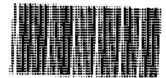

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EPA Contract No. 68-W6-0042
EPA Work Assignment No. 032-TATA-0105

EPA Project Officer: Diana King
EPA Remedial Project Manager: Richard Goehlert

FINAL SAMPLING AND ANALYSIS PLAN FOR TECHNICAL ASSISTANCE

APPENDIX B: DAS SPECIFICATIONS

Ottati and Goss/Kingston Steel Drum Superfund Site
Kingston, New Hampshire

April 1999

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Ottati and Goss/Kingston Steel Drum Superfund Site
Kingston, New Hampshire

April 1999

Prepared By:

FINAL SAMPLING AND ANALYSIS PLAN
TECHNICAL ASSISTANCE
OTTATI AND GOSS SUPERFUND SITE
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B-1. DAS ANALYTICAL SERVICES SPECIFICATIONS

FINAL SAMPLING AND ANALYSIS PLAN
TECHNICAL ASSISTANCE
OTTATI AND GOSS SUPERFUND SITE

APPENDIX B-1

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Analytical Specification for the Analysis of Volatile Organic Compounds in Soil Samples

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Analytical Specification for the Analysis of Inorganic Anions by Ion Chromatography in Aqueous Samples (Method 300.0)

ANALYTICAL SPECIFICATION

FOR THE ANALYSIS OF

VOLATILE ORGANIC COMPOUNDS

IN SOIL SAMPLES

Prepared by:

Metcalf & Eddy Inc.
Wakefield, Massachusetts
Revision 1
July 1998

1. SCOPE

This specification is for the analysis of volatile organic compounds (VOCs) in soil samples using a modified version of the EPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organics Analysis, OLMO3.2. This specification includes procedures described in Method 5035 from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition including updates, for the collection and analysis of soil samples for VOC analysis. Quality assurance/quality control (QA/QC) requirements are adapted from SW-846 as well as the EPA SOW OLM03.2. The target compounds and the required reporting limits are presented in Attachment A. Performance evaluation (PE) samples may be submitted for analysis. If PE samples are submitted, instructions for preparation and analysis will be provided in the sample shipping container.

2. PURPOSE

The data derived using this specification will be used to: determine if ecological and human health risk criteria have been exceeded, provide input to risk assessments, define the nature and extent of volatile organic contamination in soil samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, and/or for other purposes.

3. DEFINITION OF WORK

Soil samples will be analyzed in accordance with this specification for volatile organic compounds. Field samples plus the associated QC samples will be submitted for analysis. Soil samples for VOC analysis will be collected into five gram Encore™ soil samplers in accordance with the procedures presented in EPA Method 5035. Soil samples will be shipped in the Encore samplers to the laboratory daily by an overnight courier.

Soil matrix samples are to be analyzed by EPA SOW OLM03.2 with the modifications presented within. These modifications are described in Section 7, Analytical Procedures. Samples will be submitted in sample delivery groups (SDGs). An SDG is as defined in EPA SOW OLM03.2 Exhibit A, Section 4.2.2.1.1. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

Laboratory Soil Sampler Requirements

The laboratory will provide a total of three Encore, 5 gram capacity, soil samplers for each sampling location. Two of these samplers will be submitted for low concentration VOC analysis. The third sampler will provide soil for high concentration (VOCS > 200 µg/Kg) analysis if this is necessary. M&E will provide an additional sample jar to allow a percent solids determination for each sample and possibly for sample screening.

4. SCHEDULE

Target sampling dates will be provided in each work order. Samples will be shipped daily. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Bruce Livingston, Metcalf & Eddy Inc. at (781) 224-6437 or the person specified in the work order.

Holding Times

The samples must be analyzed within 48 hours of sample collection. If analysis is not possible within 48 hours of sample collection, the soil must be transferred to soil sample vials containing organic-free water and sodium bisulfate for the low concentration analysis and methanol for the high concentration analysis in accordance with Method 5035. Transferred soil samples must be analyzed within 14 days of sample collection.

Delivery of Data

All sample data must be delivered under chain of custody. Data delivered to M&E will be sent to the following:

Mr. Bruce Livingston
Metcalf & Eddy, Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

5. ANALYTICAL REFERENCES

The analytical method reference is the EPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.2. Reference is also made to Method 5035, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition with updates. Quality assurance/quality control (QA/QC) requirements are adapted from OLM03.2. The target compounds and the required reporting limits are presented in Attachment A.

6. SAMPLE PRESERVATION

Sample Collection and Preservation

All soil samples not intended for percent solids determination will be collected using five gram Encore soil samplers. A four ounce wide mouth jar will be filled to capacity and

provided to the laboratory for percent solids determination and possibly for sample screening. All samples will be iced or refrigerated to 4 °C (± 2 °C) from the time of collection and the samples will also be protected from light by the Encore samplers. Cooler temperature indicators will be placed in the sample shipping containers . If the cooler temperature exceeds 6 °C upon sample receipt, the laboratory will contact M&E immediately regarding the temperature deviation to obtain direction on whether or not to prepare and analyze the affected samples. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

Procedure for Sample Storage

The samples must be refrigerated from the time of receipt until 60 days after delivery of a complete, reconciled, sample-data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants. If analysis for VOCs is not conducted within 48 hours, the soil samples must be transferred to soil sample vials containing organic-free water and sodium bisulfate for the low concentration analysis and methanol for the high concentration analysis in accordance with Method 5035.

7. ANALYTICAL PROCEDURES

Percent Solids Determination

A percent solids determination will be conducted on all soil samples using the sample bottle submitted expressly for this purpose. The laboratory must use the percent moisture determination provided in OLM03.2 Exhibit D Volatiles, Section 10.3.

Sample Preparation

Prior to sample analysis, all soil samples will be transferred to sample analysis vials. The laboratory must determine the mass of the vials, organic-free water and sodium bisulfate before sample addition and after the samples are extruded from the Encore samplers to determine the mass used for analysis. In accordance with OLM03.2, results must be recorded to the nearest 0.1 grams. The results must be recorded in a laboratory notebook and submitted with the data package.

Laboratory Fortified Blank

One LFB meeting the criteria presented in Section 8 will be analyzed daily prior to sample analysis on each instrument used for sample analysis according to this specification. The LFB will consist of 5 grams of VOC-free soil matrix placed into a VOC analysis vial spiked with all of the target compounds specified in Attachment A, such that LFB concentrations are at the specified reporting limits. The parent LFB spiking solution must be from a source other

than the initial and continuing calibration standards.

The LFB target compounds must meet the percent recovery criteria provided in Section 8, Quality Control Requirements, prior to sample analysis. The LFB surrogates and internal standards must also meet the recovery criteria presented in Section 8.

Matrix Spike/Matrix Spike Duplicate

Selection and analysis of MS/MSDs will be performed according to OLM03.2, Exhibit D, Volatiles, Section 12.2. If the sampling chain of custody forms do not identify the samples to be used for the MS/MSD, the laboratory will contact M&E to obtain additional instructions.

Matrix spike recovery and relative percent difference will be calculated according to the equations presented in OLM03.2, Exhibit D, Volatiles Sections 12.2.4.1 and 12.2.4.2. Technical acceptance criteria will be as specified in Section 12.2.5 of the same exhibit. All MS/MSDs must be analyzed on a GC/MS system meeting the BFB tuning criteria, the initial calibration and continuing calibration technical acceptance criteria, the blank technical acceptance criteria, and the frequency described in Section 12.2.2 of the same exhibit. The percent recovery and RPD criteria for each spiking compound are presented in Section 8, Quality Control Requirements, and corrective actions are as per OLM03.2, Exhibit D, Volatiles, Section 12.2.6.

Instrument Tuning

The GC/MS system must be tuned using bromofluorobenzene to meet the ion abundance criteria presented in Table 1 of Exhibit D VOA of OLMO3.2. The tuning must be performed prior to initial and continuing calibration and before samples are analyzed.

Initial and Continuing Calibration

Initial and continuing calibration of the GC/MS system must be performed in accordance with OLM03.2. The acceptance criteria for the initial and continuing calibration are the same as OLMO3.2 and these are presented in Section 8 of this specification.

Internal Standards

The internal standards must be the same compounds specified as in OLM03.2 and they must be spiked at the concentrations presented in Exhibit D VOA Section 7.2.4.3. Internal standard responses for all samples and calibration checks must not differ by more than a factor of two (- 50% to + 100%) when compared to the appropriate calibration standard specified by OLM03.2. As with all target compounds, internal standards must be within ± 0.5 minutes between any sample and the most recent continuing calibration standard analysis.

Surrogate Compounds

All field samples and QA/QC samples including standards and method blanks will be monitored with the use of the surrogate compounds or system monitoring compounds specified in OLM03.2. Recovery of all surrogates must be as per Table 7 of Exhibit D Volatiles of OLM03.2 for all samples and QC samples. If these criteria are not met, the sample or QC sample must be reanalyzed. If in the second analysis, the surrogate recoveries again fall outside of criteria, report both analyses, note the problem in the case narrative, and flag the data with an asterisk. Surrogate standards must fall within ± 0.06 RRT units of its relative retention time in the continuing calibration standard.

Method Blanks

Method blanks must be analyzed at the frequency specified in OLM03.2. The frequency, procedure, technical acceptance criteria, and corrective actions are specified in Exhibit D VOA Section 12.1.

8. QUALITY CONTROL REQUIREMENTS

The following QC checks must achieve the limits provided and be analyzed at the designated frequencies.

QC Check	Frequency	Acceptance Limits	Corrective Action
Sample Preservation	Every field sample and field QC sample	Analyze within 48 hours of sample collection or transfer to analysis vial	Notify M&E immediately if analysis is beyond 48 hours and the samples were not transferred.
GC/MS Instrument Tuning	Every 12 hours	As per Table 1 of Exhibit D VOA of OLM03.2	As per Section 9.2.5 of Exhibit D VOA in OLM03.2
Initial Calibration	When a corrective action may change the initial calibration or if the continuing calibration criteria have not been met	RSD ≤ 20.5%, and RRF must meet minimum for all target compounds and surrogates as designated in Table 5 of Exhibit D VOA	Reanalyze ICAL. Perform system maintenance to remedy cause of problem
Continuing Calibration	Every 12 hours	%D ≤ 25%, and RRF must meet minimum for all target compounds and surrogates as designated in Table 5 of Exhibit D VOA	Reanalyze CCAL, reanalyze ICAL if necessary

QC Check	Frequency	Acceptance Limits	Corrective Action
Surrogate (System Monitoring Compound) Recoveries	All samples, QC samples and standards	As per Table 7 of Exhibit D Volatiles of OLM03.2	As per Section 11.4.3.1 of Exhibit D Volatiles of OLM03.2
Internal Standard Areas	All samples, QC samples and standards	-50% to +100% of the area of the corresponding IS in the most recent cont. calibration standard	As per Section 11.4.3.1 of Exhibit D Volatiles of OLM03.2
Method Blank	After initial calibration sequence, after each continuing standard, before sample analysis.	Target analytes <½ of the quantitation limits presented in Attachment A.	Must be met prior to sample analysis. Find the source of problem and reanalyze. Blank must be compliant before analysis of samples.
Solid Matrix Lab Fortified Blank form a source other than the calibration standards	At the beginning of each 24 hour period during which samples are run, prior to sample analysis	Percent recovery must be 60-140% for all target compounds.	Reanalyze CCAL and LFB until met; If necessary, perform ICAL, CCAL, and LFB until met. LFB must be compliant before analysis of samples.
Matrix Spike/Matrix Spike Duplicate	1 per SDG	Recoveries and Precision must be as in Table 8 Exhibit D Volatiles of OLM03.2, and Section 12.2.6	Because the values in Table 8 are advisory no corrective action for recoveries is required. Flag the QC noncompliance on Form 3B as per OLM03.2 .
Performance Evaluation Sample	1 per SDG	Not Relinquished	Will be conducted on a case by case basis.

