

17. While the procedures and emails I received indicate the methods in use are adapted from referenced sources, the Director of the laboratory indicated that performance demonstrations are not available to document the suitability of methods used to provide results comparable to those generated by recognized EPA or other prescribed methods.
18. I was not provided with any analysis plan describing methods to be used, detection limits expected, or required quality control for this project.
19. Specific quality control data indicate analytical difficulties with the sediment analysis. For example, the PCB method blank contains PCB congeners, the endrin ketone spike for the pesticides was reported as not detected for the laboratory control sample when 250 parts per billion (“ppb”) was expected, and three pesticides were present in the method blank provided with the pesticide quality control data. In addition, the inability to separate and quantify chrysene and isochrysene as well as the anthracene and phenanthrene PAH compounds (See ¶ 21.f) indicates problems with the analytical process and data review.
20. Other observations during the meeting include a statement from the laboratory Director that in order to have had the testing conducted in a manner consistent with EPA methodologies, it would have been necessary to develop a Quality Assurance /Quality Control (“QA/QC”) plan prior to the analysis.
21. With respect to specific analytes, I observed the following upon review of the procedures provided and discussion with the laboratory Director:
  - a. Regarding the PCB analysis, an appropriate analytical method is EPA 8082. The Director of the laboratory appears to have used a method adapted from various

other methods but did not implement the requirements of EPA 8082. The laboratory deviated from EPA-approved extraction methods (EPA 3550) by using water bath sonication instead of the prescribed horn-sonicator. In addition, surrogates were not used to document extraction efficiency. The analysis of method blanks, which should have indicated an absence of PCBs, are reported as having the same or similar magnitude as concentrations reported in sediment, indicating contamination or carryover. Fourteen of twenty-three analytes in the method blank reported measurable concentrations (range from 0.23 to 2.86 ppb). These deviations rendered the analysis inappropriate for comparison or for any regulatory purposes.

- b. Regarding the pesticide analysis, an appropriate analytical method is EPA 8081. The Director of the laboratory appears to have used a method adapted from various other methods but does not implement the requirements of EPA 8081. In analyzing pesticides the laboratory again deviated from EPA-approved extraction methods (EPA 3550) by using water bath sonication instead of the prescribed horn-sonicator, and not using surrogates to document extraction efficiency. In addition, no matrix spike was processed, as specified by EPA methods. The laboratory control sample (“LCS”) reported non-detect for endrin ketone and heptachlor, but the expected value was 250 ppb. Positive results for endrine ketone were reported in the samples. The QA/QC data sheet for pesticides also includes a column labeled “MS” that is actually method blank results. Positive results in the method blank were reported for beta-BHC, Aldrin, and p,p’-DDE.

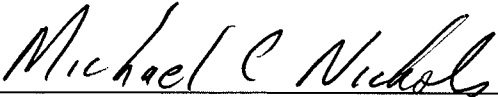
These deviations rendered the analysis inappropriate for comparison or for any regulatory purposes.

- e. For PAHs, the Director of the laboratory provided revised results that were significantly lower than those reported by UCR/AR or provided in the May 8, 2006, report from USFWS. For example, Benzo(a)pyrene at sample location 3 was originally reported as 1251 but restated as 210 ug/Kg, and at sample location 7 was originally reported to be 685 but restated as 143 ug/Kg. Other analytes show similar differences between the original spreadsheet and the data provided June 9, 2006. No units were reported with these results and the units reported here are based on our discussion with the Laboratory director on June 9, 2006.
- f. Also for PAHs, an appropriate analytical method is EPA 8270. The laboratory appears to have used a method adapted from various other methods but does not implement the requirements of EPA 8270. No performance demonstration is available from the laboratory that documents the ability of the procedure used to provide accurate measurements. Surrogate spike data is not routinely collected to document extraction efficiency and matrix spikes are not routinely performed to detect interferences or analytical problems. In addition, we noted that chrysene and isochrysene were reported at the same concentrations for specific sampling locations and a similar pattern of pair-wise identical concentrations were apparent for anthracene and phenanthrene. This pattern persists in the recalculated data set. The laboratory Director indicated he could not separate these compounds and considered the results to be a mixture of the two compounds in each case. In our experience, these compounds are separable when using EPA 8270 and the

inability to separately identify and quantify these compounds indicates an analytical and data review deficiency.

- g. Lastly, with respect to PAHs, I was provided with a copy of the integrator output which included run-time conditions but did not include analytical data that could be correlated with reported results.
  - h. For aniline and benzene derivatives, the laboratory Director indicated the data should not have been distributed. No procedure information was provided. In addition, Compounds 2 and 3 (dichlorobenzenes) have identical concentrations and are present at all locations in a pattern similar to that noted for PAHs.
  - i. For TOC, no procedure or method was provided by the laboratory. However, I observed during my tour of the laboratory that routine quality control graphs of performance were kept only through mid-2004. When I inquired about the routine recording of quality control data, the laboratory Director indicated that such records were no longer recorded because of the time required.
22. In conclusion, based upon experience, my observations and review of the data and procedural information provided, the results of this sediment analysis cannot be used for regulatory purposes or compared to data developed with standard laboratory methods.

DATED this 23 day of June, 2006.

