164666

Olin

P.O. BOX 248, 1186 LOWER RIVER ROAD, NW, CHARLESTON, TN 37310-0248
(423) 336-4000 FAX (423) 336-4183

Via: Airborne Express

May 30, 1997

Mr. Eugene P. Wingert
Remedial Project Manager
U.S. Environmental Protection Agency (3HW41)
841 Chester Building
Philadelphia, PA 19107

RE: Analytical Methods Study for the Olin Area Hanlin-Allied-Olin Site, Moundsville, West Virginia
EPA Docket No. III-94-29-DC

Dear Mr. Wingert:

Olin Corporation is pleased to submit the results of the Analytical Method Study prepared by DynCorp Information & Engineering Technology (DynCorp) and Lancaster Laboratories. The non-target compound list semivolatile organic compounds identified in the Engineering Evaluation/Cost Analysis (EE/CA) Work Plan (RUST, May 1996) were included in the method development process. These chemicals are aniline; 2,6-dinitrophenol; diphenyl; 4,4'-methylene dianiline (MDA); 2,4- and 2,6-toluenediamine (TDA); o-toluidine; 1-, 2-, 3-, and 4-methyl-1-cyclohexylamine; monoethanolamine (MEA); and 2-, 3-, and 4-methylcyclohexanone.

The study has culminated in the development of two analytical methods, applicable to soil/sediment and water matrices, that are being submitted with this letter for USEPA review and comment. The following discussion provides a summary of the method development process and recommendations for the elimination of the methylcyclohexylamine isomers and MEA from further consideration based upon analytical difficulties, low toxicity, low prevalence, and lack of environmental persistence.

1.0 ANALYTICAL METHOD DEVELOPMENT

The complex process of analytical method development for the nontarget chemicals was begun in 1996 by DynCorp at the request of Olin Corporation. Approximately 70 laboratories were initially identified by DynCorp based upon the availability of instrumentation. Thirty percent of these laboratories responded to extensive surveys on instrumentation, detection limits and previous experience with the chemicals of interest. Five candidate laboratories were ultimately

2.0 COMPOUNDS NOT SELECTED FOR METHOD DEVELOPMENT

MEA and the methycyclohexylamine isomers were found to be very problematic during the method validation study. The study indicated that recoveries and isomer resolution were very poor. The chemicals, which are relatively strong bases, have very different chemical properties than TDA and MDA. There is also considerable question whether MEA could be analyzed by mass spectroscopy because of the lack of abundant ions for monitoring (only m/z 30 is abundant in its mass spectrum).

Olin proposes the removal of these chemicals from further consideration in the EE/CA based upon an evaluation of toxicity, potential prevalence, and environmental persistence, and this is discussed below.

2.1 Monoethanolamine (MEA)

MEA is a constituent of many consumer products, such as detergents, soaps, other surfactants, and hair waving solutions, and it is used as a dispersing agent for agricultural chemicals (Howard 1990). It occurs naturally in mammals and is a normal constituent of urine (Binks et al. 1992). Mammalian metabolic studies demonstrate that MEA is readily metabolized to urea, or may be methylated to choline and converted to serine and glycine (Patty 1981, Klain et al. 1985).

Toxicity ug/l

USEPA has not developed health-based criteria for MEA. Available data indicate that MEA would be considered a noncarcinogen. A battery of genotoxicity studies used as indicators of the potential for carcinogenic effects revealed that MEA produced negative responses (Binks et al. 1992). MEA is widely used in industry and is monitored in the workplace. The American Conference of Governmental Industrial Hygienists (ACGIH) has published a threshold limit value-time weighted average (TLV-TWA) of 8,000 Pg/m3 and a short-term exposure limit (STEL) of 15,000 Pg/m3 for MEA exposures in occupational settings (ACGIH 1996a). The acute oral rat LD_{50} is 1,720 mg/kg which is fairly high; in comparison, the same value for sodium chloride is 3,000 mg/kg (RTECS 1997).

Aquatic life toxicity criteria have not been developed for MEA, but 96 hour LC_{50} values for common aquatic test organisms were estimated for this evaluation based upon Quantitative Structural-Activity Relationships (QSARs). QSARs relate the structure and physicochemical properties of molecules to their biological activities. The QSAR system used in this analysis is a joint project of the USEPA Environmental Protection Agency Environmental Research Laboratory in Duluth, Minnesota, and Montana State University (TDS Numerica 1997). This screening-level information is useful for providing an indication of potential toxicity of a chemical

and the need for closer consideration. The toxicity parameters provided in the analysis were the 96 hour lethal concentrations (LC_{50}) in seven common test organisms, as well as the 30 day chronic "no effect" level for the Fathead Minnow.

The estimated LC_{50}s and the chronic "no-effect" level provided in Table 3 below do not indicate a potential problem with respect to these parameters. A substantial elevation of pH in the water system would, in fact, be observable before these levels were approached. For example, the pH of a solution containing 6,000 mg/L of MEA would be approximately 12 (Merck Index 1989).

Table 3

[illegible]	[illegible]
Daphnia	21,000
Fathead Minnow	34,000
Rainbow Trout	43,000
Catfish	31,000
Goldfish	49,000
Bluegill	50,000
Mosquitofish	38,000
30 Day No Effect Level	8,400

Prevalence

The potential prevalence of MEA at the site also was considered in the decision to not continue with additional method development. Based upon an understanding of the manufacturing processes that occurred at the facility from 1956 to 1984, MEA is not anticipated to be prevalent in environmental media at the site. This is because the chemical was used within a closed or "hermitized" system to absorb carbon monoxide from the hydrogen/carbon monoxide production process. Thus, MEA was recycled within the system, handled infrequently and was not used as a raw material or intermediate in the manufacturing process. Potential fugitive releases from process vents may have occasionally occurred.

Persistence

Fugitive releases of MEA to the atmosphere would have been rapidly degraded by photochemically generated hydroxyl radicals. The estimated half-life of MEA in the atmosphere is 4 to 11 hours (Dow Chemical 1980, Eisenreich et al. 1981, Atkinson 1987). In the event that small amounts of MEA escaped to other environmental media, fate data strongly suggests that the chemical is not persistent. Shukla and Turner (1980) found ten taxonomically diverse species to be capable of using MEA as a sole nitrogen source, which indicates that the compound is very degradable. The work of Shukla and Turner is corroborated by several researchers who have shown substantial degradation of the chemical in biodegradation screening tests using sewage sludge over time periods ranging from 5 to 50 days (Bridie et al. 1979; Kawaski 1980; Kitano 1978; Lamb and Jenkins 1952; Sasaki 1978; Young et al. 1968; Mills and Stack 1954). In an environmental study using river water samples from the River Aire in Leeds, Emtiazi and Knapp (1994) found MEA to be the most degradable of all of the linear amines that were evaluated, with complete degradation observed within 1 to 2 days. In another environmental study using soil, researchers found that MEA in soil and sediment degraded rapidly after a relatively short acclimation time at temperatures near 25°C and observed degradation under both aerobic and anaerobic conditions (Gallagher et al. 1996). Although biodegradation is a complex phenomenon with an efficiency that depends upon many factors, the weight-of-evidence indicates that MEA residues should not be persistent at the site.

There is also no indication that MEA would partition into biota and thus bioconcentrate or biomagnify. Accumulation in biota is observed for lipophilic compounds which tend to partition into fat and remain in an organism. MEA is an extremely polar molecule that will exist predominantly as a protonated or positively charged species in the environment as evidenced by its pKa of 9.48 at 25°C (Howard 1990). In an aquatic system, adsorption onto negatively charged clay particles and humic materials in soil and sediment due to this positive charge will limit mobility to some extent, but some migration into surface water would also occur. In surface water, the enhanced polarity of a formal charge will limit the partitioning of MEA into lipid, as demonstrated by its very low log octanol-water partition coefficient (log K_{ow}) of -1.31 (Hansch and Leo 1985). Several data bases report a bioconcentration factor (BCF) of <1 for MEA, which indicates that bioconcentration does not occur, reflecting its polar nature (HSDB 1997). Rather than accumulate, the chemical is readily metabolized in animal systems to compounds such as urea, choline, serine and glycine (Patty 1981, Klain et al. 1985, Binks et al. 1992).