9. ANALYTICAL DELIVERABLES

A. Whenever possible, the forms provided in OLM03.2 must be used, and instructions presented in Exhibit B, Section 3, Forms Instructions, OLM03.2, must be followed. All information for which QC criteria are presented in this specification must be clearly presented on such forms. Additional instructions follow.

- A case narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the M&E-assigned sample numbers must be cross-referenced in the Case Narrative. An example calculation must be provided for positive results and quantitation limits reported. If there are no detected compounds in the field samples, then the laboratory must use the matrix spike results for the example calculations.

- A copy of this analytical specification must be provided.

- Results for all samples, blanks, LFBs, MS/MSDs, and PE samples must be reported on Form Is that include all target compounds. All sample results must be reported on a dry-weight basis in µg/kg. The data qualifiers provided in OLM03.2 must be applied to the data generated. Laboratory qualifiers may be used by the laboratory, however they must be completely defined in the Case Narrative.

- The data package must be paginated and good copy quality is required.

- The CLP SOW-required header information must be supplied on all Forms whenever applicable. The volume of methanol from any high concentration samples which is injected into 5 ml purge volume and analyzed must be recorded on the Form I. On Form IA, this information will be placed in the "Soil Aliquot Volume" field.

- Surrogate recoveries will be presented on Form IIF. All standards, blanks, samples, and QC samples that were analyzed must be reported on the form. The results must be flagged according to OLM03.2 procedures.

- The matrix spike and matrix spike duplicate sample results must be reported on a form similar to OLM03.2 Form IIIB for the spiked compounds. The results must be flagged according to the procedures presented in Section 8 of this specification. Raw data must be included. Unspiked or "native" volatile organic compounds must be reported in the MS/MSD as per OLM03.2.

- The method blanks and associated samples must be summarized on OLM03.2 Form IVA.

- Continuing calibration checks will be presented on Form VIIA. The concentration and source of the standards analyzed must be provided. Raw data must be included for all standards analyzed.

- Results for the internal standards used must be provided on Form VIIIA. The retention time and area or height of the peak for the internal standards in all blanks, samples and QC samples must be reported on this form.

- The analytical sequences will be presented on Form VIIID.

- All raw data must be provided for all blanks, spikes, standards, PE samples and field samples as per OLM03.2. All chromatograms must indicate the peaks used for quantitation, chromatographic conditions, instrument identification number, and injection volume. Quantitation reports must provide area counts (or peak heights) for all peaks present in the chromatograms.

- The Laboratory Fortified Blank (LFB) must be reported in tabular format on Form I. Raw data must be included. The source of the spike and the QC acceptance limits must also be reported. The percent recoveries for all compounds in the LFB will be calculated and presented on forms similar to Form III.

- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.

- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, the M&E chain of custody, and any telephone logs referring to the samples, must be provided in the data package.

- The laboratory must provide photocopies of any logbook or notebook pages that the laboratory generated in processing the samples including, but not limited to, the following: pages indicating all weights recorded for each sample and internal standard concentrations and volumes added.

- The laboratory must include the concentration of the surrogates, calibration standards, LFB, and matrix spike components on all relevant reporting Forms and raw data.

- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

B. Complete Sample Delivery Group File (CSF) Audit

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG, The CSF Completeness Evidence Audit Forms, which are included in Attachment B, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using those audit forms, the

laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks, and QC samples, as well as any other documents required by OLM03.2 and this analytical specification are contained in the data package deliverable for each SDG.

Resubmittals for missing, inaccurate, and/or questionable data will be requested by facsimile followed by a telephone call. The resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

10. EXCEPTIONS

If the laboratory has any questions, or if the laboratory experiences problems during any time from the sample scheduling/receipt through analysis, immediately contact:

Mr. Bruce Livingston
Metcalf & Eddy, Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

ATTACHMENT A

TARGET COMPOUND LIST

Target Compound	Required Quantitation Limit (μg/Kg)
Chloromethane	5.0
Bromomethane	5.0
Vinyl Chloride	5.0
Chloroethane	5.0
Methylene Chloride	5.0
Acetone	25
Carbon Disulfide	5.0
1,1-Dichloroethene	5.0
1,1-Dichloroethane	5.0
cis-1,2-Dichloroethene	5.0
trans-1,2-Dichloroethene	5.0
Chloroform	5.0
1,2-Dichloroethane	5.0
2-Butanone	25
1,1,1-Trichloroethane	5.0
Carbon Tetrachloride	5.0
Bromodichloromethane	5.0
1,2-Dichloropropane	5.0
cis-1,3-Dichloropropene	5.0
Trichloroethene	5.0
Dibromochloromethane	5.0
1,1, 2-Trichloroethane	5.0
Benzene	5.0

Target Compound	Required Quantitation Limit (µg/Kg)
trans-1,3-Dichloropropene	5.0
Bromoform	5.0
4-Methyl-2-Pentanone	25
2-Hexanone	25
Tetrachloroethene	5.0
1,1,2,2-Tetrachloroethane	5.0
Toluene	5.0
Chlorobenzene	5.0
Ethylbenzene	5.0
Styrene	5.0
Total Xylenes	5.0

ANALYTICAL SPECIFICATION FOR THE ANALYSIS OF METHANE, ETHANE, AND ETHENE IN AQUEOUS SAMPLES

Prepared by:

Metcalf & Eddy
Wakefield, Massachusetts

Revision 2
February 1999

1. SCOPE

This specification is for the analysis of aqueous matrices for dissolved methane, ethane, and ethene. This specification includes creation and equilbration of a helium headspace over an aqueous sample followed by injection of an aliquot of the headspace into a gas chromatograph (GC) that employs a flame ionization detector (FID) for quantitation of methane, ethane, and ethene. This specification requires second column confirmation for detected methane, ethane, and ethene. The target compounds and required reporting limits are presented in Attachment A.

2. PURPOSE

The data derived from these analyses will be used to determine the concentration and extent of methane, ethane, and ethene in groundwater, surface water, or other aqueous media, for use in determining if intrinsic bioremediation is occurring and natural attenuation is a feasible alternative for sites contaminated with volatile organic compounds. The data may also be used to determine the quality of data generated by PRP consultants and for other applications.

3. DEFINITION OF WORK

Aqueous samples will be analyzed for methane, ethane, and ethene in accordance with this specification including all of the procedures presented within. Confirmation of detected analytes is required on a secondary analytical column in addition to the primary analytical column. Samples that are nondetected for methane, ethane, and ethene may be analyzed on the primary column only. Aqueous samples will be collected into 60-ml serum vials with crimp-top caps, as detailed in Section 6 of this specification.

The laboratory must provide with the bid package one of the following proofs of laboratory capability generated during the past year of operation:

- A method detection limit (MDL) study conducted according to 40 CFR Part 136 Appendix B with practical quantitation limits (PQL) of < 10 µg/L.
- A laboratory fortified blank (LFB) analysis containing methane, ethane, and ethene at a concentration of 1000 µg/L or lower with supporting data and with a recovery of 70 to 130 percent of the true value.
- An initial calibration (IC) meeting the criteria presented in Sections 7 and 8 of this specification.

Should one of these proofs of capability not be available for delivery with the bid, it may be submitted after the bid, but one of these will be required to be submitted and accepted by Metcalf & Eddy prior to the analysis of any samples.

Samples will be submitted in sample delivery groups (SDGs). An SDG is defined in EPA SOW OLM03.2 Exhibit A, Section 4.2.2.1.1. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

4. SCHEDULE

Target sampling dates will be specified in each work order. Samples will be shipped at most one day after collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Mr. Bruce Livingston, Metcalf & Eddy Inc., (781) 224-6437, or the person identified in the work order.

Holding Time:

> Analyses are required to be performed within fourteen (14) days of sample collection for preserved aqueous samples, and seven (7) days for unpreserved aqueous samples. Sample preservation will be noted on the chains of custody. When aqueous samples are not preserved due to effervescence, this will be indicated on the chain of custody.

Delivery of Data:

> Data is required to be delivered to Metcalf & Eddy or the person identified in the work order within thirty-five (35) days of laboratory receipt of the last sample of each SDG of twenty (20) samples or less. Data must be delivered under chain of custody. Data delivered to Metcalf & Eddy must be sent to Mr. Bruce Livingston, Metcalf & Eddy, Inc., 30 Harvard Mill Square, Wakefield, MA 01880-5371.

5. ANALYTICAL REFERENCES

The references include two papers published in scientific journals *Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique* found in the Journal of Chromatographic Science, Volume 36, May 1998 and *Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique* from the International Journal of Environmental Analytical Chemistry, Volume 36, pp249-257. Two standard operating procedures from the USEPA R. S. Kerr Environmental Research Laboratory in Ada, Oklahoma are also referenced including *Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique* (RSK 175) 8/11/94 and *Gas Chromatographic Analysis of Gaseous*

Samples for Part per Million Levels of Nitrous Oxide, Methane, Ethylene, and Ethane (RSK147) 1/14/93. Reference is also made to the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organic Analysis, OLM03.2 and to Method 8000B from Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods, SW-846 USEPA, Third Edition, September 1986, with updates.

6. SAMPLE PRESERVATION

All aqueous samples will be preserved by chilling and maintaining them at 4±2°C and protecting them from light. Aqueous samples will be collected into 60-ml serum bottles filled without headspace, and preserved with 1:1 sulfuric acid. The amount of sulfuric acid necessary will be determined by filling a test bottle with sample, adding acid, and testing the pH. If the aqueous test sample is found to effervesce during addition of acid for sample preservation, the samples will not be preserved and the laboratory will be notified concerning the absence of preservative. Each serum bottle will be capped and sealed using Teflon-lined silicone septa and aluminum crimp seals. USEPA cooler temperature indicators will be placed in the sample shipping containers. If the cooler temperature exceeds 6°C upon sample receipt, the laboratory will contact Metcalf & Eddy immediately regarding the temperature deviation to obtain direction on whether or not to prepare and analyze the affected samples. Cooler temperature should be recorded upon sample log-in. The laboratory is not required to check sample pH at log-in.

7. ANALYTICAL PROCEDURES

The following procedures must be used for the determination of methane, ethane, and ethene in aqueous samples:

Methane, ethane, or ethene detected in any samples must be confirmed on a secondary analytical column in addition to analysis on the primary analytical column. The laboratory is required to quantitate detected compounds using two different analytical columns in order to meet the requirements of this specification. This may mean a single gas chromatograph having two FIDs and two columns, or two gas chromatographs with separate columns and detectors. Both analytical results must be delivered with the package and both results must be compliant with the QC requirements. This specification requires that each positive result be confirmed on the secondary analytical column and be within 30% difference for aqueous samples.

One of the following must be supplied with the laboratory's bid or proposal or one of these must be conducted prior to the analysis of any samples using this specification:

> A method detection limit study may be submitted as proof of capability. This study must follow the requirements described in 40 CFR Part 136 Appendix B using at least seven replicate analyses of calibration standard at a concentration within three

to five times the determined MDLs. The study must demonstrate MDLs and present reporting limits acceptable to Metcalf & Eddy. MDL studies not meeting these requirements will not be considered. The MDL study may be a study performed within the last year.

or:

A Laboratory Fortified Blank (LFB) containing all target analytes at a concentration of 1,000 µg/L or lower. The percent recovery for each compound must be within 70 to 130 percent of the true value. The LFB must have been performed in the last six months.

or:

An initial calibration meeting the criteria presented in Section 7 and Section 8 of this specification. The initial calibration must have been performed in the last six months.