  
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Michael C. Nichols

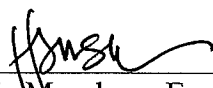
SUBSCRIBED and SWORN to before me this 23 day of June, 2006 by

Wanda Wanda Williams  
Print Name: Wanda Williams  
Notary Public in and for the State of Georgia  
County of Henry  
My commission expires: 01/09/2010

CERTIFICATE OF SERVICE

I hereby certify that I have on this day caused the foregoing to be served upon each person on the Official Service List in this proceeding, pursuant to Rule 2010(a) of the Commission's Rules of Practice and Procedure.

DATED at Atlanta, Georgia, this 23 day of June, 2006

  
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Hallie Meushaw, Esquire

**Exhibit A**

**Affidavit of Michael C. Nichols  
Dated June 23, 2006**



Results of the extraction and analysis of perchlorobiphenyls (PCB's) in Chatthaohchee river sediments:

4/26/2006

Results:

Ser #	Target Compounds	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1)	Biphenyl-4-chloro	bdl	bdl	bdl	0.22	bdl	0.76	bdl	bdl	0.12	bdl
2)	Biphenyl-3-chloro	bdl	bdl	bdl	bdl	bdl	0.71	0.30	bdl	bdl	bdl
3)	Biphenyl-2,5-dichloro	bdl	1.66	bdl	0.10	bdl	0.16	bdl	bdl	bdl	bdl
4)	Biphenyl-2,3,5-trichloro	1.05	1.40	0.59	bdl	0.38	bdl	0.33	0.33	0.98	bdl
5)	Biphenyl-2,3,6-trichloro	bdl	bdl	bdl	0.12	0.04	0.20	0.17	bdl	0.14	bdl
6)	Biphenyl-2,2',5,5'-tetrachloro	bdl	bdl	0.49	0.25	bdl	1.36	0.29	0.48	0.11	bdl
7)	Biphenyl-2,3,3',4,4'-pentachloro	bdl	2.44	0.60	bdl	bdl	1.55	0.34	bdl	bdl	bdl
8)	Biphenyl-2,3,4',5,6-pentachloro	bdl	0.14	0.40	0.41	bdl	bdl	bdl	bdl	bdl	bdl
9)	Biphenyl-2,3,3',4,6-pentachloro	bdl	bdl	0.17	0.43	bdl	bdl	bdl	bdl	bdl	bdl
10)	Biphenyl-2,2',4,4',6,6'-hexachloro	bdl	2.09	1.00	1.18	0.21	bdl	bdl	bdl	bdl	bdl
11)	Biphenyl-2,3,3',4,4',5-hexachloro	bdl	1.07	bdl	1.14	1.85	bdl	0.37	0.32	bdl	bdl
12)	Biphenyl-2,2',3,4',5,5'-hexachloro	bdl	2.95	0.65	0.74	2.61	1.01	1.01	bdl	bdl	0.11
13)	Biphenyl-2,3',4,4',5,5'-hexachloro	bdl	2.95	0.65	0.74	2.61	1.01	1.01	bdl	bdl	0.52
14)	Biphenyl-2,3,3',4',5,5',6-heptachloro	1.17	6.32	2.34	bdl	bdl	bdl	bdl	0.11	0.45	bdl
15)	Biphenyl-2,2',3,4,4',5,6-heptachloro	bdl	0.76	bdl	bdl	bdl	bdl	0.22	0.00	0.19	bdl
16)	Biphenyl-2,6-dichloro	0.12	6.74	0.63	bdl	bdl	1.21	0.21	0.08	0.96	bdl
17)	Biphenyl-4,4'-dichloro	bdl	1.61	bdl	bdl	bdl	0.16	bdl	bdl	bdl	bdl
18)	Biphenyl, trichloro	0.46	bdl	0.21	bdl	bdl	0.58	0.54	bdl	bdl	bdl
19)	Biphenyl-2,4,5-trichloro	0.58	bdl	0.20	bdl	bdl	bdl	0.55	0.50	0.46	0.10
20.)	Biphenyl-3,4,4'-trichloro	bdl	bdl	bdl	0.45	0.07	bdl	0.16	bdl	bdl	bdl
21)	Biphenyl-2,4,6-trichloro	bdl	bdl	1.37	bdl	0.17	bdl	bdl	bdl	bdl	bdl
22)	Biphenyl-3,3',4,4'-tetrachloro	1.68	4.01	5.30	4.61	1.92	6.44	3.47	2.06	33.70	1.05
24)	Biphenyl-3,3',4,5'-tetrachloro	1.09	bdl	bdl	0.43	bdl	bdl	bdl	0.00	0.00	2.07
26)	2,3-Dichlorobiphenyl	0.23	3.47	0.38	0.56	0.38	2.59	0.79	0.58	1.06	1.81
27)	2,4,5-Trichlorobiphenyl	bdl	bdl	0.14	bdl	bdl	bdl	bdl	bdl	bdl	0.47
28)	2,2',4,4'-Tetrachlorobiphenyl	0.14	bdl	bdl	bdl	0.17	0.25	bdl	0.11	bdl	0.36
29)	2,2',3',4,6-Pentachlorobiphenyl	0.25	0.43	bdl	0.39	0.60	1.46	0.14	0.20	bdl	bdl
30)	2,2',4,4',5,6-Hexachlorobiphenyl	bdl	bdl	0.19	0.39	bdl	bdl	bdl	0.32	bdl	bdl
31)	2,2',3,3',4,4',6-Heptachlorobiphenyl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
32)	2,2',3,3',4,5',6'-Octachlorobiphenyl	bdl	0.12	0.11	0.13	bdl	1.02	6.98	0.41	bdl	0.28