In summary, MEA is not expected to be a risk-driving chemical at the site based upon the criteria of toxicity, prevalence and persistence, and was therefore not selected for special method development after attempts to include it in the modified CLP method were unsuccessful. The chemical was used in a closed system during manufacturing operations, which would have limited

handling and hampered its release to the environment. The preponderance of environmental fate data indicates that the chemical is not persistent in air, soil, water or biota.

2.2 Methylcyclohexylamine Isomers

Toxicity

There are no published health-based criteria for these chemicals. No relevant toxicity studies were identified in the literature that would provide useful information. In order to evaluate the potential toxicity of these chemicals, a structural analog is therefore required.

USEPA has calculated risk-based concentrations (RBCs) for cyclohexylamine, a common industrial chemical, with a published noncancer reference dose (RfD) of 0.2 mg/kg-day. For the residential ingestion of tap water, the RBC is 7,300 Tg/L, and a value of 14,600 Tg/L can be calculated for the consumption of water during industrial land use. The RBC for a residential soil ingestion scenario is 16,000 mg/kg or 1.6%, while the industrial soil ingestion RBC is 410,000 mg/kg or 41% (USEPA 1996). Three chronic animal studies designed to evaluate the potential for carcinogenic effects in rodents were all negative (Gaunt et al. 1976, Oser et al. 1976, Hardy et al. 1976). The American Conference of Governmental Industrial Hygienists (ACGIH) has placed this chemical in their category A4, which means that there is inadequate data on which to classify this chemical in terms of carcinogenicity to humans or animals. ACGIH has published a threshold limit value-time weighted average (TLV-TWA) of 41,000 Tg/m^3 for cyclohexylamine exposures in occupational settings (ACGIH 1996a). This information is indicative of the low toxicity of the general class of chemicals.

No aquatic life toxicity criteria are available for methylcyclohexylamine, but aquatic toxicity data for cyclohexylamine suggest that these cyclic amine compounds are relatively nontoxic to aquatic life. Calamari et al. (1980) reported 96-hour LC_{50} values for rainbow trout in the range of 44 to 90 mg/L. Christensen and Luginbyhl (1975) reported even higher concentration limits for fish in in the range of 100 to 1,000 mg/L. Invertebrate toxicity was similarly high. Algae were slightly more sensitive than invertebrates or fish, with growth inhibition occurring at median effective concentrations in the range of 20 mg/L. Overall, acute toxicity values in this range are typically regarded as relatively nontoxic (Meyer and Barclay 1990). A significant elevation in the pH of the water system would be observable before these levels are reached. For example, a 14 mg/L solution of methylcyclohexylamine is estimated to have a pH of approximately 10 based upon analogy to cyclohexylamine (Butler 1966).

Prevalence

The methylcyclohexylamine isomers are not expected to be prevalent on Olin property, or be present at concentrations higher than TDA, a potential human carcinogen for which an analytical method has been developed. The methylcyclohexylamine isomers were unwanted by-products generated during the TDA/TDI manufacture that occurred between 1956 to 1984. As unwanted by-products, they were formed in small quantities in comparison to TDA, with which they would be associated.

Persistence

If methylcyclohexylamine isomers were released to the environment, available environmental fate data suggest that the chemicals are not persistent. Cyclohexylamine at a concentration of 10 mg/L in water from river mud was found to entirely degrade within 14 days (Calamari et al. 1980). Screening-level QSAR analyses predict that methylcyclohexylamine isomer residues should degrade under environmental conditions, with half-lives ranging from 2 to 15 days in soil (TDS Numerica 1997). If present in surface soil, a vapor pressure of 8.8 mm Hg at 25°C indicates that some volatilization into the atmosphere would occur (Howard 1990). Aliphatic amines in the atmosphere are expected to react with photochemically produced hydroxyl radicals, with a calculated half-life of approximately 2 days for this class of chemicals (Calvert and Pitts 1966). The preponderance of the data therefore indicate that cyclohexylamines are not persistant in the environment.

The chemical properties of the methylcyclohexylamines indicate that there is little tendency for these chemicals to partition into biota, and thus, bioconcentrate or biomagnify. For example, the methylcyclohexylamine isomers in aquatic environments will be in the form of protonated or charged molecules by analogy to cyclohexylamine, which has a reported pKa of 10.66 at 24°C (Howard 1990). The polarity of the chemicals greatly reduces their potential for bioconcentration or biomagnification in aquatic species. For example, the log K_{ow} and BCF of the protonated form of 2-methylcyclohexylamine would be even lower than the estimated log K_{ow} of 1.38 and BCF of 5 (TDS Numerica 1997) of the neutral or uncharged form of the same chemical (Hansch and Leo 1995). USEPA considers BCFs less than 300 as insignificant in aquatic systems (USEPA 1989).

In summary, the methylcyclohexylamine isomers are not expected to be risk-driving chemicals at the site based on the criteria of toxicity, prevalence and persistence, and were therefore not selected for special method development after attempts to include it in the modified CLP method were unsuccessful. During the operation of the facility, the chemicals were not purchased as raw materials, but rather were generated in small amounts as by-products of the TDA/TDI manufacturing process; an analytical method has been developed for TDA, a compound with

greater toxicity. Finally, the preponderance of environmental fate data indicates that the chemicals are not persistent in air, soil, water or biota.

3.0 SCHEDULE

Although Lancaster Laboratories conducted most of the laboratory work involved with the Analytical Method Study, we have chosen IEA to conduct analysis of site samples. Our choice of IEA is based entirely on cost for the upcoming analytical work. IEA is currently practicing the analytical protocols for the six compounds discussed in Section 1 of this letter. As we previously discussed, we request that you review the two enclosed analytical methods and reply within two weeks. Your expedited review will allow us to begin field work on or about the week of June 23, 1997. IEA is also scheduled to begin receiving samples from the site the week of June 23, 1997.

If you have any questions, please call me at 423-336-4576.

Sincerely,
OLIN CORPORATION

Richard W. McClure

Richard W. McClure, PG, REM
Associate Project Coordinator

RWM/ljp

Enclosure (2) (DynCorp methods study reports)

cc (letter only):
Tom O'Brien, Olin
Lorraine Miller, Olin
Bob Higgins, Olin-Moundsville, WV
Jeff Jackson, Rust-Greenville, SC
Dale Skoff, Rust-Wexford, PA
Lorraine Pearsall, WEINBERG-Washington, D.C.

REFERENCES

American Conference of Governmental and Industrial Hygienists (ACGIH). 1996a. Threshold Limit Values for Chemical Substances and Physical Agents. Biological Exposure Indices. Cincinnati, OH: ACGIH.

American Conference of Governmental and Industrial Hygienists (ACGIH). 1996b. Documentation of the Threshold Limit Values and Biological Exposure Indices. Supplements to Sixth Edition. Cincinnati, OH: ACGIH.

Atkinson, R. 1987. Inter. J. Chem. Kinet. 19:799-828. As cited in Environmental Fate Information (HSDB 1997).

Binks, S.P., Smillie, M.V., Glass, D.C., Fletcher, A.C., Shackleton, S., Robertson, A.S., Levy, L.S., and Chipman, J.K. 1992. Occupational Exposure Limits, Criteria Document for Ethanolamine. Commission of the European Communities. Office for Official Publications of the European Communities. Luxembourg.

Bridie, A.L., Wolff, C.J.M., and Winter, M. 1979. BOD and COD of some petrochemicals. Water Res. 13:627-630. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Butler, J.N. 1966. Ionic Equilibrium: A Mathematical Approach. Reading, MA: Addison-Wesley Publishing Company, Inc.