Headspace Development/Equilibration Aqueous samples will be submitted to the laboratory in 60-ml serum bottles capped and sealed using Teflon-lined silicone septa and aluminum crimp seals. The laboratory will prepare the samples for analysis by simultaneously removing 6 mls of sample from the serum bottle, and replacing it with 6 mls of ultrapure helium, according to the following procedure: The serum bottle is placed upside down in a three-fingered clamp attached to a ring stand. A 20-gauge needle attached to a 10-mL Luer-lok™ glass syringe set for dead volume is inserted through the [illegible] n 8-cm 20-gauge needle attached to Teflon tubing and a needle valve is inserted [illegible] septum up to the bottom of the bottle. The Teflon tubing is plumbed to a two-stage regulator on a cylinder of high-purity helium, and the helium is passed through the needle at 5mL/min or less. The helium will force water out of the bottle and into the syringe. When the volume of water in the syringe reaches 6 mL, the 8-cm needle is pulled out, followed by the syringe. This will create a 6-mL headspace volume in the serum bottle.

The serum bottles will then be shaken on either a wrist action or rotary shaker for five minutes. After shaking, the bottles will next be placed in a 40°C oven or water bath for a 30 minute equilibration time. It is imperative that the laboratory maintain good temperature control at 40°C in order to achieve precise initial calibration results and accurate continuing calibration and sample results.

All standards, QA/QC samples, and blanks will be prepared for analysis in this manner (i.e. using a 60-ml serum bottle, and creating a 6-ml headspace volume by removing water) Other sample aliquot and serum bottle volumes are acceptable, but only [illegible] prior approval by Metcalf & Eddy. Standards and QA/QC samples must be prepared [illegible] the same bottles and headspace volumes as the field samples.

Once the headspace is created and equilibrated the samples and standards are ready for analysis. Nominally, a 300 µl volume must be withdrawn from the headspace using a gas tight syringe. Other standard injections volumes are acceptable, but only with prior approval by Metcalf & Eddy. The 300 µl headspace aliquot is injected into the GC where the components are separated and quantitated with the FID. No more than two 300 µl aliquots of headspace may be withdrawn from any one serum bottle. If methane, ethane, or ethene is at a concentration above the calibration range in any sample, then a smaller headspace volume must be withdrawn and injected into the GC so that the on-column mass falls within the calibration range. The volume injected for each sample must be indicated on the Form 1 results page.

Initial Calibration The laboratory must prepare a five point initial calibration curve prior to the analysis of environmental samples. The calibration range should span from nominally 2x up to 500x the practical quantitation limit. For example, for a practical quantitation limit of 10 μg/l, the calibration range will span from nominally 20 µg/L up to 5,000 µg/L. Concentrations of 2x, 10x, 100x, 250x, and 500x the practical quantitation limit (20, 100, 1,000, 2,500 and 5,000 µg/L for the example) are recommended, although other calibration ranges are acceptable, but only with prior approval by Metcalf & Eddy. Standards will be made using analyte-free, distilled, laboratory water. The methane, ethane, and ethene present in samples will partition between the gaseous headspace and the water in accordance with Henry's Law. The headspace concentration will be determined using this specification from which the initial concentration in the samples will be determined. Standards may be prepared from known concentrations of methane, ethane, and ethene in helium expressed as parts per million by volume or ppmv. Other standard preparation techniques may be used but only with prior approval by Metcalf & Eddy.

At one atmosphere and 25°C, the concentration of a standard in ppmv may be converted to ng/ml with the following equation:

$$\text{ng/ml} = \frac{\text{ppmv x molecular weight}}{24.5}$$

An example for preparation of the low concentration standard for methane from a 1,000 ppmv gas standard is as follows: A 1,000 ppmv gas standard of methane (molecular weight = 16.043 g), using the equation above, is equal to 654.8 ng/ml. A 1.654 ml injection of 654.8 ng/ml (1,000 ppmv) methane into a serum bottle yields 1080 ng or 1.08 µg of methane. If this 1.08 µg of methane were from the 54.0 ml aliquot of sample, the equivalent concentration would be 1.08 µg/54.0 ml or 0.02 µg/ml, which equals 20 µg/L.

The appropriate volume of gas standard is injected into a 60-ml serum vial, containing analyte-free, distilled laboratory water. The laboratory must inject the gas standard, and generate the appropriate headspace volume (6 ml) with ultra-pure helium, while maintaining normal atmospheric pressure in the serum bottle. After addition of the standard, and

generation of headspace, the standard is shaken and heated in the same manner as the field samples, as described in the second paragraph under "Headspace Development / Equilibrium." The laboratory must clearly document the preparation of all calibration standards in a laboratory notebook and provide these in the data package deliverable.

The initial calibration of the GC must be performed when the continuing calibration criteria are not met, whenever instrument maintenance could affect the initial calibration, and the first time the laboratory uses this specification. The relative standard deviation (RSD) of the relative response factors (RRF) for each standard must be ≤30% for methane, ethane, and ethene. The initial calibration criteria must be met prior to analysis of blanks and samples. The initial calibration must also be conducted on the secondary analytical column.

The retention time windows for methane, ethane, and ethene must be determined according to Section 7.6 of Method 8000B for each column used. Retention time shifts of the target compounds outside the determined retention time windows will require a new initial calibration and reanalysis of affected samples. Additionally, all other requirements of Method 8000B must be followed for analysis.

Continuing Calibration A continuing calibration standard must be analyzed at a frequency of once every ten injections, and at the end of the analytical batch. The concentration of the standard must be at the midpoint of the initial calibration curve, 1,000 µg/L. The percent difference (%D) between the relative response factor for the continuing calibration and the initial calibration must be ≤30%. If the continuing calibration does not meet this requirement, then another continuing calibration standard must be analyzed. If the second continuing calibration also fails the %D criterion, a new initial calibration is required. All calibration criteria must be met prior to blank and sample analysis. The continuing calibration must also be conducted on the secondary analytical column.

Laboratory Fortified Blank One laboratory fortified blank (LFB) containing methane, ethane, and ethene at a concentration of 1,000 µg/L must be analyzed on a daily basis prior to sample analysis. The parent solution must be from a source other than the initial calibration standard and continuing calibration standard. The preparation of the LFB spike must be recorded in a laboratory and photocopies of these pages must be provided in the data deliverable. The percent recovery for methane, ethane, and ethene must be within the range of 70 to 130 percent.

Laboratory Duplicate A minimum of one laboratory duplicate per SDG must be analyzed and reported by the laboratory. These laboratory duplicates must be prepared using 300 µl aliquots taken from the same 60-ml serum bottles. The percent difference for detected methane, ethane, or ethene must be less than 30% for concentrations of 100 µg/L or greater and less than 50% for concentrations less than 100 µg/L. If the laboratory duplicate criteria are not met, a second laboratory duplicate must be prepared and analyzed. In this instance, report the results from both sets of laboratory duplicates.

Method Blanks One method blank of laboratory pure analyte-free water must be analyzed with each analytical batch. Blanks must be analyzed after the last calibration standard and

before analysis of samples. Target compounds detected in the blank must be less than one-half the reporting limit for all target analytes. The method blank must meet specifications before samples can be analyzed.

Matrix Spike/Matrix Spike Duplicates Matrix spike/matrix spike duplicates (MS/MSD) must be analyzed at a frequency of one pair per SDG. The spiking solution must contain methane, ethane, and ethene at a concentration of 1,000 µg/L. Recovery limits for each compound are from 70% - 130% with a maximum RPD of 15% between the MS and MSD recoveries.

8. QC REQUIREMENTS

QC Element Required	Frequency of Performance	Acceptance Limits	Corrective Action
MDL Study, LFB, or Initial Calibration	Once, to be delivered with laboratory bid, or prior to analysis of samples	Must meet the requirements in Section 7	Laboratory not considered without MDL study, LFB or initial calibration proof of capability
Initial 5 point Calibration (ICAL)	Once with first use of this specification, when instrument maintenance could affect ICAL, and when CCAL criteria are not met	≤ 30% RSD for RRFs for methane, ethane, and ethene	Rerun until all criteria are met. Must meet criteria prior to analysis of samples
Continuing Calibration (CCAL)	Every 10 injections and at the end of the analytical batch	%D ≤ 30%	Rerun one continuing calibration standard. If still not compliant, conduct a new initial calibration.
Laboratory Fortified Blank	Daily, prior to analysis of samples	Recoveries within 70 to 130% of the true value.	Reanalyze LFB. LFB criteria must be met prior to sample analysis on a daily basis

QC Element Required	Frequency of Performance	Acceptance Limits	Corrective Action
Laboratory Duplicate	One per SDG	Within 30% D for concentrations ≥100 μg/L, and within 50% D for concentrations <100 μg/L	If the Lab Duplicate criteria are not met, reanalyze another Lab Duplicate. Report the results for both lab duplicates.
Matrix spike/ matrix spike duplicate	One pair per SDG	Recovery must be 70% to 130% with a 15% RPD maximum	The MS/MSD recovery criteria are advisory. No corrective action is necessary. Flag recoveries or RPDs outside QC criteria on the Form III.
Second column confirmation and quantitation	Every standard, blank, and sample with methane, ethane, or ethene detected on the primary column	Positive results should be within 30% difference for aqueous samples	If the percent difference is outside the criteria, flag the results on the Form I with an asterisk and note this in the case narrative.

9. ANALYTICAL DELIVERABLES

A. Whenever possible, the forms provided in the CLP SOW OLM03.2 must be used, and the instructions presented in Exhibit B, Section 3, Forms Instructions, OLM03.2, must be followed. Since the forms presented for volatile organic analysis in OLM03.2 are designed for a GC/MS method, some forms from the GC based pesticide/PCB analysis may be more appropriate. In cases where the OLM03.2 form can not be used, substitute forms will be in a similar format, and will contain as much of the same information as is pertinent to the GC method described in this specification. All information for which QC criteria are presented in this specification must be clearly presented on such a form. Additional instructions follow.

- A narrative must be provided describing the procedure performed by the laboratory, the volume of sample injected, type of standardization and any

deviations from the method. Problems encountered during analysis, problem resolution and any factors which may affect the validity of the data must be addressed. This specification, signed, and dated chain of custody documentation, shipping airbills, and telephone logs must be included. The data package must be paginated and good copy quality is required.

- Results for all samples, blanks, LFBs, Laboratory Duplicates, and MS/MSDs must be reported on a CLP Form I that has been modified to include all target compounds. The data qualifiers provided in OLM03.2 must be applied to the data generated. The laboratory qualifiers may be used by the laboratory, however they must be completely defined in the Case Narrative.

- All raw data must be provided for all blanks, spikes, standards, and field samples as per OLM03.2. All chromatograms must be properly scaled according to guidance provided for analysis of Pesticides/Aroclors, Exhibit D, Sections 9.2.5.10, 9.3.5.8, 10.2.3, and 11.1.2. All chromatograms must indicate the peaks used for quantitation, chromatographic conditions, instrument identification number, and injection volume. Quantitation reports must provide area counts (or peak heights) for all peaks present in the chromatograms.

- Quantitative results must be reported on Form Is from the primary analytical column. If, for any reason, the laboratory chooses to report results from the secondary column (e.g. suspected interference) this must be noted in the case narrative.

- The raw data must be provided for both columns, for all blanks, spikes, standards, and field samples and must include:

  - Gas chromatograms for each sample analyzed on each column

  - Instrument quantitation reports containing the following information: laboratory sample identification number, Metcalf & Eddy sample number, date and time of analysis, retention time of each compound, individual peak area or peak height, analyte concentration, copy of area table from data system, GC instrument ID, lab file ID, column, and operating conditions

  - Standard chromatograms with each individual compound labeled for each column must be provided.

- The analytical sequences will be presented on a form similar to CLP Form VIII.

- The matrix spike and matrix spike duplicate sample results on both [illegible]ns for all compounds must be tabulated on CLP Form I. The conce[illegible]ion added, percent recoveries and relative percent differences must be reported on a modified CLP Form III for the spiked compounds. The results must be flagged according to the procedures contained in Section 8 of this specification. Raw data must be included.

- The method blanks and associated samples must be summarized on modified CLP Form IV.