**Results of the extraction and analysis of chlorinated pesticides in Chatthaohchee river sediments:**

4/26/2006

**Results:**

Ser #	Wt of sediment, g										Concentration, ug/l
	S 1	S 2	S 3	S 4	S 5	S 6	S 7	S 8	S 9	S 10	
1)	BDL	810.0	75.9	16.5	12.9	261.7	BDL	BDL	BDL	BDL	612.2
2)	BDL	BDL	1.4	3.6	1.1	4.4	BDL	BDL	BDL	BDL	0.9
3)	0.7	BDL	BDL	BDL	BDL	BDL	BDL	0.7	BDL	BDL	BDL
4)	BDL	7.3	26.3	6.0	24.2	95.1	BDL	15.9	44.1	BDL	BDL
5)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
6)	BDL	BDL	0.3	1.4	BDL	BDL	BDL	0.3	BDL	BDL	0.6
7)	3.3	22.6	3.6	0.4	2.0	27.2	BDL	2.1	9.3	BDL	BDL
8)	BDL	BDL	BDL	7.2	54.3	114.8	BDL	0.4	BDL	BDL	BDL
9)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	3.9	BDL	BDL
10)	BDL	0.2	BDL	BDL	BDL	0.9	BDL	0.5	0.2	0.4	BDL
11)	BDL	BDL	BDL	BDL	BDL	167.2	BDL	57.2	62.3	BDL	BDL
12)	BDL	BDL	BDL	BDL	1.9	BDL	BDL	BDL	0.8	BDL	BDL
13)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.4
14)	BDL	666.2	BDL	BDL	32.5	314.2	BDL	3.8	866.7	BDL	BDL
• 15)	BDL	BDL	BDL	BDL	1.8	BDL	BDL	BDL	53.8	BDL	BDL
16)	19.6	81.4	BDL	14.1	BDL	BDL	BDL	1.6	BDL	BDL	BDL
17)	9.0	1,092.1	30.6	36.3	29.0	30.2	3.5	6.1	135.9	53.9	BDL
18)	108.3	250.5	236.9	891.1	335.8	96.8	428.7	395.1	BDL	BDL	BDL

alice palmers soil texture sample results from 10 sediment samples  
a micropipette method for soil mechanical analysis, Miller, WP and DM Miller, 1987  
4 g used.

	% sand	% silt	% clay
1	88.3%	11.7%	10.0%
2	70.4%	29.6%	25.3%
3	57.7%	42.3%	9.8%
4	71.0%	29.0%	10.1%
5	51.1%	48.9%	10.4%
6	72.6%	27.4%	12.6%
7	86.1%	14.0%	12.8%
8	86.0%	14.0%	11.6%
9	88.3%	11.7%	11.6%
10	87.5%	12.6%	11.3%
4 rep	69.2%	30.8%	9.1%
6 rep	73.3%	26.7%	11.6%

c:anal\_results06/TEX\_#1432\_AliceP\_10Apr06.xls

**Results of the analysis of polynuclear aromatic hydrocarbons (PAH's) in sediments:**

4/25/2006

**Procedure:**

A certain wt of the sediment was extracted in 40 ml screw capped bottle by dichloromethane in ultrasonic bath. Centrifuge and separate the organic layers each to a 50 ml conical flask. Repeat the extraction with 10 ml of dichloromethane. Combine the 2 extracts and evaporate almost to dryness. Dissolve the residue with 2 ml of methanol and keep for GC/MS analysis.

Target Compounds	L.O.D. ug/l	S 1	S 2	S 3	S 4	S 5	S 6	S 7	S 8	S 9	S 10
1) Naphthalene	0.4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
2) Acenaphthylene	0.4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
3) Acenaphthene	0.5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
4) 9H-Fluorine	0.4	bdl	bdl	bdl	bdl	bdl	bdl	3.6	bdl	6	bdl
5) Anthracene	0.4	13	37	29	39	22	62	102	33	161	66
6) Phenanthrene	0.4	13	37	29	39	22	62	102	33	161	66
7) Fluoranthene	0.5	47	154	220	257	113	179	323	130	370	223
8) Pyrene	0.4	40	122	187	217	104	142	249	103	269	176
9) Benzo[k]fluoranthene	0.4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
10) Benzo[a]pyrene	0.4	bdl	bdl	1,251	bdl	bdl	bdl	685	bdl	bdl	bdl
11) Chrysene	0.4	54	143	266	252	105	151	256	122	146	218
12) Isochrysene	0.4	54	143	266	252	105	151	256	122	146	218
13) Benzo[b]fluoranthene	0.4	bdl	bdl	1,251	bdl	bdl	bdl	685	bdl	bdl	bdl