Calamari, D., DaGasso, R., Galassi, S., Privini, A., and Vighi, M. 1980. Biodegradation and toxicity of selected amines on aquatic organisms. Chemosphere. 9:753-762.

Calvert, J.G. and Pitts, J.N., Jr. 1966. Photochemistry. New York: John Wiley & Sons. Pp. 899. As cited in Environmental Fate Information (HSDB 1997).

Christensen, H.E. and T.T. Luginbyhl. 1975. Registry of Toxic Effects of Chemical Substances. U.S. Department of Health, Education, and Welfare. As cited in Calamari et al. (1980).

Dow Chemical Company. 1980. The Alkanolamines Handbook. Midland, MI: Dow Chemical Co. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Eisenreich, S.J. et al. 1981. Environ. Sci. Technol. 15:30-38. As cited in Environmental Fate Information (HSDB 1997).

Emtiazi, G., and Knapp, J.S. 1994. The biodegradation of piperazaine and structurally-related linear and cyclic amines. Biodegradation 5:83-92.

Mills, E.J., Jr. and Stack, V.T., Jr. 1954. Biological oxidation of synthetic organic chemicals. Proceedings of 8th Industrial Waste Conference, Eng. Bull., at Purdue University. Eng. Ext. Ser. Pp. 492-517. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Oser, B.L., Carson, S., Cox, G.E., et al. 1976. Long-term and multi-generation toxicity studies with cyclohexylamine hydrochloride. Toxicol. 6:47-65. As cited in ACGIH 1996b.

Patty's Industrial Hygiene and Toxicology (Patty's). 1981. 3rd Edition. Vol. 2B. New York: Wiley-Interscience. As cited in Environmental Fate Information (HSDB 1997).

Registry for Toxic Effects of Chemical Substances (RTECS). 1997. National Institutes of Occupational Safety and Health (NIOSH). National Library of Medicine, Bethesda, MD.

Rust Environment & Infrastructure (RUST). 1996. Engineering Evaluation/Cost Analysis (EE/CA) Work Plan. May.

Sasaki, S. 1978. The scientific aspects of the chemical substance control law in Japan. In Hutzinger, O., Von Letyoeld, L.H., and Zoeteman, B.C.J. (eds.). Aquatic Pollutants: Transformation and Biological Effects. Oxford: Pergamon Press. Pp. 283-298. As cited in the Hazardous Substance Data Base (TDS Numerica 1997).

Shukla, S.D. and Turner, J.M. 1980. Microbial metabolism of amino alcohols. Biochem. J. 186:13-9. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Technical Database Services (TDS) Numerica. 1997. New York, NY.

U.S. Environmental Protection Agency (USEPA). 1996. Risk-Based Concentration Table. USEPA Region III, Technical and Program Support Branch. Philadelphia, PA.

U.S. Environmental Protection Agency (USEPA). 1989. Risk Assessment Guidance for Superfund Volume II: Environmental Evaluation Manual. Interim Final. EPA/540/1-89/001.

Young, R.H.F., Ryckman, D.W., and Buzzell, J.C., Jr. 1968. An improved tool for measuring biodegradability. J. Water Pollut. Contr. Fed. 40:354-368. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Gallagher, J.R., Thompson, J.S., Sorenson, J.A., and Schmit, C.R. 1996. An Assessment of the Subsurface Fate of Monoethanolamine at Sour Gas Processing Plant Sites - Phase I Report. Grand Forks: Energy & Environmental Research Center, University of North Dakota.

Gaunt, I.F., Hardy, J., Grasso, P. et al. 1976. Long-term toxicity of cyclohexylamine hydrochloride in the rat. Food Cosmet. Toxicol. 14:255-267. As cited in ACGIH 1996b.

Hansch, C. and Leo, A. 1995. Exploring QSAR: Fundamentals and Applications in Chemistry and Biology. Washington, DC: American Chemical Society.

Hansch, C. and Leo, A. 1985. MedChem Project. Claremont, CA: Pomona College. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Hardy, J., Gaunt, I.F., Hoosen, J., et al. 1976. Long-term toxicity of cyclohexylamine hydrochloride in mice. Food Cosmet. Toxicol. 14:269-276. As cited in ACGIH 1996b.

Hazardous Substance Data Bank (HSDB). 1997. National Library of Medicine, Bethesda, MD.

Howard, P.H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Vol. II. Solvents. Chelsea, MI: Lewis Publishers.

Kawaski, M. 1980. Experiences with the test scheme under the chemical control law of Japan: An approach to structure-activity correlations. Ecotoxic. Environ. Safety 4:444-454. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Kitano, M. 1978. Biodegradation and bioaccumulation test on chemical substances. OECD Tokyo Meeting. Reference Book TSU-No. 3. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Klain, G.J., et al. 1985. Fundam. Appl. Toxicol. 5(6, Pt. 2):S127-S133. As cited in the Hazardous Substance Data Bank (HSDB 1997).

Lamb, C.B. and Jenkins, G.F. 1952. BOD of synthetic organic chemical. Proceedings of 8th Industrial Waste Conference at Purdue University. Pp. 326-329. As cited in the Environmental Fate Data Base (TDS Numerica 1997).

Merck Index, The. 1989. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals. Eleventh Edition. Rahway, NJ: Merck & Co., Inc.

Meyer, F.P. and Barclay, L.A. 1990. Manual on the Investigation of Fish Kills. U.S. Department of the Interior. Resource Publication #177.

Compound	Water Mean Recovery		Water Method Detection Limit		Soil/Sediment Mean Recovery	
	Laboratory A	Laboratory B	Laboratory A	Laboratory B	Laboratory A	Laboratory B
3-Methylcyclohexanone	–	95.3	–	2.4	–	100.0
4-Methylcyclohexanone	89.7	105.9	1.2	3.0	99.0	104.0
4,4'-Methylene dianiline	65.2	68.3	1.8	6.3	17.8	30.0
2,6-Dinitrophenol	11.5	61.8	3.1	7.7	157.7	161.0
Aniline	69.5	67.8	2.3	2.9	110.6	39.0
O-Toluidine	71.5	74.3	1.1	3.1	53.6	35.0
Monoethanolamine [1]	–	–	–	–	–	–
Methylcyclohexylamine [1]	0.2 3.4 1.5	17.1	0.1 1.3 0.6	3.9	–	6.7
2,4-Toluenediamine [1]	49.9	11.6[2]	1.9	3.5[2]	3.1	9.1[2]
2,6-Toluenediamine [1]	52.5		1.9		3.1	

RPD

[1] These compounds are not amenable to analysis by this method.
[2] Reported as total (i.e., unresolved isomers).

The validation study indicated that MEA, the methycyclohexylamine isomers and the TDA isomers were very difficult to analyze. These chemicals exhibited very poor or nonexistent recoveries in water and soil/sediment with the modified CLP method. While MDA exhibited reasonable recoveries in water, recoveries were poor in soil.

The decision to include or exclude chemicals from further method development at this stage of the process was based upon an evaluation of toxicity, environmental persistence, and the likelihood of a chemical to be prevalent on the Olin property. The classification of a chemical as a possible human carcinogen by USEPA or the International Agency for Research on Cancer (IARC) was considered a sufficient reason to pursue further method development. USEPA has classified 2,4-TDA as a probable (B2) carcinogen, and IARC has classified MDA as a possible (2B) human carcinogen. The TDA isomers (2,4- and 2,6-TDA) and MDA were therefore selected as candidates for further method development. The 2,6-TDA isomer, a noncarcinogen, was included because resolution of this isomer from the 2,4-TDA isomer is important.

1.2 Soil and Water Extraction Method with High-Volume Injection GC/MS

Lancaster Laboratories developed a high volume injection GC/MS method for analyzing 2,4-TDA, 2,6-TDA and MDA in soil and water. This method, entitled **"Determination of 2,4-Diaminotoluene, 2,6-Diaminotoluene, and 4,4'Methylenedianiline in Water by Solid-Phase Extraction (SPE) and Soil by Accelerated Solvent Extraction (ASE) using High-Volume Injection Gas Chromatography-Mass Spectrometry (HVI/GC/MS)"** is enclosed with this letter for USEPA review and comment.