- The initial calibration results must also be reported in tabular format on a modified CLP Form VI for both columns. The response factors and the percent relative standard deviation must be calculated for all analytes for each column. The concentration and source of the standards analyzed must be provided. Raw data must be included for all standards analyzed.

- The 1,000 μg/L continuing calibration standard must be reported for both columns in a tabular format on modified CLP Form VII. The raw data must be included. The percent differences [illegible] daily response factors must be reported for all analytes. A CLP Form [illegible] must be provided if the initial calibration standard curve midpoint st[illegible] was used for quantit[illegible] of samples. A standard chromatogram for each detector of each c[illegible]n is required.

- The Laboratory Fo[illegible] Blank (LFB) must be reported for both columns in tabular format on [illegible]P Form I modified to include all target com[illegible]s. Raw data must be included. The percent recoveries must be quantit[illegible]d spike concentrations summarized on the modified CLP Form I or CL[illegible]a III. The source of the spike and the acceptable recovery limits must also be reported.

- Provide the external standards results on a modified CLP Form VII. The retention time and area counts of the individual peaks for the exte[illegible]l standards must be reported on this form.

- Provide an example calculation for positive results for each column and detection limits reported.

- Provide a summary of the retention time windows for both analytical columns using a modified CLP Form X.

- Provide a summary of the target compounds detected in each sample, the LFB, and MS/MSD including the retention time, retention time window, concentration from each column, and the percent difference in concentrations using a modified CLP Form X.

- Provide copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, and any telephone logs referring to the samples, in the data package.

- Provide copies of records (telecons) of communication with field personnel, the project chemist, or the Metcalf & Eddy Lead Chemist.

B. Complete Sample Delivery Group File (CSF) Audit

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment B, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using these audit forms, the laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks, and QC samples, as well as any other documents required by OLM03.2 and this analytical specification are contained in the data package deliverable for each SDG.

Resubmittals for missing, inaccurate, and/or questionable data will be requested by facsimile followed by a telephone call. The resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

10. EXCEPTIONS

If QC requirements or action limits are exceeded, or if analytical samples are destroyed or lost; or if matrix interference is suspected, contact:

Mr. Bruce Livingston
Metcalf & Eddy, Inc.
(781) 224-6437

ATTACHMENT A

Analyte	**Practical Quantitation Limit (μg/L)***
Methane	1.0
Ethane	2.0
Ethene	3.0

* The practical quantitation limits presented are those published in *Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique* found in the Journal of Chromatographic Science, Volume 36, May 1998. Should the laboratory be unable to achieve these quantitation limits, quantitation limits of ≤ 10 μg/L for each analyte will be considered.

ANALYTICAL SPECIFICATION
FOR THE ANALYSIS OF
LOW CONCENTRATION PESTICIDES
AND POLYCHLORINATED BIPHENYLS
IN AQUEOUS AND SOLID SAMPLES

Prepared by:

Metcalf & Eddy, Inc.
Wakefield, Massachusetts
Revision 1
December 1996

1. SCOPE

This specification is for analysis of organochlorine pesticides and polychlorinated biphenyls (PCBs) in aqueous, soil/sediment, and other solid samples using USEPA (EPA) Contract Laboratory Program (CLP) Statement Of Work (SOW) for Organics Analysis, OLM03.1, with modifications to reach lower concentrations. The modifications require concentration of the sample extract to 2.0 ml instead of 10.0 ml. The target compounds and the required quantitation limits are listed in Attachment A. Samples may include groundwater, surface water, soil, sediment or other matrices which will be identified in each work order. In the event that historical results are available, the range of past concentrations reported will be provided to the laboratory. Performance Evaluation (PE) samples may be submitted for analysis. If PE samples are submitted, instructions for preparation and analysis of the PE samples will be provided in the sample shipping container.

2. PURPOSE

Data generated using this specification will be used to: determine if ecological and human health criteria have been met, determine the quality of data generated by another consulting firm, characterize the nature and extent of pesticide and PCB contamination, define excavation limits, confirm onsite laboratory or field test kit screening results, determine the efficacy of remedial activities, and for other purposes.

3. DEFINITION OF WORK

Groundwater, surface water, soil, sediment, or other matrices will be analyzed for low concentrations of pesticides and PCBs. The number of samples and the matrix will be identified in each work order. Samples will be submitted in sample delivery groups (SDGs). An SDG is defined as in EPA SOW OLM03.1, Exhibit A, Section 4.2.2.1.1.

4. SCHEDULE

Target sampling dates will be provided in each work order. Samples will be shipped at most one day after collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping, the anticipated sample collection dates, and the number of samples will be specified in each work order. Data delivery inquiries may be made to Bruce Livingston, Metcalf & Eddy, Inc., (M&E) Wakefield, MA, (781) 224-6437 or the person identified in the work order.

Holding Time:

The samples must be extracted within 7 days of sample receipt. Samples must be analyzed within twenty-one (21) days of extraction.

Delivery of Data:

Sample data must be delivered to M&E or the person identified in the work order within thirty-five (35) days of laboratory receipt of the last sample per SDG. Results must be delivered under chain of custody. Data delivered to M&E should be sent to:

Bruce Livingston
Metcalf & Eddy Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

5. ANALYTICAL REFERENCE

The analytical reference method is EPA CLP SOW for Organics Analysis, OLM03.1. Based on field screening readings, the method may be modified to reach lower quantitation limits. The M&E Chain-of-Custody will indicate whether EPA CLP SOW or modified detection limits will be required.

6. SAMPLE PRESERVATION

Samples are to be cooled and maintained at $4 \pm 2°C$. USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler exceeds 6°C upon sample receipt, the laboratory must contact M&E immediately regarding the temperature deviation.

7. ANALYTICAL PROCEDURE

The laboratory will follow the instructions of the EPA CLP SOW for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.1. The following are the specific modifications that must be followed.

- The laboratory will receive 1000 ml or more of aqueous sample, which will be

concentrated to a final extract volume of 2.0 ml. Soil/Sediment samples will be supplied with sufficient mass for sample extraction, percent moisture determination, and to provide a nominal 30 gram aliquot. The final extract volume for the soil extracts will be 2.0 ml. See Attachment A for analyte-specific quantitation limits. The laboratory may receive PE samples and must follow the instructions provided for PE sample analysis.

- The concentrations of the individual standards, multicomponent standards, resolution check mixture, performance evaluation mixture, GPC calibration solution, and the florisil cartridge check solution must be the same as specified in SOW OLM03.1. The surrogate and matrix spiking solutions should be prepared at one fifth of the OLM03.1 concentration to account for the 2.0 ml final extract volume versus the 10.0 ml final extract volume specified in OLM03.1.

- The samples are to be extracted and prepared as specified in OLM03.1 except for the final extract volumes. Florisil cartridge cleanup is required and GPC cleanup is mandatory for all soil extracts. Sulfur cleanup may be performed as specified in OLM03.1 to achieve acceptable chromatographic separation and definition of pesticide/PCB peaks. The laboratory should contact M&E regarding any additional extract cleanups deemed necessary to achieve the required quantitation limits.

- The mass of solid sample extracted must be adjusted for percent moisture prior to analysis so a nominal 30 grams equivalent dry weight are used. All solid sample results must be reported on a dry weight basis.

- Follow the analytical sequence for Pesticides/PCBs as provided in Exhibit D Section 10.2.2.1 of OLM03.1. Analysis of instrument blanks, performance evaluation mixtures, and 12 hour continuing calibration standards are required. Analyze all samples, blanks and QC samples on both columns.

- Matrix spike and matrix spike duplicate samples must be prepared and analyzed as specified in OLM03.1 except the concentration of the spiking should be one fifth of the OLM03.1 concentration to account for the smaller final volume.

- Method blanks must be extracted and analyzed as specified in OLM03.1. The method blank may not contain any of the analytes listed in Attachment A above one-half the listed quantitation limits.

- The laboratory will prepare a laboratory fortified blank (LFB) for each SDG extracted. The LFB will be spiked with all of the target compounds (except multi-response) at concentrations equal to the required quantitation limits and surrogates at the equivalent of 40 ng/l and must be extracted and analyzed prior to sample analysis.

- All samples, blanks, and QC samples must be spiked with both surrogates.

tetrachloro-m-xylene and decachlorobiphenyl, as specified in the OLM03.1.

- Wherever OLM03.1 refers to the list of CRQLs in Exhibit C, the laboratory will substitute the quantitation limits presented in Attachment A.

8. QUALITY CONTROL REQUIREMENTS

The following are the QC Checks required, frequency of QC Checks, QC limits, and required corrective actions.

QC Checks Required	Frequency of QC Checks	Limits	Corrective Action
Resolution Check Mixture	At the beginning of the initial calibration sequence	As per the CLP SOW OLM03.1.	As per the CLP SOW OLM03.1.
Initial Calibration (for both columns)	As per the CLP SOW OLM03.1.	RSD $\pm$ 20.% (Per OLM03.1.	Calibration criteria must be met prior to sample analysis
Method Blanks	1 per Sample Delivery Group, per extraction day.	< One half of the Quantitation Limit listed in Attachment A.	If the criteria are exceeded, the source of the contamination must be investigated and appropriate corrective measures must be taken <u>and</u> documented before sample analysis. Reanalyze the method blank and associated samples.
Surrogates	All standards, samples, and QC samples	% Recovery = 30 - 150 %	As per the CLP SOW OLM03.1.
Instrument Blanks	As specified in the CLP SOW OLM03.1.	As specified in CLP SOW OLM03.1.	As per the CLP SOW OLM03.1.
Continuing Calibration	As specified in the CLP SOW OLM03.1.	% D $\pm$ 25.%	As per the CLP SOW OLM03.1.
Matrix Spike/ Matrix Spike Duplicate	1 per Sample Delivery Group per Matrix	As specified in the CLP SOW OLM03.1.	If limits are exceeded note in the narrative and flag the matrix spike and unspiked sample data
Laboratory Fortified Blank	1 per day samples are extracted	% Recovery of <u>each</u> analyte = 60 - 140 %	Note recoveries outside of the limits in the case narrative

QC Checks Required	Frequency of QC Checks	Limits	Corrective Action
Pesticide Breakdown Products	Every PEM QC check standard	Endrin or p.p'-DDT breakdown ≤ 20.%, combined ≤ 30.%	Maintenance of the column/injector may be required
Performance Evaluation Sample	Up to 1 per Sample Delivery Group	Not relinquished	As required on a case by case basis

9. ANALYTICAL DELIVERABLES

a. The laboratory deliverables must resemble as closely as possible the CLP RAS Organic SOW OLM03.1 format. Reference is made to data reporting forms provided in SOW OLM03.1. The data package must be of good readable copy quality and any missing deliverable must be provided within 48 hours from the time requested at no additional charge. The following items are required as documented deliverables as well as meeting the required quantitation limits stated in Attachment A:

- All applicable deliverables required in the SOW OLM03.1 SOW for Organics Analysis, Multi-Media, Multi-Concentration, must be provided.

- All sample tracking reports, chain of custody forms, custody seals, and any telephone logs referring to the samples must be provided.

- A copy of this Analytical Specification must be provided.

- Copies of sample log in sheets indicating the cooler temperature and the sample arrival time and date must be provided.

- Bench sheets for method of sample extraction, surrogate solution identification and surrogate amounts added, matrix spike solution identification, and amounts added, quantitation dates and instrument run times, dates and pH determination must be provided.

- Clearly noted run numbers and concentrations of the surrogates used for the initial calibration, continuing calibration, blanks, samples, QC samples, and PE samples must be provided. The percent recovery must be calculated.

- The source of all standardizing materials and the concentrations of all standards must be provided.

- An example of an actual calculation where a positive result was found (if

none detected then a surrogate should be used in the example) must be provided.

- A case narrative explaining the methodology used, problems encountered, and problem resolutions must be provided. The narrative must also show all laboratory sample numbers and their corresponding field sample numbers.