river sediment samples from Alice Lawrence of the US F&WS

Sample	Organic C (%)
1	0.1454
2	5.184
3	0.8214
4	1.306
5	0.9881
6	3.061
7	0.5867
8	0.3186
9	0.3414
10	0.8739

c:/anal\_results06/CNS\_#1432\_AliceP\_11Apr06.xls

**Exhibit B**

**Affidavit of Michael C. Nichols  
Dated June 23, 2006**

*12/18/06 dry wt*

Results of the analysis of polynuclear aromatic hydrocarbons (PAH's) in sediments:												
4/25/2006												
<b>Procedure:</b>												
A certain wt of the sediment was extracted in 40 ml screw capped bottle by dichloromethane in ultrasonic bath.												
Centrifuge and separate the organic layers each to a 50 ml conical flask. Repeat the extraction with 10 ml of dichloromethane.												
Combine the 2 extracts and evaporate almost to dryness. Dissolve the residue with 2 ml of methanol and keep for GC/MS analysis.												
												9
Target Compounds												
1) Naphthalene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2) Acenaphthylene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3) Acenaphthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
4) 9H-Fluorine	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5) Anthracene	2.593843	13.73063	4.85906	7.001795	3.96293	27.99097	21.22789	6.25	20.6808	12.53561		
6) Phenanthrene	2.593843	13.73063	4.85906	7.001795	3.96293	27.99097	21.22789	6.25	20.6808	12.53561		
7) Fluoranthene	9.259186	56.82657	36.91275	46.14004	19.87643	80.81264	67.22164	24.62121	47.5273	42.35518		
8) Pyrene	7.868918	45.01845	31.37584	38.95871	18.34069	64.10835	51.82102	19.50758	34.55363	33.4283		
9) Benzo[k]fluoranthene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
10) Benzof[a]pyrene	BDL	BDL	209.8993	BDL	BDL	BDL	142.5598	BDL	BDL	BDL	BDL	BDL
11) Chrysene	10.73883	52.76753	44.63087	45.24237	18.48191	68.17156	53.27784	23.10606	18.75401	41.40551		
12) Isochrysene	10.73883	52.76753	44.63087	45.24237	18.48191	68.17156	53.27784	23.10606	18.75401	41.40551		
13) Benzo[b]fluoranthene	BDL	BDL	209.8993	BDL	BDL	BDL	142.5598	BDL	BDL	BDL	BDL	BDL

*NOT Present*

**Exhibit C**

**Affidavit of Michael C. Nichols  
Dated June 23, 2006**

## LABORATORY FOR ENVIRONMENTAL ANALYSIS

**Date:** 6/1/2006  
**Last Updated:** 6/1/2005  
**Responsible Analyst:** Sayed M. Hassan

### ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS USING GAS CHROMATOGRAPHY MASS SPECTROMETRY

#### 1.0 SCOPE AND APPLICATION

1.1. This method is used to determine the concentration of polynuclear aromatic hydrocarbon compounds (PAH's) in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The compounds listed below can be determined:

Naphthalene, Acenaphthylene, Acenaphthene, 9H-Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Benzo[k]fluoranthene, Benzo[a]pyrene, Chrysene, Isochrysene, and Benzo[b]fluoranthene.

#### 2.0 SUMMARY OF METHOD

- 2.1. The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation and, if necessary, sample cleanup procedures.
- 2.2. The PAH compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.
- 2.3. Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion using a calibration curve.

#### 3.0 INTERFERENCES

- 3.1. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine the source of interference –if any- and take corrective action to eliminate the problem.
- 3.2. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is reduced by the analysis of solvent in between samples to check for cross-contamination.

#### 4.0 APPARATUS AND MATERIALS

- 4.1 Gas chromatograph/mass spectrometer system
  - 4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including an automatic liquid sampler, syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
  - 4.1.2 Column - 30 m x 0.25 mm ID x 0.5 um film thickness silicone-coated fused-silica capillary column (HP-5 Trace Analysis).
  - 4.1.3 Mass spectrometer
    - 4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

4.1.3.2 GC/MS interface is directly connected to the capillary column.

4.1.5 Data system - A computer system interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can search any GC/MS data file for ions of a specific mass and can plot ion abundances versus time. The software also includes a Mass Spectral Library containing 275,000 spectra of organic compounds.

4.2 Syringe - 10- $\mu$ L.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.00001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the 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.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methanol or other suitable solvent and dilute to volume in a 10-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10EC or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 GC/MS tuning standard - A methylene chloride solution containing 50 ng/ $\mu$ L of perfluoro-t-butylamine (PFTBA) is used as recommended by the manufacturer.

5.5. Laboratory control standards. These are prepared by dilution of purchased certified standards preferably from sources other than the calibration standards.

## 6.0 SAMPLE PRESERVATION AND HANDLING

6.1 Store the samples and extracts at -10EC, protected from light, in sealed containers.

## 7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Soils/sediments are extracted by applying "ULTRASONIC EXTRACTION PROCEDURE". The methylene chloride extract is evaporated almost to dryness by placing in a suitably heated water bath and dissolving the residue in 2 ml of methanol.

7.2 Extract cleanup. The methanol extract is further purified by evaporation almost to dryness and re-dissolution in 2 ml of methanol. The process is repeated until a clean transparent extract is obtained.