The method involves a specialized extraction for both soil and water. Analytes are separated from a water matrix by passing the sample through a cartridge containing a copolymer. The copolymer is then extracted with solvent (solid-phase extraction or SPE) and analyzed by GC/MS. Soil samples are extracted using the accelerated solvent extractor (ASE) under elevated temperature and pressure.

The use of the SPE for waters and ASE for soils with HVI/GC/MS yielded generally lower water method detection limits and higher mean recovery values for all three compounds when compared to the values obtained using the modified CLP method as can be seen in Table 2 below. The recovery of MDA in water using the SPE extraction method with HVI/GC/MS was comparable to the recoveries obtained with the modified CLP method, but the detection limits were lower with the HVI/GC/MS method.

Table 2

Water Method Detection Limits		
Compound	SPE-HVI/GC/MS Method	Modified OLM03.2
2,4-Diaminotoluene	0.37	1.913
2,6-Diaminotoluene	0.38	1.881
4,4'-Methylenedianiline	0.62	1.852

Average Percent Recoveries				
Compound	Water		Soil/Sediment	
	Solid Phase Extraction	Modified OLM03.2 Method	Accelerated Solvent Extraction	Modified OLM03.2 Method
2,4-Diaminotoluene	69%	49.9%	73%	3.1%
2,6-Diaminotoluene	77%	52.5%	51%	3.1%
4,4'-Methylenedianiline	61%	65.2%	93%	17.9%

culled from the list of participating laboratories upon review of the survey responses. These five labs were closely evaluated on their ability to develop a modified Contract Laboratory Program (CLP) method that would address isomer resolution, chemical recovery and detection limits for all the chemicals of interest in both a soil and water matrix. They were also evaluated with respect to their quality assurance plan, standard operating procedures and previous experience with method development. The final evaluation resulted in the selection of two laboratories for an actual method validation study of the nontarget chemicals: Lancaster Laboratories of Pennsylvania (Laboratory A) and Centre Analytical Laboratories (Laboratory B).

The primary goal of the validation study was to determine whether CLP Method OLM03.2 for the analysis of semivolatile compounds in soil and water by gas chromatography/mass spectrometry (GC/MS) could be used for the nontarget chemicals. Use of the existing CLP method was the most desirable situation because laboratories efficiently work with established procedures. A second goal of the study was to develop, if necessary, a different analytical method for those chemicals that are not amenable to the modified OLM03.2 and are believed to be of potential concern with respect to human health and the environment.

1.1 Modified Contract Laboratory Method OLM03.2 for Semivolatiles

The validation study revealed that most of the nontarget chemicals are amenable to analysis with the existing CLP method for semivolatiles. Aniline, 2,6-dinitrophenol, diphenyl, o-toluidine and 2-, 3-, and 4-methylcyclohexanone were extracted with reasonable recoveries from both soil/sediment and water matrices as shown in Table 1 below. MDA demonstrated reasonable recoveries in water, but relatively low recoveries in soil/sediment. A modified CLP Method OLM03.2 incorporating the cyclohexanone isomers, MDA, diphenyl, 2,6-dinitrophenol, aniline, and o-toluidine as additional compounds was developed by DynCorp. The method, entitled **"Analysis of Semivolatile Compounds in Soil and Water for Olin Corporation's Moundsville Project"** is provided with this letter for USEPA review and comment.

Table 1
Mean Recoveries and Method Detection Limits

Compound	Water				Soil/Sediment	
	Mean Recovery		Method Detection Limit		Mean Recovery	
	Laboratory A	Laboratory B	Laboratory A	Laboratory B	Laboratory A	Laboratory B
Diphenyl	84.8	81.7	1.1	1.2	95.9	83.0
2-Methylcyclohexanone	71.3	71.8	0.9	1.9	76.9	74.0

Determination of 2,4-Diaminotoluene, 2,6-Diaminotoluene, and 4,4'-Methylenedianiline in Water by Solid-Phase Extraction (SPE) and Soil by Accelerated Solvent Extraction using High-Volume Injection Gas Chromatography-Mass Spectrometry (HVI/GC/MS)

Scope:

This method is suitable for the determination of 2,4-diaminotoluene, 2,6-diaminotoluene, and 4,4'-methylenedianiline at low ppb levels found in groundwater or surface waters and soil samples. Conditions such as high levels of organic compounds may interfere with normal detection limits.

Compound	CAS Number	EQL[1] (µg/L)
2,4 -diaminotoluene	95-80-7	2
2,6-diaminotoluene	823-40-5	2
4,4'-methylenedianiline	101-77-9	3
1-nitronaphthalene*	86-57-7	

Basic Principles:

The analytes and surrogate are extracted from a water sample by passing the sample through a solid-phase cartridge containing 500 mg of divinylbenzene/vinylpyrrolidone copolymer. The disk is eluted with 15 mL of 1:1

1 = Estimated Quantitation Limits. Values based on single laboratory method detection limit study performed on water.

* = surrogate standard

ethyl acetate/methylene chloride. Soil samples are extracted using the accelerated solvent extractor (ASE) at 50°C and 1500 psi using methylene chloride and a basic modifier (1,6-hexanediamine in methanol). After drying through sodium sulfate, the solvent is then evaporated to 1.0 mL to concentrate the analytes. The diaminotoluene isomers and 4,4'-methylenedianiline are separated by narrow-bore capillary gas chromatography and can be identified by their retention times and differences in their mass spectra. Quantification is performed using an internal standard calibration.

Sample Collection and Storage:

Water samples should be collected in 1-L amber glass bottles and stored at 4° ± 2°C. Soils should be collected in 8-oz wide-mouth glass jars and stored at 4° ± 2°C. Water samples must be extracted within 7 days of sample collection. Soil samples must be extracted within 14 days of sample collection. All extracts must be analyzed within 40 days of sample extraction.

Apparatus:

1. Hewlett-Packard Model 5890 gas chromatograph or equivalent
2. Hewlett-Packard Model 5971 mass selective detector or equivalent
3. Pro Sep 800 High Volume Injector - Apex Technologies, Inc. (Cincinnati, OH)
4. Water extraction apparatus - SPE vacuum manifold
5. Accelerated solvent extractor (ASE 200) or equivalent, Dionex Corp., Sunnydale, CA
6. Sodium sulfate column and graduated ampule for concentration
7. 70-mL SPE sample reservoirs

8. 11-mL stainless steel extraction vessels or equivalent, Dionex Corp.

9. ASE circle filter discs, 1.91 cm, Dionex Corp., P/N 049458

Reagents and Consumable Materials:

1. Waters Porapak® R_{DX} (500 mg divinylbenzene/vinylpyrrolidone) sep-pak cartridge (Waters PN WAT047220)

2. Reagent Ottawa sand, EM Science or equivalent

3. Methylene chloride, Baker Ultra Resi-Analyzed or equivalent

4. Ethyl acetate, Baker Ultra Resi-Analyzed or equivalent

5. Acetonitrile, Baker Ultra Resi-Analyzed or equivalent

6. Methanol, Baker Instra-Analyzed or equivalent

7. Sodium sulfate, Fisher or equivalent - Prepared by baking at 400°C for 4 hours prior to use to remove contaminants.

8. Potassium phosphate dibasic (K_2HPO_4), Baker Analyzed or equivalent

9. Phosphoric acid 85%, Fisher or equivalent

10. 1,6-Hexanediamine, Sigma Chemical or equivalent

11. Phosphate buffer (2 M) - Dissolve 34.82 g of K_2HPO_4 in reagent water and dilute to a final volume of 1 L in a volumetric flask. Adjust to pH 7.0 with phosphoric acid (85%).

12. Soil extraction fluid - Dissolve 5 g of 1,6-hexanediamine in methanol and dilute to 100 mL in methanol. Transfer to a 2-L volumetric flask and dilute to volume with methylene chloride.