- All chromatograms (with peaks used for quantitation noted, chromatographic conditions, volume injected, and instrument number) for calibration verifications, surrogate recoveries, samples, QC samples, PE samples, and spike recoveries must be included in the data package.

- The laboratory will use the case number provided and field sample numbers when reporting sample results.

- The data package must be paginated.

b. Complete Sample Delivery Group File (CSF) Audit

Region I EPA requires that all analytical data and all tabulated raw or supporting data be delivered with each SDG. With each SDG the CSF Completeness Evidence Audit must be completed. The CSF Completeness Evidence Audit Forms are included in Attachment B and must accompany each data package. The laboratory using these audit forms must show that each piece of sample data, raw data, calibration data, QC data and any other requirement of the statement of work or analytical specifications are included in the data package.

The forms included in Attachment B are for all types of data packages. For this analytical specification the laboratory will use the forms supplied to the best of their ability where deliverable items are applicable.

10. EXCEPTIONS

If QC requirements or QC acceptance limits are exceeded; or if analytical samples are destroyed, compromised or lost; or if matrix interference is suspected; or there are any other problems immediately contact:

Bruce Livingston
Metcalf & Eddy Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

ATTACHMENT A

TARGET ANALYTE LIST

AND

QUANTITATION LIMIT REQUIREMENTS

QUANTITATION LIMIT REQUIREMENTS

	Pesticides/PCBs	CAS Number	Quantitation Limits	
			Water (µg/l)	Solids (µg/kg)*
1.	α-BHC	319-84-6	0.01	0.40
2.	β-BHC	319-85-7	0.01	0.40
3.	δ-BHC	319-36-8	0.01	0.40
4.	γ-BHC (Lindane)	58-89-9	0.01	0.40
5.	Heptachlor	76-44-8	0.01	0.40
6.	Aldrin	309-00-2	0.01	0.40
7.	Heptachlor epoxide	1024-57-3	0.01	0.40
8.	Endosulfan I	959-98-8	0.01	0.40
9.	Dieldrin	60-57-9	0.02	0.70
10.	p,p'-DDE	72-55-9	0.02	0.70
11.	Endrin	72-20-8	0.02	0.70
12.	Endosulfan II	33213-65-9	0.02	0.70
13.	p,p'-DDD	72-54-8	0.02	0.70
14.	Endosulfan sulfate	1031-07-8	0.02	0.70
15.	p,p'-DDT	50-29-3	0.02	0.70
16.	Methoxychlor	72-43-5	0.10	4.0
17.	Endrin ketone	53494-70-5	0.02	0.70
18.	Endrin aldehyde	7421-36-3	0.02	0.70
19.	α-Chlordane	5103-71-9	0.01	0.40
20.	γ-Chlordane	5103-74-2	0.01	0.40
21.	Toxaphene	8001-35-2	1.0	35.
22.	Aroclor-1016	12674-11-2	0.20	7.0
23.	Aroclor-1221	11104-28-2	0.40	14.
24.	Aroclor 1232	11141-16-5	0.20	7.0
25.	Aroclor-1242	53469-21-9	0.20	7.0
26.	Aroclor-1248	12672-29-6	0.20	7.0
27.	Aroclor-1254	11097-16-5	0.20	7.0
28.	Aroclor-1260	11096-82-5	0.20	7.0

* Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, based on dry weight basis as requested in this specification, may be slightly higher.

ANALYTICAL SPECIFICATION

FOR THE ANALYSIS OF

ORGANOCHLORINE PESTICIDES

AND POLYCHLORINATED BIPHENYLS (AROCLORS)

IN SEDIMENT/PEAT SAMPLES

Prepared by:

Metcalf & Eddy Inc.
Wakefield, Massachusetts
Revision 1
September 1997

1. SCOPE

This specification is for the analysis of organochlorine pesticides, and polychlorinated biphenyls (PCBs) in sediment/peat samples using a modified version of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organic Analysis, OLM03.1 The target compounds are listed in Exhibit C, Section 3 of the SOW with one additional target compound, o,p'-DDT. The target compounds and the required quantitation limits are presented in Attachment A.

Method modifications include lowered quantitation limits, procedures for handling and preparing samples with low solids content, mandatory GPC and sulfur cleanup for all extracts, and mandatory sulfuric acid cleanup for extracts to be analyzed for Aroclors. Mass spectral confirmation of all pesticide and Aroclor detects is required if concentrations permit. These modifications are briefly described below and are detailed in Section 7, Analytical Procedures.

An initial percent solids determination will be conducted on all samples. All samples will be prepared using freeze drying to increase the percent solids. Once the freeze drying is complete, the samples will be ground to a uniform dry solid and the percent solids on the freeze dried samples will then be determined. Additional freeze dried sample weight will be extracted so that 30 grams of dry weight equivalent is extracted. If a minimum percent solids of greater than 50% is not obtained after freeze drying, then the laboratory must immediately contact M&E to obtain additional instructions.

All samples will then be extracted and subjected to GPC and sulfur cleanup. The extracts will be split: one-half will undergo sulfuric acid cleanup and be analyzed for Aroclors. The other half will be analyzed directly for pesticides.

Performance evaluation (PE) samples will be submitted for analysis. Instructions for preparation and analysis of the PE samples will be provided in the sample shipping container.

2. PURPOSE

Data derived using this specification will be used to: determine if ecological and human health risk criteria have been exceeded, provide input to risk assessments, define the nature and extent of pesticide/PCB contamination in sediment/peat samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, and/or for other purposes.

3. DEFINITION OF WORK

Sediment/peat samples will be analyzed for organochlorine pesticides and PCBs. The shipment of samples will be assigned a unique Case Number. A Case consists of one or

more Sample Delivery Groups (SDGs). An SDG is defined by the following, whichever is most frequent: each Case of field samples, or each 20 field samples within a Case, or each 14 calendar day period during which field samples in a Case are received by the laboratory. Samples may be assigned to SDGs by matrix at the discretion of the laboratory. The laboratory must use the matrix assigned on the chain-of-custody records to make this determination. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

The matrix of the samples will be sediment/peat, therefore, provision must be made in laboratory procedures for sample storage and preparation. Additional laboratory sample storage space may be required. Extra bottles will be submitted to provide the sample weight necessary to meet the project objectives. It is expected that the sediment density will be close to but slightly greater than 1.0 gm/ml and the percent solids will be approximately 10%. Given these assumptions, one 32 fluid ounce sample container will hold approximately 94 grams of dry weight sample. M&E will submit two 32 ounce bottles for each sample with six bottles each for MS/MSD and laboratory fortified sample (LFS) designated samples.

4. SCHEDULE

Holding Times:

The sediments must be extracted within ten days of sample collection. Samples must be analyzed within forty days following the start of extraction.

The extraction holding times do not apply for PEs received as standard extracts.

Delivery of Data:

The sampling event data must be delivered to M&E within 35 days of laboratory receipt of the last sample per SDG. Sample data must be delivered under chain of custody. Data delivered to M&E should be sent to:

Mr. Bruce Livingston
Metcalf & Eddy Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

5. ANALYTICAL REFERENCES

The analytical method reference is the USEPA Contract Laboratory Program Statement of Work for Organic Analysis, OLM03.1. soxhlet extraction by SW-846 Method 3540B, and sulfuric acid cleanup of PCB extracts by SW-846 Method 3665, Sulfuric Acid/Permanganate Cleanup, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition (and updates).

6. SAMPLE PRESERVATION

Sample Collection and Preservation

All samples will be iced or refrigerated at 4°C (± 2°C) from the time of collection. Cooler temperature indicators will be placed in the sample shipping containers. If the cooler temperature exceeds 6°C upon sample receipt, contact M&E immediately regarding the temperature deviation and to obtain direction on whether or not to prepare and analyze the affected samples. If the initial sample shipments arrive at a temperature above 6°C, M&E will conduct corrective action to include more ice in subsequent shipments to properly chill the samples. If the initial shipments arrive at a temperature below 2°C, the sample storage prior to shipment will be evaluated. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

Procedure for Sample Storage

The samples must be protected from light and refrigerated at 4°C (± 2°C) from the time of receipt until 60 days after delivery of a complete reconciled sample data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

Procedure for Sample Extract Storage

Sample extracts must be protected from light and refrigerated at 4°C (± 2°C) until 365 days after delivery of a complete reconciled data package.

Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

Samples, sample extracts and standards must be stored separately.

7. ANALYTICAL PROCEDURES

Sediment/peat samples will be submitted to the laboratory.

Percent Solids Determinations

The laboratory must decant any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples prior to sample extraction and analysis. A second percent solids determination must be conducted following freeze drying of each sediment sample. Prior to the second percent solids determination, the laboratory must grind the dried sample to a uniform powder using a clean mortar and pestle. All percent solids determinations must be performed according to the requirements contained in Exhibit D Pesticides/Aroclors Section 10.1.5.2. A balance calibration check must be conducted in accordance with guidance from NIST. The NIST guidance references ASTM E 617 which for this application requires Type II S grade weights that meet Class 2 tolerances. Prior to performing the post-drying weighing of samples for any percent solids determination associated with this analytical specification, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample as well as the start and stop times for the post-drying weighing session must be documented in the sample preparation logbook.

Sample Preparation, Extraction and Cleanup

All samples will be freeze dried to increase the percent solids content. The nominal freeze drying conditions will include a unit temperature of -50°C, a condenser temperature of -80°C, a vacuum of 133x10E-3 mBar, and a 10 hour minimum (overnight) freeze drying time. However, the laboratory should consult the freeze dryer manufacturer's instructions for the specific model planned for use with this specification. Changes to these nominal operating conditions should be discussed with M&E prior to the initiation of freeze drying. The sediment samples should be frozen using dry ice prior to placement in the freeze drying apparatus. Care should be taken to freeze the samples to create a uniform, as thin as possible, coating of sediment on the inside surface of the freeze drying vessel to promote complete drying.

Following freeze drying the laboratory must grind the dried sample to a uniform powder using a clean mortar and pestle. Using the percent solids following freeze drying, the laboratory will proportionately increase the sample weight extracted to achieve extraction of 30 grams of dry weight sample. The surrogate solution will be added to the sample just prior to sample extraction. The samples must be extracted using 50:50 acetone/hexane for 18 hours in accordance with SW-846 Method 3540B. The extraction start and stop times must be recorded in a laboratory notebook and provided in the final data package. The extracts

must be concentrated and solvent exchanged into hexane following the procedures presented in Method 3540B.

Prior to performing the post-drying weighing of samples subjected to freeze drying, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample as well as the start and stop times for the post-drying weighing session must be documented in the sample preparation logbook. The laboratory must document when the last desiccant regeneration was performed or when new desiccant was added to each desiccator.

If a minimum percent solids of greater than 50% is not obtained after freeze drying, then the laboratory must immediately contact M&E to obtain additional instructions. Additionally, if the laboratory has difficulty obtaining sufficient percent solids and/or adequate sample weight for any of the sediment/peat samples, then M&E must be immediately contacted to obtain additional instructions.

The laboratory must add the surrogates Tetrachloro-m-xylene (TCX) and Decachlorobiphenyl (DCB) to all field samples, method blanks, and QC samples at a concentration that results in sample surrogate concentrations at the midpoint of both the pesticide and PCB curves (taking into account the increased sample weight extracted and the required extract volume of 1.0 ml that will be split: one-half for analysis of pesticides and one-half for analysis of PCBs). The concentration and volume of surrogate solution added to each sample must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

All field sample, method blank, and QC sample extracts must be subjected to GPC and sulfur cleanup following the OLM03.1 procedures and requirements contained in this analytical specification. The field sample, method blank and QC sample extracts must be concentrated to a volume of 1.0 ml to achieve the required quantitation limits. If concentration of any sample extract to 1.0 ml is problematic, contact M&E immediately to obtain additional instructions. The final concentrated extract volume for each sample must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

The resulting field sample and method blank extracts will be split: one-half of each extract will undergo sulfuric acid cleanup according to SW-846 Method 3665 and shall be analyzed for PCBs (Aroclors) according to the procedures presented later in this section. Applicable PE, LFS, and MS/MSD QC sample extracts shall also undergo sulfuric acid cleanup and be analyzed for PCBs.