7.3. Analysis. Analyze 1-2  $\mu\text{L}$  of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each target analyte. The injection volume must be the same for all blanks, standards and sample extracts. Calculate response factors (RF) for each target analyte as follows;

$$\text{RF} = A/C$$

where:

A = Peak area of the analyte

C = Concentration of the analyte. in  $\mu\text{g/L}$ ,

7.3.1. Calibration check compounds (CCCs)

7.3.1.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column

7.3.1.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 20% for each target analyte. However, the RSD for each individual CCC must be less than or equal to 30%.

7.3.1.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.2 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units.

7.3.3 Linearity of target analytes - If the RSD of any target analytes is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.2.1. If the RSD of any target analyte is greater than 20%, a new initial calibration must be performed.

7.3.2.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4. GC/MS calibration verification - Calibration verification is performed at the beginning of each 12-hour analytical shift.

7.4.1. A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

7.5 GC/MS analysis of samples

7.5.1. Inject a 1-2  $\mu\text{L}$  aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration. The injection volume must be the same volume used for the calibration standards.

7.5.2. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed.

7.5.3. The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. Since SIM may provide a lesser degree of confidence in the compound identification, multiple ions are monitored for each compound.

7.6. Quantitative analysis

7.6.1. Quantitation of compounds will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.6.2. If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data.

## 8.0 QUALITY CONTROL

### 8.1. Instrument QC requirements:

8.1.1. The MS system must be tuned to meet the criteria of the manufacturer.

8.1.2. There must be an initial calibration of the GC/MS system.

8.1.3. The GC/MS system must meet the calibration verification acceptance criteria as recommended by the manufacturer.

8.1.4. The RRT of the sample components must fall within a window of  $\pm 0.06$  units

8.2. Lab Demonstration of Proficiency. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Dr. Sayed Hassan, who handles the organic analysis has earned a Ph.D. and Master degrees in analytical chemistry (method development) supported by 15+ years of experience in GC/MS work at the EPA and UGA. Labs.

8.2.1. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.2.2. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, .etc,

8.2.3. The effect of the matrix is documented by duplicate analysis of field samples. The difference should not exceed  $\pm 20\%$ . One Duplicate field sample is carried out every 10 samples or one per batch for smaller groups of samples.

## 9.0 REFERENCES

1. Eichelberger, J.W., Harris, L.E., and Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems", Analytical Chemistry, 47, 995-1000, 1975.

2. Lucas, S.V., Kornfeld, R.A., "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes ", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

3. Engel, T.M., Kornfeld, R.A., Warner, J.S., and Andrews, K.D., "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

4. Lopez-Avila, V. (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV, October 1991; EPA 600/X-91/140.

QA/QC Data	PAH's			
	MS	LCS		
		Stated/ ppb	Found/ ppb	% Recovry
Naphthalene	N.D.	40,000.0	38,218.2	95.55
Acenaphthylene	N.D.	40,000.0	43,294.7	108.24
Acenaphthene	N.D.	40,000.0	33,603.9	84.01
9H-Fluorine	N.D.	40,000.0	33,114.3	82.79
Anthracene	N.D.	40,000.0	33,237.8	83.09
Phenanthrene	N.D.	40,000.0	33,237.8	83.09
Fluoranthene	N.D.	4,000.0	4,772.8	119.32
Pyrene	N.D.	4,000.0	4,520.6	113.02
Benzo[k]fluorant	N.D.	2,000.0	N.D.	
Benzo[a]pyrene	N.D.	4,000.0	2,045.2	51.13
Chrysene	N.D.	4,000.0	4,669.0	116.73
Isochrysene	N.D.	N.A.	4,669.0	
Benzo[b]fluorant	N.D.	4,000.0	2,045.2	51.13

## LABORATORY FOR ENVIRONMENTAL ANALYSIS

Date: 6/3/2006  
Date Last Revised: 6/1/2005  
Responsible Analyst: Sayed M. Hassan

### DETRMINATION OF ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY MASS SPECTROPHOTOMETRY

#### 1.0. SCOPE AND APPLICATION

1.1. The method is used to determine the concentration of various organochlorine pesticides in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with mass spectrum detector (MSD). The compounds listed below may be determined:

alpha-BHC, gama-BHC, beta-BHC, delta-BHC, Heptachlor, Aldrin, Heptachlor Epoxide, Endosulfan I, Dieldrin, p,p'-DDE, Endrin, Endosulfan II, p,p'-DDD, Endrin Aldehyde, Endosulfan Sulfate, p,p'-DDT, Endrin Ketone, and Methoxychlor.

#### 2.0. SUMMARY OF METHOD

- 2.1. A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.
- 2.2. Liquid samples are extracted at neutral pH with methylene chloride using a set of separatory funnels, or other appropriate technique.
- 2.3. Solid samples are extracted with methylene chloride using ultrasonic extraction.
- 2.4. After cleanup, the extract is analyzed by injecting a 1-2  $\mu$ L sample into a gas chromatograph with a narrow-bore fused silica capillary column and mass spectrophotometric detector (GC/MSD).
- 2.5. Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion using a calibration curve.