Preparation of Standards:

1. Combined stock standard (1000 µg/mL) - Weigh 25.0 ± 0.1 mg of each 2,4-diaminotoluene, 2,6-diaminotoluene, and 4,4'-methylenedianiline into a 25-mL volumetric flask and dilute to volume with methanol. Store in a freezer at -15°C. Remake every 3 months.

2. Surrogate stock standard (1000 µg/mL) - Weigh 25.0 ± 0.1 mg of 1-nitronaphthalene into a 25-mL volumetric flask and dilute to volume with methanol. Store in a freezer at -15°C. Remake every 3 months.

3. Intermediate combined standard (100 µg/mL) - Place 5.0 mL of the combined stock standard into a 50-mL volumetric flask and dilute to volume with methanol. Store in a freezer at -15°C. Remake every 3 months.

4. Intermediate surrogate standard (100 µg/mL) - Place 5.0 mL of the surrogate stock standard into a 50-mL volumetric flask and dilute to volume with methanol. Store in a freezer at -15°C. Remake every 3 months.

5. Spiking solution (analyte at 10 µg/mL and surrogate at 5 µg/mL) - Place 5.0 mL of the intermediate combined standard and 2.5 mL of the intermediate surrogate standard into a 50-mL volumetric flask and dilute to volume with methanol. Store in a freezer at -15°C. Adding 1.0 mL of this methanolic solution to 100 mL of water will produce analyte concentrations of approximately 0.1 µg/mL and a surrogate concentration of 0.05 µg/mL. Replace monthly.

6. Surrogate spiking solution (5 µg/mL) - Place 5.0 mL of the intermediate surrogate standard into a 100-mL volumetric and dilute to volume with methanol. Store in a freezer at -15°C. Replace monthly.

7. Calibration standards - Prepare the appropriate five levels of standards (see below) by diluting the intermediate combined standard and the intermediate surrogate standard appropriately in ethyl acetate. Store in a refrigerator at 4°C. Replace weekly.

Preparation of Glassware:

All glassware is rinsed with tap water and soaked in dilute Chem-Solv for a minimum of 2 hours. The glassware is then rinsed with warm tap water followed by deionized water and baked in a drying oven for at least 1 hour or until dry.

Safety Precautions:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available, such as fume hoods, lab coats, and gloves.

Water Extraction Procedure:

1. Set up the SPE vacuum manifold and position the R_{DX} cartridges on the manifold. Normally, the vacuum is not required to condition the cartridges or load the samples.

2. Condition each cartridge with approximately 10 mL of acetonitrile (ACN). After allowing the ACN to soak into the resin for several minutes, allow the ACN to drip through the cartridge until the solvent reaches the top of the resin bed. Stop the flow.

3. Continue to condition each cartridge with 10 mL of deionized water. Allow the water to drip through the cartridge until the water reaches the top of the resin bed. Stop the flow.

4. After agitating the sample, measure 100 mL of sample into a 100-mL volumetric flask . Add 1 mL of the 5 µg/mL methanolic solution of the 1-nitronaphthalene surrogate standard and, if required, the matrix spiking solution. Add 2.5 mL of the phosphate buffer and mix.

5. Add the water sample to the sep-pak cartridge and attach the sample reservoir. Fill the sample reservoir with the water sample and allow the sample to gravity feed through the cartridge at a fast drip rate (ca. 10 mL/min). After the sample has completely passed through the cartridge, turn on the vacuum (ca. 20 psi) and pull air through the cartridges for 15 minutes. After drying the cartridges, turn off the vacuum.

6. Remove the reservoirs and the manifold head which holds the sep-pak cartridges. Insert the collection vessels (25 × 100 mm glass test tubes).

7. Elute the cartridges with 15 mL of 1:1 ethyl acetate/methylene chloride using a steady drip under gravity.

8. Pour the eluent through a sodium sulfate column containing approximately 2 cm of sodium sulfate. Rinse the collection vessel and the sodium sulfate column with two 3-mL aliquots of 1:1 ethyl acetate:methylene chloride. Collect the extract and rinses in a 24-mL ampule.

9. Concentrate the extract using an N-Evap with a bath temperature of about 35°C until the volume reaches just below 1 mL.

10. Bring the volume to 1.0 mL with ethyl acetate. Place the extract into an amber autosampler vial. Cap securely and store at 4° ± 2°C.

Soil Extraction Procedure:

1. Decant and discard any water layer on a sediment sample. Mix samples thoroughly. Discard any foreign objects such as sticks, leaves, and rocks.

2. Place the end cap on the exit end of the 11-mL ASE stainless steel extraction cell. Using the tamping rod, push a circle filter disk to the bottom of the exit side of the cell and cover the disk with a layer of Ottawa reagent sand (approximately 0.5 cm in depth).

3. Weigh 5 to 10 g of soil (weighed to the nearest 0.01 g) directly in the ASE stainless steel extraction cell. Soil samples which contain high levels of water and are not free flowing should be weighed in a weighing dish and mixed with an equal weight of sodium sulfate prior to placing in the extraction cell.

4. Add 1.0 mL of the surrogate spiking solution (5 µg/mL 1-nitronaphthalene in methanol) to the top of the soil in the extraction cell. Also add 1.0 mL of the spiking solution to the matrix spikes and the laboratory control sample(s). Use Ottawa sand for laboratory control samples.

5. After filling any void volume in the extraction cell with sand, screw the top end cap onto the 11-mL ASE stainless steel extraction cell. Make sure both ends are securely tightened.

6. Load the extraction cells on the top carousel of the ASE with the exit end (side with the filter paper) down.

7. Place labeled 40-mL collection vials in the appropriate locations on the lower carousel of the ASE.

8. Extract each cell on the ASE under the following conditions:

Temperature	50°C
Pressure	1500 psi
Static time	5 minutes
Flush volume	60%
Purge time	60 seconds
Cycles	3
Extraction fluid	Approx. 20 mL of 95/5 v/v methylene chloride/5% 1,6-hexanediamine in methanol

9. After the extraction has been completed, check that each collection vial contains 15 to 20 mL of extraction fluid. A low volume may indicate a malfunction of the ASE during the extraction.

10. Pour the extract through a sodium sulfate column containing about 2 cm of sodium sulfate. Rinse the collection vial and the column with two 3-mL aliquots of methylene chloride. Collect the extract and the rinses in an ampule.

11. Concentrate the extract using an N-evap with a bath temperature of 35°C until volume reaches about 1 mL.

12. Dilute to an appropriate final volume with ethyl acetate if high concentrations of analytes are known to be present in the soil or reconcentrate to a final volume of 1.0 mL on the N-evap. Place the extract (1.0 mL) in an amber autosampler vial. Cap securely and store at 4° ± 2°C.

Percent Moisture Determination

1. Immediately after weighing the sample for extraction, weigh 5 - 10 g of the soil into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a dessicator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of soil.

$$\% \text{ Moisture} = \frac{\text{grams of wet sample} - \text{grams of dry sample}}{\text{grams of wet sample}} \times 100$$

Instrumental Conditions:

Below are the recommended operating conditions for the Pro Sep 800 High-Volume Injector, the HP 5890 GC, and the HP 5971 MSD.

1. Pro Sep 800 High-Volume Injector
   Precolumn - MIDI II 240 x 2 mm ID coated with HT-5 phase
   Pro Sep temperature program - Start at 90°C and hold for 0.2 minutes; Ramp at 300°C/min to 300°C, hold for 26 minutes
   He flow through injector - 100 mL/min

2. HP 5890 GC

Injector temperature	260°C
Injection volume	5 µL
Split valve program	Open at 0.00 min, close at 0.05 min and open at 3.0 min.