The other half of each field sample and method blank extract, and all applicable PE, LFS,

and MS/MSD QC sample extracts, shall be analyzed directly for pesticides following the OLM03.1 procedures and requirements contained in this analytical specification. The final pesticide extract volume and the final PCB extract volume (after sulfuric acid cleanup) must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

Laboratory Fortified Sample (LFS)

Three aliquots of one field sample per SDG must be prepared as LFS samples. The sampling chain-of-custody forms shall identify the samples to be used for LFS samples. If the sampling chain-of-custody forms do not identify the samples to be used for LFS samples, then contact M&E to obtain additional instructions.

The purpose of the LFSs is to evaluate loss/degradation of target compounds during freeze drying. The laboratory fortified spike solution shall be added to the sample after the initial percent moisture determination has been performed and **before** the sample undergoes freeze drying. The surrogate spike solution shall be added to the sample after the initial percent moisture determination has been performed and **after** freeze drying has been completed.

One sample aliquot shall be spiked with the target compounds in the Individual A pesticide mixture, one shall be spiked with the target compounds in the Individual B pesticide mixture, and one shall be spiked with Aroclor 1232. All spike concentrations shall result in LFS concentrations at the midpoint of the calibration curves (taking into account the increased sample weight extracted and the required final extract volumes). One of the pesticide LFSs must contain o,p'-DDT (as determined by the pesticide calibration resolution requirements which are provided later in this section).

The LFSs must meet the percent recovery criteria provided in Section 8 of this analytical specification. If these criteria are not achieved, then all Form I sample results for that LFS and field samples that underwent freeze drying with that LFS must be flagged and a discussion of those results must be included in the data package narrative.

Matrix Spike/Matrix Spike Duplicate(MS/MSD)

Three matrix spike/matrix spike duplicate pairs must be extracted and analyzed per SDG. The matrix spike and surrogate spike solutions shall be added to the sample after the initial percent moisture determination has been performed and after freeze drying. The sampling chain-of-custody forms shall identify the samples to be used for matrix spike/matrix spike duplicates. If the sampling chain-of-custody forms do not identify the samples to be used for matrix spike/matrix spike duplicates, then contact M&E to obtain additional instructions.

One pair will be spiked with the target compounds specified in OLM03.1 at concentrations that result in matrix spike concentrations at the midpoint of the calibration curves (taking into account the increased sample weight extracted and the required final extract volumes).

The second pair must be spiked with o,p'-DDT at a concentration that results in matrix spike concentrations at the midpoint of the calibration curve (taking into account the increased sample weight extracted and the required final extract volumes). The o,p'-DDT MS/MSD shall follow the established 4,4'-DDT OLM03.1 criteria for matrix spike/matrix spike duplicate frequency, acceptance limits (recovery and RPD) and corrective action procedures.

The third matrix spike/matrix spike duplicate pair must be spiked with Aroclor 1232 at a concentration that results in matrix spike concentrations at the midpoint of the calibration curve (taking into account the increased sample weight extracted and the required final extract volumes). The PCB MS/MSD pair must be subjected to the same preparation, extraction and cleanup procedures as the field samples. The PCB MS/MSD must meet the percent recovery and RPD criteria provided in Section 8 of this analytical specification. If these criteria are not achieved, then the Form I sample results for the unspiked sample must be flagged and a discussion of those results must be included in the data package narrative.

Analysis

The calibration requirements presented below apply to both GC columns used for analysis of pesticide and PCB extracts.

GC/MS confirmation of pesticide and PCB results for field samples is required as per Section 11.1.2 of OLM03.1.

All chromatograms must be properly scaled as described in Sections 9.2.5.10, 9.3.5.8, 10.2.3, & 11.3 of OLM03.1.

All technical acceptance criteria for sample analysis must be met as per Section 11.3 or effective corrective actions must be performed as per Section 11.4 of OLM03.1.

Pesticide Calibration

External standard calibration must be performed following Section 9.2 of OLM03.1. Include the additional compound o,p'-DDT in either the Individual A or B standard mixture, whichever provides greater than or equal to 90% resolution of o,p'-DDT with both adjacent peaks in the initial calibration midpoint concentration Individual A or B standard. The concentration of this compound in the low through high point standards must follow the general instructions provided in OLM03.1 Section 7.2: the low point concentration **must be at the quantitation limits required in this analytical specification**, the midpoint concentration must be at 4 times the low point concentration and the high point must be at least 16 times that of the low point (but a higher concentration for the high point initial calibration standard may be chosen by the laboratory if the instrument linearity requirement in Section 8 of this analytical specification is achieved).

Follow the procedures outlined in OLM03.1 Sections 9.2.4, 9.2.5 and 9.2.6 for the determination, acceptance criteria and corrective actions for: initial calibration, absolute

retention times, retention time windows, instrument linearity, calibration factors, percent breakdown of DDT and endrin, PEM percent differences, and all resolution checks. Eliminate the Aroclor standards from the initial calibration sequence (since a separate PCB-only sequence must be performed as outlined in the section below).

Calibration verification must be performed according to Section 9.3 of OLM03.1. Follow the procedures outlined in OLM03.1 Sections 9.3.2 through 9.3.6 for the instrument blanks, PEMs, and midpoint Individual A and B standards, which comprise the calibration verification. The o,p'-DDT must be included in either the Individual A or B standard, whichever had acceptable resolution as determined during the initial calibration procedure.

PCB-only Calibration

The PCB analytical sequence should be performed as follows:

	Initial Calibration
1	Low Aroclor 1016/1260
2	Low Aroclor 1221
3	Low Aroclor 1232
4	Low Aroclor 1242
5	Low Aroclor 1248
6	Low Aroclor 1254
7	Mid Aroclor 1232
8	High Aroclor 1232
9	Method Blank
10	Laboratory Fortified Sample
11	Instrument Blank
	Continuing Calibration Group 1
12	10 Field Samples (including MS/MSD)
13	Method Blank (if needed)
14	Laboratory Fortified Sample (if needed)

15 plus	Continuing Calibration Standard(s): Mid Aroclor #1 (for detected PCBs) High Aroclor #1 Mid Aroclor #2, 3, etc. as required (for detected PCBs) High Aroclor #2, 3, etc. as required (for detected PCBs)
16	Instrument Blank
	Continuing Calibration Group 2
17	10 Field Samples
18	Method Blank (if needed)
19	Laboratory Fortified Sample (if needed)
20 plus	Continuing Calibration Standard(s): Low Aroclor 1016/1260 Mid Aroclor #1 High Aroclor #1 Mid Aroclor #2, 3, etc. as required High Aroclor #2, 3, etc. as required
21	Instrument Blank
	Continuing Calibration Group 3
22	Etc.

PCB Initial Calibration Sequence

Runs 1-11 constitute the initial calibration portion of the PCB analytical sequence.

The concentration of the low point standard for each Aroclor **must be equal to the quantitation limits required in this analytical specification**. The midpoint concentration for all Aroclors in the analytical sequence shall be at 4 times the low point concentration and the high point concentration shall be at least 16 times the low point concentration (but a higher concentration may be used by the laboratory if the linearity criteria provided in Section 8 of this analytical specification are achieved).

A full curve is required for Aroclor 1232 in the initial calibration, since that Aroclor is spiked in the LFS and MS/MSD. The Aroclor 1232 three point calibration curve must meet the linearity criteria provided in Section 8 of this analytical specification prior to the analysis of

the remaining QC samples (method blank, LFS, and instrument blank) in the initial calibration sequence. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures, and re-analyze the three point calibration curve prior to analyzing the remaining QC samples in the PCB initial calibration sequence.

The method blank must meet the frequency, acceptance limits, and corrective action requirements specified in Section 8 of this analytical specification prior to the analysis of the LFS.

The instrument blank must meet the frequency, acceptance limits, and corrective action requirements specified in Section 8 of this analytical specification prior to the analysis of any field samples contained in Continuing Calibration Group 1.

PCB Continuing Calibration Sequence

The continuing calibration for every 12 hour time period must begin and end with an instrument blank. Run 11 serves as the beginning instrument blank for Continuing Calibration Group (CCG) 1, and the instrument blank that ends the previous CCG serves as the beginning instrument blank for the next CCG.

Each CCG must include at least one midpoint and high point Aroclor standard, which must be analyzed after the field samples as shown in the table above. The Aroclor used for midpoint and high point Aroclor standards must consist of Aroclors detected in the environmental samples. Multiple sets of midpoint/high point standards may have to be analyzed in a single CCG in order to accurately quantitate Aroclors detected in the field samples for that CCG. If more than one Aroclor is detected in the field samples in a CCG, then a midpoint and high point standard for each of those Aroclors must be analyzed during that CCG's continuing calibration. If no Aroclors are detected in the field samples in a particular CCG, then the laboratory must run a midpoint and high point standard containing an Aroclor for which a curve has yet to be generated. All three point calibration curves (generated using the low point standard from the initial calibration and the midpoint and high point standards from the continuing calibration) must meet the linearity criteria provided in Section 8 of this analytical specification. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures, generate new three point calibration curves for the affected Aroclors, and re-analyze all field and QC samples that were quantitated using those curves.

Once a demonstrated linear three point curve has been generated for all 6 Aroclor standards, then the high point standard can be eliminated from the continuing calibration standards for all remaining CCGs. The continuing calibration for those CCGs shall just contain one (or more) midpoint standards for Aroclors detected in the field samples for that CCG (if no Aroclors are detected in the field samples for that CCG, then run a midpoint Aroclor standard for an Aroclor that was detected in any of the field samples in previous

CCGs or, if no Aroclors have been detected in any field samples, then run one of the 6 midpoint Aroclor standards on a rotational basis). The percent difference criteria in Section 8 of this analytical specification must be achieved for those midpoint continuing calibration standards. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures (including curve re-analysis, if necessary), and re-analyze all field and QC samples that were analyzed since the last acceptable midpoint continuing calibration standard for that Aroclor.

In addition, the low point Aroclor 1016/1260 standard must be analyzed once every 24 hour time period after the start of the initial calibration sequence to demonstrate continued instrument sensitivity. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures (including curve re-analysis, if necessary), and re-analyze all field and QC samples that were analyzed since the last acceptable low point Aroclor 1016/1260 standard.

The continuing calibration standards and an instrument blank must be the last analyses performed within the analytical sequence.

If sample concentrations exceed the calibration range, a dilution must be performed to bring the sample concentrations to the mid to upper end of the calibration range. All original and diluted sample analyses must be reported in the final data package.

If, in the analyst's judgement, higher chlorinated Aroclors such as 1262 and/or 1268 appear to be present in any of the field samples, then M&E must be contacted immediately to obtain additional instructions. M&E may instruct the laboratory to analyze standards for those Aroclors and re-analyze field sample extracts for those Aroclors at no additional cost.