#### 3.0 INTERFERENCES

- 3.1. Sources of interference can be grouped into three broad categories.
  - 3.1.1. Contaminated solvents, reagents, or sample processing hardware.
  - 3.1.2. Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
  - 3.1.3. Compounds extracted from the sample matrix to which the detector will respond.
  - 3.1.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is reduced by the analysis of solvent in between samples to check for cross-contamination
- 3.2. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130EC for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.
- 3.3. Waxes, lipids, and other high molecular weight materials can be removed by gel-permeation cleanup.

#### **4.0 APPARATUS AND MATERIALS**

##### **4.1. Gas chromatograph/mass spectrometer system**

4.1.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including an automatic liquid sampler, syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2. Column - 30 m x 0.25 mm ID x 0.5  $\mu$ m film thickness silicone-coated fused-silica capillary column (HP-5 Trace Analysis).

##### **4.1.3. Mass spectrometer**

4.1.3.1. Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

4.1.3.2. GC/MS interface is directly connected to the capillary column.

4.1.4. Data system - A computer system interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can help search any GC/MS data file for ions of a specific mass and can plot ion abundances versus time. The software also includes a Mass Spectral Library containing 275,000 spectra of organic compounds.

4.2. Syringe - 10- $\mu$ L.

4.3. Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4. Balance - Analytical, capable of weighing 0.00001 g.

4.5. Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

#### **5.0. REAGENTS**

5.1. Pesticide grade chemicals shall 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.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4EC in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards are prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

5.2. All solvents used in the extraction and cleanup procedures should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

5.3. Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.4. Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.4.1. Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5. Composite stock standard - May be prepared from individual stock solutions.

5.5.1 For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at a concentration of 1000 mg/L, add solvent, and mix the solutions

in a 25-mL volumetric flask. This composite solution can be further diluted to obtain the desired concentrations.

5.5.2. For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50 mL, 100 mL), and follow the procedure described above.

5.6. Calibration standards should be prepared by dilution of the composite stock standard with methanol or other suitable solvent. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

## 6.0. SAMPLE PRESERVATION AND HANDLING

6.1. Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

## 7.0. PROCEDURE

7.1. Sample extraction. In general, water samples are extracted at a neutral pH with methylene chloride using separatory funnels or other appropriate technique. Solid samples are extracted with either methylene chloride alone or methylene chloride-acetone mixture (1:1) using the ultrasonic extraction 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 must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

7.2. Extract cleanup. Cleanup procedures may not be necessary for a relatively clean sample matrix. Some extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements.

7.2.1. If a sample is of biological origin, or contains high molecular weight materials, the use of EPA Method 3640 (GPC cleanup, pesticides) is recommended. Frequently, an additional procedure in which one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

7.2.2. Alumina may be used to remove phthalate esters.

7.2.3. Florisil may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

7.2.4. Silica gel may be used to separate some industrial interferants.

7.3. Analysis. Analyze 1-2  $\mu$ L of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each target analyte. The injection volume must be the same for all blanks, standards and sample extracts. Calculate response factors (RF) for each target analyte as follows;

$$RF = A/C$$

where:

A = Peak area of the analyte

C = Concentration of the analyte. in  $\mu$ g/L,

7.3.1. Calibration check compounds (CCCs)

7.3.1.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column

7.3.1.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 20% for each target analyte. However, the RSD for each individual CCC must be less than or equal to 30%.

7.3.1.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.2. Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units..

7.3.2.1. Before establishing the RRT, make sure the gas chromatographic system is operating within optimum conditions.

7.3.3 Linearity of target analytes - If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.2.1. If the RSD of any target analyte is greater than 20%, a new initial calibration must be performed.

7.3.3. When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4. GC/MS calibration verification - Calibration verification is performed at the beginning of each 12-hour analytical shift.

7.4.1. A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

7.5 GC/MS analysis of samples

7.5.1. Inject a 1-2  $\mu\text{L}$  aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration. The injection volume must be the same volume used for the calibration standards.

7.5.2. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed.

7.5.3. The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. Since SIM may provide a lesser degree of confidence in the compound identification, multiple ions are monitored for each compound.

7.6. Quantitative analysis

7.6.1. Quantitation of compounds will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.6.2. If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data.

## 8.0 QUALITY CONTROL

8.1. Instrument QC requirements:

8.1.1. The MS system must be tuned to meet the criteria of the manufacturer.

8.1.2. There must be an initial calibration of the GC/MS system.

8.1.3. The GC/MS system must meet the calibration verification acceptance criteria as recommended by the manufacturer.

8.1.4. The RRT of the sample components must fall within  $\pm 0.06$  units

8.2. Lab Demonstration of Proficiency. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Dr. Sayed Hassan, who handles the organic analysis has earned a Ph.D. and Master degrees in analytical chemistry (method development) supported by 15+ years of experience in GC/MS work at the EPA and UGA. Labs.

8.2.1. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank

should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.2.2. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc.

8.2.3. The effect of the matrix is documented by duplicate analysis of field samples. The difference should not exceed  $\pm 20\%$ . One Duplicate field sample is carried out every 10 samples or one per batch for smaller groups of samples.

8.3. Whenever silica gel or Florisil cleanups are used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel or Florisil or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. When compounds are found in two fractions, add the concentrations found in the fractions, and correct for any additional dilution.

8.4. Surrogate recoveries: The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory.

8.5. 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.