Capillary column	Rt_x-200 (trifluoropropylmethylpoly-siloxane) 30 m × 0.25 mm; df 0.25 mm
Oven temperature	50°C for 3 minutes; ramp at 20°C/min to 120°C; hold 1 min; ramp at 3°C/min to 154°C; ramp at 30°C/min to 300°C and hold 5 min.
Run time	28.70 minutes
Carrier gas	Helium at 1.0 mL/min constant flow

3. HP 5971 MSD

Tune	USEPA DFTPP criteria
Scan range	50 to 550 amu
Scan rate	2.2 scan/sec
Threshold	50

Initial Calibration:

1. Tune the GC/MS system with a suitable calibrant to meet the manufacturer's specifications. The mass calibration and resolution of the GC/MS system should be verified every 12 hours with the injection of 25 ng of DFTPP. The GC/MS system should meet the USEPA mass spectral ion abundance criteria for DFTPP specified below.

   A single spectrum or an average spectrum across the DFTPP peak may be used to evaluate the performance of the system. If the DFTPP does not meet the criteria in Table I, the MSD must be retuned prior to calibrating the system.

Table I
DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30% to 60% of mass 198
68	<2% of mass 69
69	mass 69 relative abundance
70	<2% of mass 69
127	40% to 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5% to 9% of mass 198
275	10% to 30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	40% to 100% of mass 198
443	17% to 23% of mass 442

2. Inject the following five levels of calibration standards using a constant injection volume ranging from 5 to 50 µL.

	Analyte Conc. µg/mL	Surrogate Std. Conc. (1-nitronaphthalene) µg/mL	Internal Std. Conc. (phenanthrene-d10) µg/mL
Level 1	0.50	5.0	5.0
Level 2	1.0	5.0	5.0
Level 3	2.0	5.0	5.0
Level 4	5.0	5.0	5.0
Level 5	10.0	5.0	5.0

3. Using the Level 4 standard, verify GC performance and separation of the diaminotoluene isomers on the Rt_x-200 column. The valley between the 2,6 and 2,4 isomers must be <25% of the average of the two peak heights of the isomers. See Figure 2 as an example on how to determine this resolution.

4. Calculate a response factor (RF) for each analyte of interest and surrogate for each level using phenanthrene-d10 as the internal standard.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

Where:

A_x = Integrated abundance of the quantitation ion of the analyte

A_{is} = Integrated abundance of the quantitation ion internal standard

Q_x = Quantity of analyte injected in ng or concentration units

Q_{is} = Quantity of internal standard injected in ng or concentration units

For each analyte and surrogate, calculate the mean RF (M) from the analyses of the five calibration solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 x (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, take action to improve GC/MS performance or, as an alternative to calculating mean response factors, use the GC/MS data system software or other available software to generate a linear regression calibration curve. An acceptable correlation coefficient of the curve will be 0.99.

Table II shows the quantitation and qualifier ions for each of the analytes:

Table II
Target and Qualifier Ions

Analyte	Quantitation Ion	Qualifier
2,6-Diaminotoluene	122.	121, 104, 94
2,4-Diaminotoluene	121	122, 104, 94
4,4-Methylenedianiline	198	197, 182, 106
1-Nitronaphthalene (SS)	115	127, 173, 101
Phenanthrene-d10	188	187, 160, 80

A spectrum for each analyte and the surrogate standard is shown in Figure 1.

Continuing Calibration:

Verify the initial calibration by injecting the Level 3, 2.0-µg/mL standard every 12-hour period or after every ten sample injections.

Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear regression is used, the calculated amount for each analyte must be ±30% of

the true value. If these conditions do not exist, corrective action should be taken which may require recalibration.

Sample Analysis:

After adding the internal standard, phenanthrene-d10 (10 µL of 500 ng/µL to 1.0 mL extract), inject an aliquot of the extract (the same volume) under the same GC/MS conditions as used in the initial and continuing calibrations.

Identification of Analytes:

Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time of the sample component should be within 0.05 minutes of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10% to 50%. Some ions, particularly the molecular ion, are of special importance and should be evaluated even if they are below 10% relative abundance.

Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

The 2,4- and 2,6-diamintoluene isomers have similar mass spectra but can be identified by the differences in the abundances of the 121, 122 ions. The 2,6-isomer has mass 122 as the quantitation ion with an abundance of 100% and 121 as a qualifier ion with a relative abundance of approximately 60%. The 2,4-isomer, which elutes after the 2,6-isomer, has 121 as the most abundant ion (100% relative abundance) and 122 at relative abundance of approximately 90%.

Acceptable resolution can also be achieved using the Rt_x-200 narrow-bore column, where the height of the valley between the two isomer peaks is <25% the average of the height of the two peaks.

Data Analysis and Calculations:

Calculate analyte and surrogate concentrations in water samples:

$$C_x = \frac{(A_x)\,(Q_{is})\,(Df)\,(V_f)}{(A_{is})\,RF\,(V_o)}$$

Where:

C_x = Concentration of analyte or surrogate in µg/L in the water sample

A_x = Integrated abundance of the quantitation ion of the analyte in the sample

A_{is} = Integrated abundance of the quantitation ion of the internal standard in the sample

Q_{is} = Concentration of internal standard added to the water sample in µg/mL

V_o = Original water sample volume in liters

V_f = Final extract volume in mL

RF = Mean response factor of analyte from the initial calibration

Df = Dilution Factor

Calculate analyte and surrogate concentrations in soil samples:

$$Cx = \frac{(Ax)\ (Qis)\ (Df)\ (V_f)}{(Ais)\ RF\ (Ws)\ D}$$

Where:

A_x, A_{is}, Q_{is} and V_f are as given for water above.

C_x = Concentration of analyte (dry weight basis) or surrogate in µg/g in the soil sample

W_s = Original soil sample weight in grams

RF = Mean response factor of analyte from the initial calibration

Df = Dilution Factor

$$D = \frac{100 - \%\ \text{moisture}}{100}$$

Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression curves.

Method Performance:

Single laboratory accuracy and data for water using the method are shown in Table III. Quadruplicate spiking studies were performed on laboratory reagent water and a background water sample taken from the site.

Table IV shows a method detection limit study conducted on laboratory reagent water and provides a calculation for the LOQ of the method.

Single laboratory accuracy and data for soil using the method are shown in Table V. Quadruplicate spiking studies were performed on laboratory reagent sand. Preliminary recovery studies on background soil taken from the site indicate high levels of organics which enhanced recoveries of the analytes when compared to a clean top soil.

Quality Assurance:

For each batch of samples, a laboratory reagent blank (LRB), a matrix spike, a matrix spike duplicate, and a laboratory fortified blank (LFB) (deionized water blank spiked with all compounds to be determined carried through the entire procedure) must be extracted. A batch is defined as the samples to be extracted within a 12-hour period, but not to exceed 20 samples. If more than 20 samples are set up, an additional LRB, spike, spike duplicate, and LFB must be prepared.

Technical Acceptance Criteria:

The following acceptance criteria were established based on single laboratory performance and are advisory.

The laboratory reagent blank must contain less than the estimated limit of quantitation in water for each target analyte.

Matrix Spike and
Surrogate Recovery Limits

Compound	% Recovery Water[2]	% Recovery Soil
2,6-Diaminotoluene	44 - 80	46 - 56
2,4-Diaminotoluene	39 - 65	68 - 78
4,4'-Methylenedianiline	49 - 91	92 - 94
1- Nitronaphthalene	78 - 97	67 - 70

Pollution Prevention:

This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

For information about pollution prevention that may be applicable to laboratory operations, 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 Street NW, Washington, DC, 20036.

Waste Management:

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste

---

[2] Limits established based on single laboratory method performance. All limits are advisory.

identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, also available from the American Chemical Society at the address in Section 14.2.