8. QUALITY CONTROL REQUIREMENTS

Pesticide/PCB Cleanup:

QC Check	Frequency of QC Check	Acceptance Limits	Corrective Action
Calibration of GPC	As per OLM03.1, Section 10.1.8.1.3.2	As per OLM03.1, Section 10.1.8.1.3.4	As per OLM03.1, Section 10.1.8.1.3.5
GPC Calibration Check	As per OLM03.1, Section 10.1.8.1.4.2	As per OLM03.1, Section 10.1.8.1.4.4	As per OLM03.1, Section 10.1.8.1.4.5
Sulfur Cleanup Blanks	As per OLM03.1, Section 12.1.3.2	As per OLM03.1, Section 12.1.3.4	As per OLM03.1, Section 12.1.3.5

Pesticide Analysis:

QC Check	Frequency of QC Check	Acceptance Limits	Corrective Action
Instrument Blank	As per OLM03.1, Section 12.1.4.2	As per OLM03.1, Section 12.1.4.4 & 11.3	As per OLM03.1, Section 12.1.4.5 & 11.4
Method Blank	As per OLM03.1, Section 12.1.2.2	As per OLM03.1, Section 12.1.2.4 & 11.3	As per OLM03.1, Section 12.1.2.5 & 11.4
Initial Calibration including o,p'-DDT	Upon award of this contract and as per OLM03.1, Section 9.2.2 and as per instructions provided in Section 7, Analytical Procedures	As per OLM03.1, Section 9.2.5 & 11.3 (apply these criteria for o,p'-DDT also)	As per OLM03.1, Section 9.2.6 & 11.4 (apply these criteria for o,p'-DDT also)
Calibration Verification including o,p'-DDT	As per OLM03.1, Section 9.3.2 and as per instructions provided in Section 7, Analytical Procedures	As per OLM03.1, Section 9.3.5 & 11.3 (apply these criteria for o,p'-DDT also)	As per OLM03.1, Section 9.3.6 & 11.4 (apply these criteria for o,p'-DDT also)
Surrogate %Rec. & RT	As per OLM03.1, Section 7.2.4.1	As per OLM03.1, Section 11.2.3.2 & 11.3	As per OLM03.1, Section 11.2.3.3 & 11.4
Laboratory Fortified Sample (one with OLM03.1 target compounds and a second with o,p'-DDT)	As per instructions provided in Section 7, Analytical Procedures	Recovery 50-150%	As per instructions provided in Section 7, Analytical Procedures

QC Check	Frequency of QC Check	Acceptance Limits	Corrective Action
Matrix Spike/Matrix Spike Duplicate (one pair with OLM03.1 target compounds and a second with o,p'-DDT)	As per OLM03.1, Section 12.2.2 & instructions provided in Section 7, Analytical Procedures	As per OLM03.1, Section 12.2.5 & instructions provided in Section 7, Analytical Procedures	As per OLM03.1, Section 12.2.6 & instructions provided in Section 7, Analytical Procedures
Performance Evaluation Samples	one per SDG	USEPA will score the results	Actions will be applied on a case by case basis

PCB Analysis:

QC Check	Frequency of QC Check	Acceptance Limits	Corrective Action
Instrument Blank	As per OLM03.1, Section 12.1.4.2	As per OLM03.1, Section 12.1.4.4 & 11.3	As per OLM03.1, Section 12.1.4.5 & 11.4
Method Blank	As per OLM03.1, Section 12.1.2.2	As per OLM03.1, Section 12.1.2.4 & 11.3	As per OLM03.1, Section 12.1.2.5 & 11.4
Initial Calibration	As per instructions provided in Section 7, Analytical Procedures	RSD <20% for Aroclor 1232	As per instructions provided in Section 7, Analytical Procedures
Continuing Calibration	As per instructions provided in Section 7, Analytical Procedures	%D <15% for any midpoint Aroclor and for low Aroclor 1016/1260 RSD <20% for any Aroclor curve	As per instructions provided in Section 7, Analytical Procedures
Surrogate %Rec. & RT (DCB only)	As per OLM03.1, Section 7.2.4.1	As per OLM03.1, Section 11.2.3.2 & 11.3	As per OLM03.1, Section 11.2.3.3 & 11.4

QC Check	Frequency of QC Check	Acceptance Limits	Corrective Action
Laboratory Fortified Sample	As per instructions provided in Section 7, Analytical Procedures	Recovery 50-150%	As per instructions provided in Section 7, Analytical Procedures
Matrix Spike/Matrix Spike Duplicate	One pair per SDG as per instructions provided in Section 7, Analytical Procedures	Rec. 50-150% & RPD <20.	As per instructions provided in Section 7, Analytical Procedures
Performance Evaluation Samples	one per SDG	USEPA will score the results	Actions will be applied on a case by case basis

9. DATA PACKAGE DELIVERABLES

The laboratory data package deliverables must resemble as closely as possible the OLM03.1 format. The general deliverables described in Section B--Exhibit 2 and the specific data described in Exhibit B-- Section 2, part 2.6.5 must be provided. That section describes the chromatograms and data system printouts. Modify the appropriate forms to include the additional compound, o,p'-DDT and the PCB only analysis. The data package must be of good readable copy quality and paginated in ascending order.

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment C, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using those audit forms, the laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks and QC samples as well as any other documents required by OLM03.1 and this analytical specification are contained in the data package deliverable for each SDG.

Resubmittals for missing, inaccurate, and/or questionable data from the laboratory will be requested by facsimile followed by a telephone call. The resubmittals must be provided under custody seal within 48 hours of the date of facsimile request at no additional cost and the resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

Data package deliverables for each SDG must include the following:

- A Case Narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the EPA assigned sample numbers must be cross-referenced in the Case Narrative. An example calculation for one pesticide target compound and one Aroclor must also be provided in the Case Narrative to demonstrate the derivation of pesticide and Aroclor target compound results that are reported on Form Is. If there are no detected compounds in the field samples, then the laboratory must utilize matrix spike results for the example calculations.

- A copy of this analytical specification must be provided.

- Results for all samples, blanks, LFSs, MS/MSDs, and PE samples must be reported on Form Is that have been modified to include all target compounds. All sample results must be reported on a dry weight basis in $\mu g/kg$. OLM03.1 sample result qualifiers must be used on all Form Is. Additional sample result qualifiers may be utilized by the laboratory (to meet the requirements contained in Sections 7 and 9 of this analytical specification), however, they must be completely defined in the Case Narrative.

- The SOW-required header information must be supplied on all Forms.

- The surrogate percent recoveries must be calculated and reported on Form IIs.

- The MS/MSD recoveries and RPD results must be reported on modified Form IIIs. Values that exceed the QC limits must be flagged with a "*".

- The LFS recoveries must be reported on a modified Form IIIs. Values that exceed the QC limits must be flagged with a "*".

- The Method Blank(s) and corresponding samples must be reported on Form IVS.

- The initial calibration results for both the Pesticide and PCB only analyses must be reported on modified Forms VI-1 through VI-7.

- The percent breakdown of DDT and endrin must be reported on Form VII-1.

- The Pesticide and PCB only Calibration Verification results must be reported on modified Form VII-2s.

- Report the pesticide analytical sequence for all columns and instruments on Form VIIIs.

- Report the PCB analytical sequence for all columns and instruments on a modified Form VIIIs.

- Report the results of all extract cleanups on modified Form IXs. Include all samples, blanks, and QC samples on the forms.

- The retention time, retention time windows, results quantitated from each column and percent difference between quantitated results must be summarized for all detected target compounds for each sample on modified Form Xs.

- All raw data, including chromatograms and quantitation reports for all standards, blanks, field samples and QC samples must be provided. All chromatograms must indicate the peaks used for quantitation, chromatographic conditions, instrument identification number, and injection volume. Quantitation reports must provide area counts for all peaks present on the chromatograms.

- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.

- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, and any telephone logs referring to the samples, must be provided in the data package.

- Provide all sample logbook pages, which have recorded the results for all % solids determinations with pre/post sample weights, start/stop times for desiccator cooling and start/stop times for post-drying sample weighing, sample weights extracted, surrogate concentrations and volumes added: reagent weights/volumes for sodium sulfate and all extraction solvents; the start and stop times for the 18 hour soxhlet extractions; all initial, intermediate and final pesticide and PCB extract volumes; and pages from any other logbook that the laboratory generated in the processing of the samples.

- Include the concentration of the surrogates, calibration standards (pesticide and PCB initial and verification), LFS, and matrix spike components on all relevant reporting Forms and raw data.

- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

10. EXCEPTIONS

If the laboratory has any questions or if the laboratory experiences problems during any time from sample scheduling/receipt through analysis contact M&E immediately.

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Wakefield, MA 01880-5371
Phone (781) 224-6437
FAX (781) 245-6293

Attachment A Target Compound and Quantitation Limit Requirements	
Target Compound	**Quantitation Limits (μg/kg)**
Aldrin	**0.17**
α-BHC	**0.17**
β-BHC	**0.17**
δ-BHC	**0.17**
γ-BHC	**0.17**
Chlordane(Technical)	**0.33**
p,p'-DDD	**0.33**
p,p'-DDE	**0.33**
o,p'-DDT	**0.33**
p,p'-DDT	**0.33**
Dieldrin	**0.33**
Endosulfan I	**0.17**
Endosulfan II	**0.33**
Endosulfan Sulfate	**0.33**
Endrin	**0.33**
Endrin Aldehyde	**0.33**
Endrin Ketone	**0.33**
Heptachlor	**0.17**
Heptachlor Epoxide	**0.17**
Methoxychlor	**1.7**
Toxaphene	**17.0**
Aroclor 1016	3.3
Aroclor 1221	6.7
Aroclor 1232	3.3
Aroclor 1242	3.3

Attachment A Target Compound and Quantitation Limit Requirements	
Target Compound	**Quantitation Limits ($\mu g/kg$)**
Aroclor 1248	**3.3**
Aroclor 1254	**3.3**
Aroclor 1260	**3.3**

* The quantitation limits listed for a solid matrix are based on 30 grams dry weight.

ANALYTICAL SPECIFICATION

FOR THE ANALYSIS OF

LOW CONCENTRATION METALS

IN SEDIMENT/PEAT SAMPLES

Prepared by:

Metcalf & Eddy, Inc.
Wakefield, Massachusetts
Revision 2
September 1997

1. SCOPE

This specification is for the analysis of low concentrations of metals in sediment/peat samples using a modified version of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-media Multi-concentration ILM04.0. To meet project objectives, modifications to ILM04.0 will be required to achieve lowered detection limits for antimony, arsenic, beryllium, cadmium, mercury and silver. The target analytes and the required quantitation limits are presented in Attachment A.

Method modifications include lowered quantitation limits, and procedures for handling and preparing samples with low solids content. These procedures are briefly described below and are detailed in Section 7, Analytical Procedures and in Attachment B.

The percent solids of all samples will be determined initially upon sample receipt. Percent solids preparation will include decanting any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples prior to sample digestion. Specific sample preparation steps will be performed as described in the Sample Preparation portion of Section 7. All samples will undergo a drying step after the initial percent solids determination. If the percent solids of the sample after the first drying step is greater than or equal to 50%, then additional sample weight must be digested so that the equivalent dry weight of sample, as described in this specification, is digested (Attachment B). If the percent solids is less than 50%, additional drying steps, as described in Section 7 of this specification, will be necessary. All percent solids determinations must be performed according to the requirements contained in ILMO4.0 Exhibit D Part F and these must be documented in a laboratory notebook.

Performance evaluation (PE) samples will be submitted for analysis during the main sampling event only. Instructions for preparation and analysis of PE samples will be provided in the sample shipping container.

2. PURPOSE

Data derived using this specification will be used to: determine if ecological and human health criteria have been exceeded, provide input to risk assessments, define the nature and extent of metals contamination in sediment/peat samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, or for other purposes.

3. DEFINITION OF WORK

Sediment/peat samples are to be analyzed for low concentrations of metals. To meet project objectives, modifications to ILM04.0 will be required to achieve lowered detection limits for

antimony, arsenic, beryllium, cadmium, mercury and silver as presented in Attachment A. The shipment of samples will be assigned a unique M&E DAS Case Number. A Case consists of one or more Sample Delivery Groups (SDGs). An SDG is defined by the following and whichever is more frequent: each Case of field samples, or each 20 field samples within a Case, or each 14 calendar day period during which field samples in a Case are received by the laboratory. Samples may be assigned to SDGs by matrix at the discretion of the laboratory, however, the laboratory must use the matrix assigned on the chain-of-custody records to make this determination. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

The matrix of the samples will be sediment/peat of low percent solids, therefore, provisions must be made in the laboratory procedures for sample storage and preparation. Additional laboratory sample storage space my be required. Extra sample bottles will be submitted to provide adequate sample weight to meet the project objectives. It is anticipated that the sediment/peat density will be close to, but slightly greater than 1.0 gm/ml and that the percent solids will be approximately 10%. Based on these assumptions, one (1) 8-ounce, plastic sample container will hold approximately 24 grams of dry weight sample. M&E will submit one 8-ounce bottle for each sample including those designated for MS or MS/MSD analysis.