## 9.0. REFERENCES

1. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", final report to the U.S. Environmental Protection Agency on Contract 68-03-3511; Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.
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QA/QC Data	Organochlorine Pesticides				
	MS		LCS		
			Stated/ ppb	Found/ ppb	% Recovery
alpha-BHC	bdl		250	250.0	100.0
gama-BHC	bdl		250	251.6	100.6
beta-BHC	0.95		250	250.8	100.3
delta-BHC	bdl		250	262.7	105.1
Heptachlor	bdl		250	N.D.	
Aldrin	1.58		250	251.2	100.5
Heptachlor Epoxid	bdl		250	231.0	92.4
Endosulfan I	bdl		250	250.0	100.0
Dieldrin	bdl		250	225.4	90.2
p,p'-DDE	0.23		250	252.7	101.1
Endrin	bdl		250	250.0	100.0
Endosulfan II	bdl		250	331.1	132.4
p,p'-DDD	bdl		250	252.8	101.1
Endrin Aldehyde	bdl		250	228.5	91.4
Endosulfan Sulfate	bdl		250	250.0	100.0
p,p'-DDT	bdl		250	250.0	100.0
Endrin Ketone	bdl		250	N.D.	
Methoxychlor	bdl		250	250.0	100.0

## LABORATORY FOR ENVIRONMENTAL ANALYSIS

**Date:** 6/1/2006  
**Last Updated:** 6/1/2005  
**Responsible Analyst:** Sayed M. Hassan

### ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBs) USING GAS CHROMATOGRAPHY MASS SPECTROMETRY

#### 1.0. SCOPE AND APPLICATION

1.1. The method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid and aqueous matrices. Open tubular, capillary columns are employed with mass spectrometer detector (MSD). The target compounds listed below may be determined. The method is also appropriate for additional congeners.

Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, 2-Chlorobiphenyl, 2,3-Dichlorobiphenyl, 2,2',5'-Trichlorobiphenyl, 2,4',5'-Trichlorobiphenyl, 2,2',3,5'-Tetrachlorobiphenyl, 2,2',5,5'-Tetrachlorobiphenyl, 2,3',4,4'-Tetrachlorobiphenyl, 2,2',3,4,5'-Pentachlorobiphenyl, 2,2',4,5,5'-Pentachlorobiphenyl, 2,3,3',4',6-Pentachlorobiphenyl, 2,2',3,4,4',5'-Hexachlorobiphenyl, 2,2',3,4,5,5'-Hexachlorobiphenyl, 2,2',3,5,5',6-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl, 2,2',3,3',4,4',5-Heptachlorobiphenyl, 2,2',3,4,4',5,5'-Heptachlorobiphenyl, 2,2',3,4,4',5',6-Heptachlorobiphenyl, 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl.

1.2. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

1.3. Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of selected individual PCB congeners.

1.4. The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations.

1.5. The PCB compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

1.5.1. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards.

- 1.5.2. Quantitation is accomplished by comparing the response of a major ion for each target compound using a calibration curve.
- 1.5.3. This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and mass detectors and skilled in the interpretation of gas chromatograms and the resulting mass spectra.

## **2.0 SUMMARY OF METHOD**

- 2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the following as guidelines.
- 2.2 Aqueous samples are extracted at neutral pH with methylene chloride using separatory funnel or other appropriate technique.
- 2.3 Solid samples are extracted with methylene chloride or methylene chloride-acetone (1:1) using ultrasonic bath.
- 2.4. After cleanup, if necessary, the PCB compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.
- 2.4.1. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards.
- 2.4.2. Quantitation is accomplished by comparing the response of a major ion for each target compound using a calibration curve.
- 2.4.3. This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and mass detectors and skilled in the interpretation of gas chromatograms and the resulting mass spectra.

## **3.0 INTERFERENCES**

- 3.1. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine the source of interference -if any- and take corrective action to eliminate the problem.
- 3.2. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is reduced by the analysis of solvent in between samples to check for cross-contamination.

## **4.0 APPARATUS AND MATERIALS**

- 4.1 Gas chromatograph/mass spectrometer system
- 4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including an automatic liquid sampler, syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 4.1.2 Column - 30 m x 0.25 mm ID x 0.5 um film thickness silicone-coated fused-silica capillary column (HP-5 Trace Analysis).
- 4.2. Mass spectrometer.
- 4.2.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.
- 4.2.2 GC/MS interface is directly connected to the capillary column.
- 4.3. Data system.
- 4.3.1 A computer system interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.
- 4.3.2. The computer has software that can search any GC/MS data file for ions of a specific mass and can plot ion abundances versus time.

4.3.3. Mass Spectral Library containing 275,000 spectra of organic compounds allow identification of the separated components.

4.2 Syringe - 10- $\mu$ L.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.00001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

## 5.0 REAGENTS

5.1. Pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4EC in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC (Sec. 8.0) indicates a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

5.2. Organic-free reagent water - All waters mentioned in this method refer to organic-free reagent water.

5.4. Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.4.1. Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

5.4.2. Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.5. GC/MS tuning standard - A methylene chloride solution containing 50 ng/ $\mu$ L of perfluoro-t-butylamine (PFTBA) is used as recommended by the manufacturer..