Revision Log:

Initiated Date: DATE

Ver. #	Effective Date	Change
00		

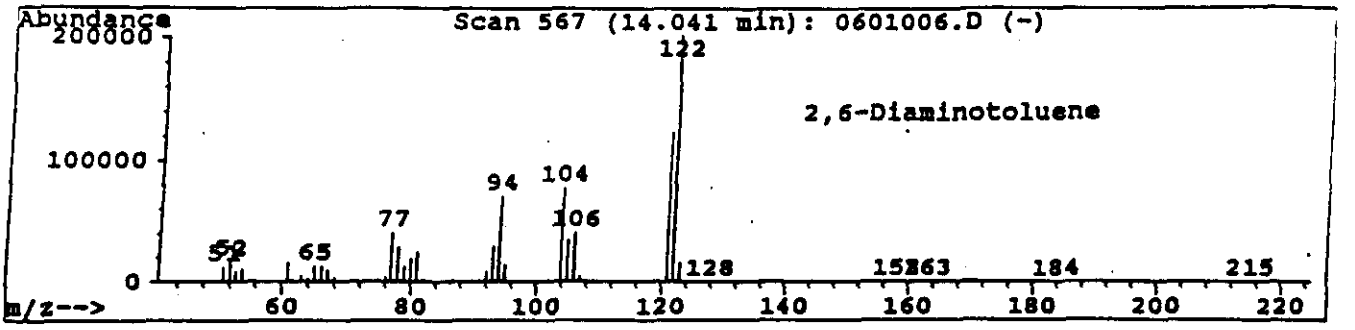
DOCID.DOC
MMDDYY

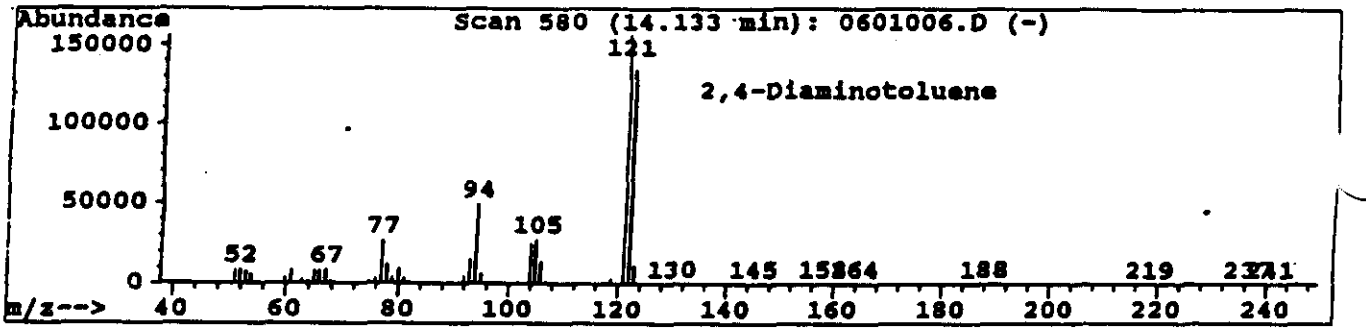
Prepared by: _____ Date: _____

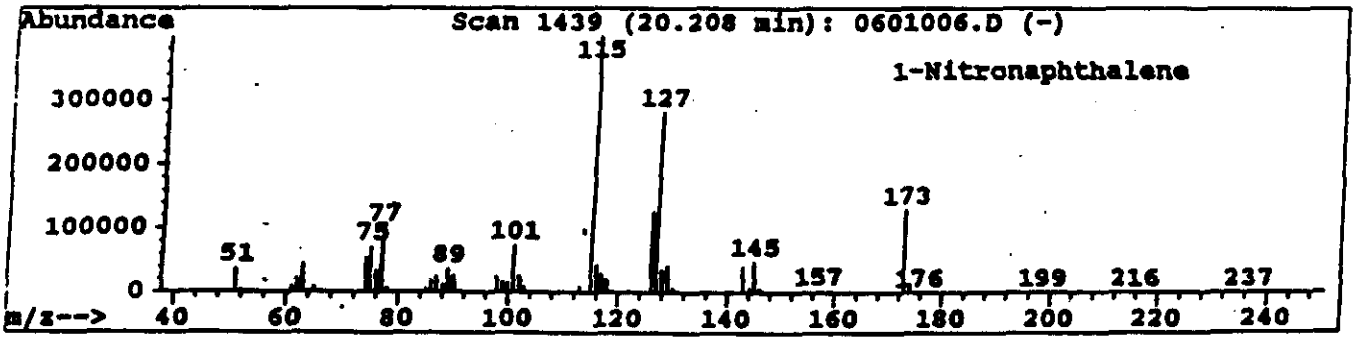
Approved by: _____ Date: _____

Approved by: _____ Date: _____

Figure 1. Spectra of Analytes and Surrogate Standard







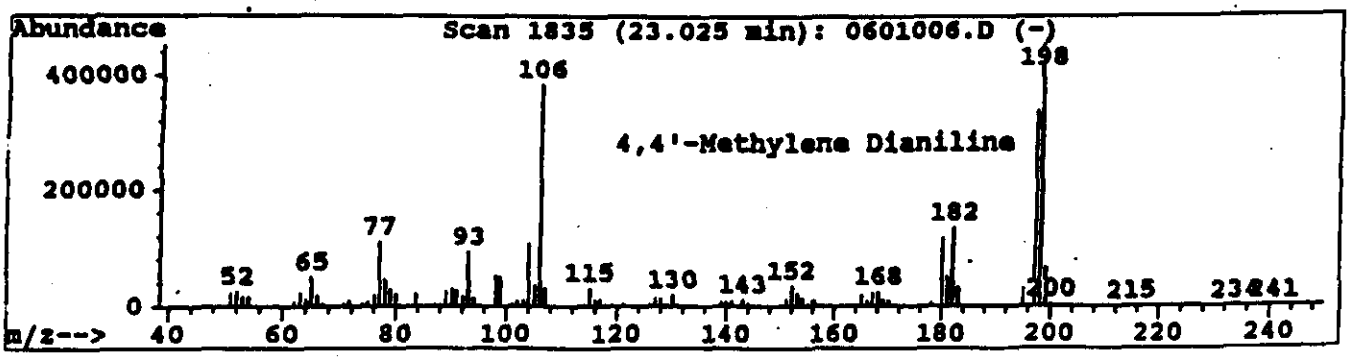


Figure 2. Resolution Check for 2,6 and 2,4-diaminotoluene

```
File        : C:\HPCHEM\1\DATA\APR20\0601006.D
Operator    :
Acquired    : 20 Apr 97    4:35 pm using AcqMethod DAMT
Instrument :    5971JLS
Sample Name: STD 5.0 UG/ML IN ETHYL ACETATE
Misc Info   :
Vial Number: 6
```

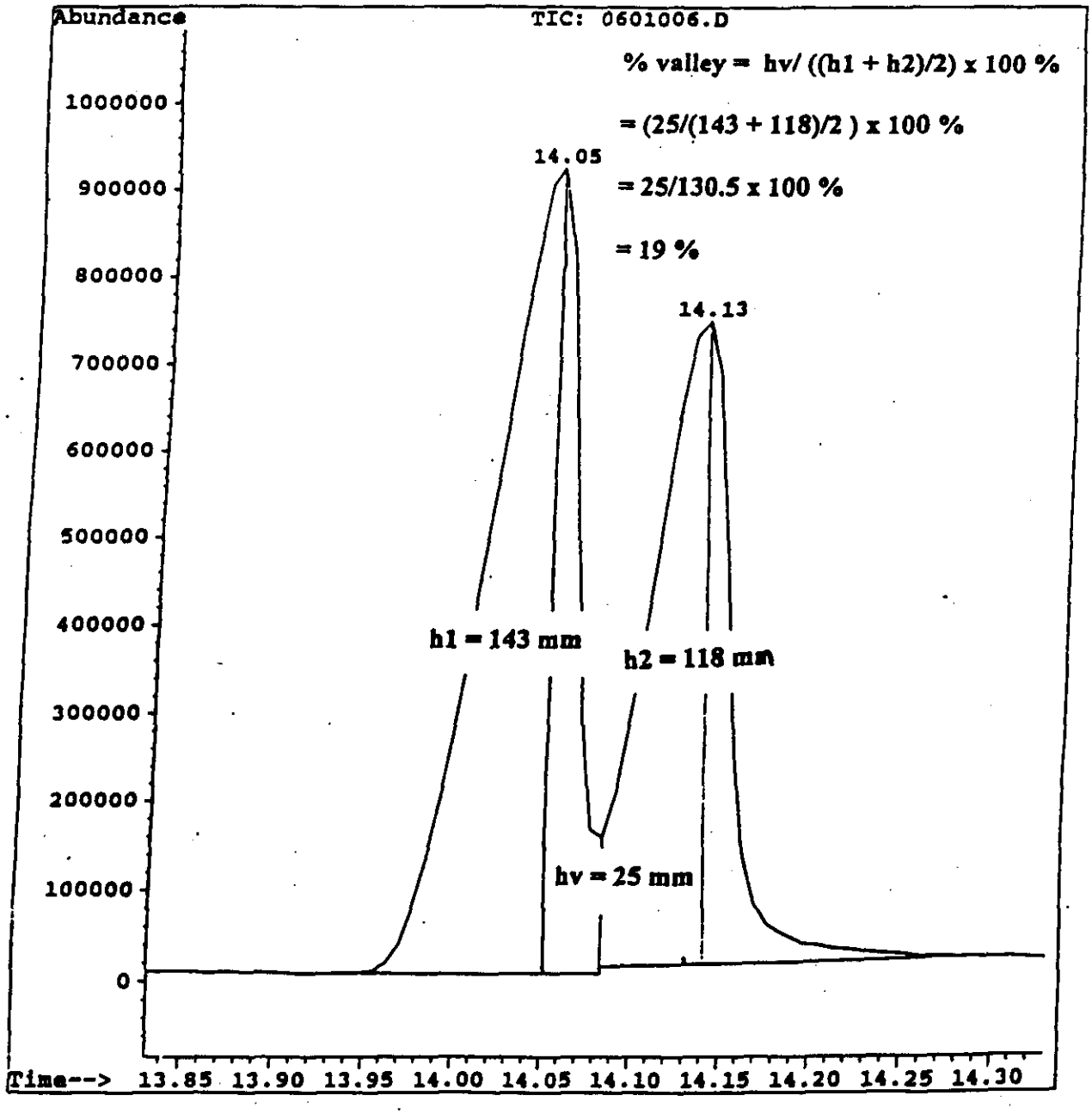


Table III. Quad Study - Solid Phase Extraction of Water

500 mg Waters RDX (divinylbenzene/vinylpyrrolidone copolymer) Porapak Cartridges
Extracted 4/16/97

DI Water -100 mL spiked at 100 ug/L

Compound	Method Blank ug/L	Spike Added ug/L	SPIKE 1 Found ug/L	SPIKE 1 Rec	SPIKE 2 Found ug/L	SPIKE 2 Rec	SPIKE 3 Found ug/L	SPIKE 3 Rec	SPIKE 4 Found ug/L	SPIKE 4 Rec	Ave Rec	RSD
2,6-Diaminotoluene	nd	104	83.4	80%	82.1	79%	69.3	67%	87.3	84%	77%	9.7%
2,4-Diaminotoluene	nd	106	75.8	72%	74.2	70%	63.5	60%	80.5	76%	69%	9.8%
4,4'-Methylene Dianiline	nd	100	64.6	65%	52.9	53%	63.3	63%	64.7	65%	61%	9.3%
1- Nitronaphthalene SS	44.2	51.9	45.2	87%	43.2	83%	38.3	74%	47.7	92%	84%	9.1%

Site Water Sample - 100 mL spiked at 100 ug/L

	Bckgrd Sample ug/L	Spike Added ug/L	Matrix Spike #1 Found ug/L	Matrix Spike #1 Rec	Matrix Spike #2 Found ug/L	Matrix Spike #2 Rec	Matrix Spike #3 Found ug/L	Matrix Spike #3 Rec	Matrix Spike #4 Found ug/L	Matrix Spike #4 Rec	Ave Rec	RSD
2,6-Diaminotoluene	nd	104	75.4	73%	67.3	65%	66.1	64%	48.0	46%	62%	18.0%
2,4-Diaminotoluene	nd	106	64.7	61%	56.8	54%	55.7	53%	45.0	42%	52%	14.6%
4,4'-Methylene Dianiline	0.7	100	89.2	89%	69.5	70%	62.6	63%	60.3	60%	70%	18.6%
1- Nitronaphthalene SS	47.4	51.9	50.5	97%	48.9	94%	47.1	91%	37.3	72%	89%	12.9%

Data Files:

DI water		Site Water	
Apr16\		Apr16\	
Blank	0901026.d	Bckgrd	1401032.d
Spike 1	1001027.d	MS1	1501033.d
Spike 2	1101028.d	MS2	1601034.d
Spike 3	1201029.d	MS3	1701035.d
Spike 4	1301030.d	MS4	2601046.d

Conducted 4/16/97 JLS/021

Inj 4/16/96 5 ul

Analysis #
Revision 1.0
Supersedes Date: N/A
Effective Date: May 1997

Table IV. Water MDL Study

500 mg Waters RDX (divinylbenzene/vinylpyrrolidone copolymer) Porapak Cartridges
Extracted 4/16/97

DI Water -100 mL spiked at 1 ug/L

Compound	Method Blank ug/L	Spike Added ug/L	MDL 1 Found ug/L	MDL 2 Found ug/L	MDL 3 Found ug/L	MDL 4 Found ug/L	MDL 5 Found ug/L	MDL 6 Found ug/L	MDL 7 Found ug/L	Ave Rec.	STD DEV ug/L	MDL ug/L	LOQ ug/L
2,6-Diaminotoluene	nd	1.04	0.33	0.17	0.25	0.43	0.16	0.13	0.08	21%	0.12	0.38	1.91
2,4-Diaminotoluene	nd	1.06	0.26	0.03	0.17	0.33	0.09	0.01	0.17	14%	0.12	0.37	1.86
4,4'-Methylene Dianiline	nd	1.00	0.68	0.62	0.64	0.39	0.56	0.31	0.16	48%	0.20	0.62	3.10
1- Nitronaphthalene SS	44.8	51.9	37.1	42.1	42.2	38.3	31.7	36.2	42.8	74%			

Data Files:

Apr16\

Blank	0801006.d
MDL 1	2101039.d
MDL 2	1001010.d
MDL 3	1101011.d
MDL 4	1201012.d
MDL 5	1301013.d
MDL 6	1401014.d
MDL 7	1501015.d

Solid Phase Extraction - 5 ul Injection on 4/16-17/97

Table V. Soil Quad Study by Accelerated Solvent Extraction (ASE)

Extraction Conditions: **ASE with 95/5 Methylene Chloride/5 % 1,6-Hexanediamine in MeOH, 1500 psi, 100 C, 5 min static, 3 cycles**

Reagent Sand 5 g Final Vol. 10 mL ethyl acetate

	Added	Blank	spike 1		spike 2		spike 3		spike 4			
		Found	Found	% Rec	Found	%Rec	Found	%Rec	Found	%Rec	Ave Rec	RSD %
	ug/g	ug/g	ug/g		ug/g		ug/g		ug/g			
2,6-Diaminotoluene	20.8	nd	10.2	49%	6.4	31%	14.2	68%	11.7	56%	51%	31%
2,4-Diaminotoluene	21.2	nd	14.6	69%	11.7	55%	19.4	92%	16.9	80%	74%	21%
4,4'-Methylenedianiline	20.0	nd	19.4	97%	19.0	95%	18.6	93%	17.3	87%	93%	5.0%
1-Nitronaphthalene SS	10.4	7.6	8.2	79%	7.8	75%	6.5	63%	6.2	60%	69%	13%

April 19, 1997 NB 17,725 p30

Data Files:

APR20\

Blank	3401033.d
spike 1	3501034.d
spike 2	3601035.d
spike 3	3701036.d
spike 4	3801037.d