5.6. laboratory control standards. These are prepared by dilution of purchased certified standards preferably from sources other than the calibration standards.

## 6.0 SAMPLE PRESERVATION AND HANDLING

6.1. Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

## 7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Soil/sediment are extracted by applying "ULTRASONIC EXTRACTION PROCEDURE". The methylene chloride extract is evaporated almost to dryness by placing in a suitably heated water bath and dissolving the residue in 2 ml of methanol.

7.2 Extract cleanup. The methanol extract is further purified by evaporation almost to dryness and re-dissolution in 2 ml of methanol. The process is repeated until a clean transparent extract is obtained.

7.3. Analysis. Analyze 1-2  $\mu$ L of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each target analyte. The injection volume must be the

same for all blanks, standards and sample extracts. Calculate response factors (RF) for each target analyte as follows;

$$RF = A/C$$

where:

A = Peak area of the analyte

C = Concentration of the analyte. in  $\mu\text{g/L}$ ,

#### 7.3.1. Calibration check compounds (CCCs).

7.3.1.1. The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column.

7.3.1.2. Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC must be less than or equal to 30%.

7.3.1.3. If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.2. Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units.

7.3.3. Linearity of target analytes - If the RSD of any target analytes is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.2.1. If the RSD of any target analyte is greater than 20%, a new initial calibration must be performed.

7.3.2.2. When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

7.4. GC/MS calibration verification - Calibration verification is performed at the beginning of each 12-hour analytical shift.

7.4.1. A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

#### 7.5 GC/MS analysis of samples

7.5.1. Inject a 1-2  $\mu\text{L}$  aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration. The injection volume must be the same volume used for the calibration standards.

7.5.2. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed.

7.5.3. The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. Since SIM may provide a lesser degree of confidence in the compound identification, multiple ions are monitored for each compound.

#### 7.6. Quantitative analysis

7.6.1. Quantitation of compounds will be based on the integrated abundance of the primary characteristic ion from the extracted ion current profile (EICP).

7.6.2. If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data

## **8.0. QUALITY CONTROL**

### **8.1. Instrument QC requirements:**

8.1.1. The MS system must be tuned to meet the criteria of the manufacturer.

8.1.2. There must be an initial calibration of the GC/MS system.

8.1.3. The GC/MS system must meet the calibration verification acceptance criteria as recommended by the manufacturer.

8.1.4. The RRT of the sample components must fall within  $\pm 0.06$  unites.

8.2. Lab Demonstration of Proficiency. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Dr. Sayed Hassan, who handles the organic analysis has earned a Ph.D. and Master degrees in analytical chemistry (method development) supported by 15+ years of experience in GC/MS work at the EPA and UGA. Labs.

8.2.1. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.2.2. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, .etc,

8.2.3. The effect of the matrix is documented by duplicate analysis of field samples. The difference should not exceed  $\pm 20\%$ . One Duplicate field sample is carried out every 10 samples or one per batch for smaller groups of samples.

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QA/QC Results	PCB				
	MB	LCS			% Recovery
		labelled	found	Concentration, ppb	
Biphenyl-4-chloro	0.51	2,500.0	3171.2	126.8	
Biphenyl-3-chloro	0.38	N.A.			
Biphenyl-2,5-dichloro	1.28	1,500.0	1689.7	112.6	
Biphenyl-2,3,5-trichloro	bdl	1,000.0	1048.2	104.8	
Biphenyl-2,3,6-trichloro	bdl	1,000.0	1076.1	107.6	
Biphenyl-2,2',5,5'-tetrachloro	0.68	2,500.0	2484.8	99.4	
Biphenyl-2,3,3',4,4'-pentachloro	bdl	2,500.0	2787.5	111.5	
Biphenyl-2,3,4',5,6-pentachloro	0.62	2,500.0	2610.3	104.4	
Biphenyl-2,3,3',4,6-pentachloro	2.16	2,500.0	3152.2	126.1	
Biphenyl-2,2',4,4',6,6'-hexachloro	bdl	N.A.			
Biphenyl-2,3,3',4,4',5-hexachloro	bdl	N.A.			
Biphenyl-2,2',3,4',5,5'-hexachloro	2.24	2,500.0	2137.5	85.5	
Biphenyl-2,3',4,4',5,5'-hexachloro	2.24	2,500.0	2137.5	85.5	
Biphenyl-2,3,3',4',5,5',6-heptachloro	2.86	N.A.			
Biphenyl-2,2',3,4,4',5',6-heptachloro	bdl	N.A.			
Biphenyl-2,6-dichloro	2.31	1,500.0	1683.7	112.2	
Biphenyl-4,4'-dichloro	bdl	1,500.0	1689.7	112.6	
Biphenyl, trichloro	bdl	N.A.			
Biphenyl-2,4,5-trichloro	1.74	1,000.0	1048.2	104.8	
Biphenyl-3,4,4'-trichloro	0.23	1,000.0	1036.6	103.7	
Biphenyl-2,4,6-trichloro	2.42	1,000.0	1038.7	103.9	
Biphenyl-3,3',4,4'-tetrachloro	2.40	1,000.0	854.2	85.4	
Biphenyl-3,3',4,5'-tetrachloro	bdl	1,000.0	780.4	78.0	