4. SCHEDULE

Specific sampling dates will be provided in each work order. Samples will be shipped no more than one day after collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Mr. Bruce Livingston, Metcalf & Eddy (781) 224-6437.

Holding Times:

> The sediment/peat samples must be analyzed for all metals, except mercury, within 180 days of sample collection. Analysis for mercury must be conducted within 26 days of sample collection. Analysis for silver must be conducted within 24 hours after sample digestion.

Delivery of Data:

> The data must be delivered to M&E, within 35 days of laboratory receipt of the last sample in the SDG. Sample data must be delivered under chain of custody. Results delivered to M&E should be sent to:

Mr. Bruce Livingston
Metcalf & Eddy
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
Fax (781) 245-6293

5. ANALYTICAL REFERENCE

The analytical reference method is the EPA CLP Statement of Work for Inorganics Analysis Multi-Media Multi-Concentration ILM04.0. Modifications to reach lower quantitation limits and for handling low solids content samples are provided in Section 7, Analytical Procedures, of this specification.

6. SAMPLE PRESERVATION

Sample Collection and Preservation

Samples will be preserved by cooling and maintaining them at 4° C (±2°C). USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler is greater than 6°C or less than 2°C upon sample receipt, the laboratory must contact M&E immediately for instructions regarding analysis of the samples. If the initial sample shipments arrive at a temperature above 6°C, M&E will conduct corrective action to include more ice in subsequent shipments to properly chill the samples. If the initial shipments arrive at a temperature below 2°C, the sample storage prior to shipment will be evaluated. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

Procedure for Sample Storage

The samples must be refrigerated at 4°C (±2°C) from the time of sample receipt until 60 days after delivery of a complete reconciled sample data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

In addition, the samples must be stored in an atmosphere demonstrated to be free of all potential contaminants. Samples and standards must be stored separately.

7. ANALYTICAL PROCEDURES

The analysis will be performed following the procedures in Sections 6,7, and 8, with the required percent recovery of 75-125% and RPD of less than or equal to 20% as specified in ILM04.0, Exhibit E, Section V Parts 6 and 7.

Percent Solids Determinations

The laboratory must decant any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples, after decanting, but prior to sample digestion. Specific sample preparation steps will be performed as described in the Sample Preparation section below. Multiple percent solids determinations may need to be performed on sediment/peat samples that contain low percent solids, before and after drying. All percent solids determinations must be performed according to the requirements presented in ILM04.0 Exhibit D Part F. A balance calibration check must also be conducted in accordance with guidance from NIST. The NIST guidance references ASTM E 617, which for this application requires Type II S grade weights that meet Class 2 tolerances. Prior to performing the post-drying weighing of samples for any percent solids determination associated with this analytical specification, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample, as well as the start and stop times for the post-drying weighing session, must be documented in the sample preparation logbook.

Sample Preparation

Preparation blanks must be carried through all steps that are conducted on sediment/peat samples at a frequency of one per SDG or per batch of samples prepared whichever is more frequent.

The percent solids of all samples will be determined initially upon sample receipt (Attachment B). Each sample will then be dried at 60°C for four hours. All samples must undergo this initial drying regardless of the initial percent solids. If the percent solids of the sample from the determination after initial drying is greater than or equal to 50%, then additional sample weight will be digested so that the equivalent dry weight of sample as specified in ILM04.0 or this specification is digested. If the percent solids is less than 50% after the four hours of drying, then the laboratory will dry the samples at 60°C for 24 hours to remove additional moisture. After 24 hours of drying, a third percent solids determination will be conducted. If the percent solids is greater than or equal to 50% additional sample weight will be digested so that the equivalent dry weight of sample as specified in ILM04.0 or this specification is digested. If the percent solids is less than 50% a second 24 hour drying at 60°C will be conducted. If the percent solids is greater than or equal to 30% after the second 24 hour drying cycle, additional sample weight will be digested so that the equivalent dry weight of sample required is digested. If the percent solids is less than 30% after this second 24 hour drying cycle, the laboratory must contact Mr. Bruce Livingston at M&E (781) 224-6437, to further discuss sample preparation and additional instructions. Preparation of sediment samples using microwave digestion is not acceptable for this

analytical specification.

In order to achieve the quantitation limits required for antimony, arsenic, beryllium, cadmium, and silver the laboratory must conduct analyses for these metals using graphite furnace atomic absorption (GFAA). The laboratory must follow the procedures provided in Methods 204.2, 206.2, 210.2, 213.2 and 272.2 of ILM04.0 for the GFAA analysis of antimony, arsenic, beryllium, cadmium and silver, respectively. Additionally, a standard equal to 2X the required quantitation limits must be analyzed along with the remaining calibration standards required in ILM04.0 for GFAA analysis. The highest concentration standards must define the upper limit of the linear range of the instrument for each metal. Any sample concentrations above the highest concentration standards must be diluted to fall within the upper half of the calibration range. A dry weight equivalent of 2 grams of sediment in 200 ml final volume must be used to ensure the quantitation limits required are achieved.

In order to achieve the quantitation limit required for mercury the initial sample weight must be increased to a dry weight equivalent of 2 grams of sediment in 100 ml final volume as opposed to the 0.2 grams specified in ILM04.0.

A laboratory fortified blank (LFB), consisting of an analyte free solid matrix such as Ottawa sand, must be analyzed with each SDG at the specification required quantitation limits or lower to demonstrate that the laboratory is able to consistently meet these quantitation limits.

The use of ICP "TRACE" analysis is allowable for all metals, except antimony, arsenic, beryllium, cadmium, silver and mercury, if the quantitation limits can be achieved and as long as interference check sample analysis is performed and documented. All requirements presented in Exhibit E Section V number 5 of ILM04.0 for interference check sample analysis must be met.

The sediment/peat samples must be analyzed unspiked and as a matrix spike/matrix spike duplicate. The spiking solution will be added prior to drying the samples at 60°C. The samples will be spiked so that the final concentration will be nominally 2.0 mg/kg on a dry weight basis depending on the actual dry weight of the spiked samples. From the stock mercury solution presented in ILM04.0 Exhibit D Method 245.5, prepare a spiking solution at a concentration of 2.0 µg/ml. Add 2.0 ml of this spike solution to the wet sediment/peat sample aliquot that is equivalent to 2.0 gms of dry weight sample for each MS and MSD. The sediment/peat samples must be oven dried at 60°C for 24 hours independent of the initial percent solids. The SRM will not be analyzed as an MS/MSD.

Along with the sample analysis requirements, the laboratory must also provide one of the following:

- A method detection limit (MDL) study within the last 6 months

demonstrating a quantitation limit for antimony at 0.30 mg/kg, arsenic at 0.20 mg/kg, beryllium at 0.040 mg/kg, cadmium at 0.01 mg/kg, silver at 0.02 mg/kg and mercury at 0.01 mg/kg. The MDL requirements are specified in section 9b.

- Laboratory fortified blank (LFB) results, consisting of an analyte free solid matrix such as Ottawa sand, spiked with all target analytes at concentrations equivalent to the quantitation limits in Attachment A demonstrating that these limits can be achieved.

8. QUALITY CONTROL REQUIREMENTS

All quality control elements of ILM04.0 must be conducted, with provisions made to achieve the detection limits provided in Attachment A. The following tables present the QC checks required, the frequency, acceptance limits, and corrective actions for samples analyzed using GFAA and ICP:

Graphite Furnace Atomic Absorption (GFAA)/Cold Vapor AA (Hg)

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Initial Calibration (See 2x equivalent low concentration standard and Section 7 text)	As per ILM04.0, Exhibit E, Section V, part 1	As per ILM04.0, Exhibit E, Section V, part 1	Recalibrate until initial calibration criteria are met. Low standard must equal the required quantitation limits in Attachment A.
Initial Calibration Verifications (ICVs)	As per ILM04.0, Exhibit E, Section V, part 2, subpart a)	As per ILM04.0, Exhibit E, Section V, part 2	Initial calibration criteria must be met or the analysis terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.
Continuing Calibrations (CCVs)	As per ILM04.0, Exhibit E, Section V, part 2, subpart b)	90 to 110 % of true value for all metals by GFAA and 80 to 120% of true value for Hg	Continuing calibration criteria must be met or stop analysis, determine the source of the problem, perform corrective action, the calibration verified and reanalysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification, and begin again with initial calibration prior to sample analysis.

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
2x equivalent Low Quantitation Limit Standard	To be conducted with initial calibration at frequency in ILM04.0 Exhibit E Section V. part 1	75-125% of the true value	If criteria are exceeded, the calibration and 2x standards will be reprepared and reanalyzed until the analysis is linear.
CRDL Standards (routine limits)	1 per 20 samples analyzed, at the beginning and end of each sample analysis run, preceding the ICS but not before the ICV.	As per ILM04.0, Exhibit E. Section V. part 3	If criteria are exceeded, the AA standards will be reprepared and reanalyzed until the analysis is linear.
Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs)	As per ILM04.0, Exhibit E. Section V. part 4. subpart a)	The absolute value of the calibration blank must less than or equal to the CRDL	If the absolute value of the blank result exceeds the IDL, the result shall be reported as specified in Exhibit B. If the absolute value of the blank result exceeds the CRDL, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding ten analytical samples or all samples analyzed since the last compliant calibration blank.
Preparation Blanks	At least one preparation blank per SDG	As per ILM04.0, Exhibit E. Section V. part 4. subpart b)	If the criteria are exceeded, all samples associated with the blank shall be redigested and reanalyzed for that analyte.
Solid Matrix Laboratory Control Sample (LCS)	As per ILM04.0, Exhibit E. Section V. part 8	The required quantitation limits must be met. Recovery not to exceed 125%.	If the criteria are not met, terminate the analysis, correct the problem, and redigest and reanalyze the analytical samples associated with the non-compliant LCS.
Matrix Spike Sample Analysis	1 per SDG	75 to 125% recovery, except if the native concentration exceeds the spiked concentration by a factor of 4 or more; ILM04.0, Exhibit E. Section V. part 6	If limits are not within the accepted criteria, note this in the narrative and all samples associated with that spike sample are flagged with the letter "N" on FORMS I-IN and V-IN.

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Duplicate Sample Analysis	1 per SDG	20% for RPD if duplicates are ≥ 5x CRDL; ±CRDL if duplicates are <5x CRDL; as per ILM04.0, Exhibit E, Section V, part 7	If results are outside the control limits, flag all the data for samples associated with that duplicate sample with an "*" on FORMS I-IN and VI-IN.
Solid Matrix Laboratory Fortified Blank spiked at the quant limits in Attachment A	1 per SDG	50 to 150% recovery	If the recoveries are outside the acceptance limits, note this in the case narrative and flag the results reported on a FORM V.
Method of Standard Addition	As per ILM04.0, Exhibit E, Section V, part 13	As per ILM04.0, Exhibit E, Section V, part 13	Report the data and flag it with a "S" or "+" depending on the exceedance and report the results on FORM I-IN and FORM VIII-IN.
Instrument Detection Limit (IDL)	Prior to field sample analysis and reported quarterly	As specified in ILM04.0 in Exhibit E, Section V, part 10	If the instrument is adjusted, the IDL for that instrument will be redetermined and established IDLs submitted.
Performance Evaluation Sample	1 per SDG	USEPA will score the results	Actions will be applied on a case by case basis.

Antimony, arsenic, beryllium, cadmium, silver and any other elements analyzed using GFAA to meet detection limit requirements, must incorporate all QC elements presented in Exhibit E Section V number 13 of ILM04.0.

Inductively Coupled Plasma (ICP)

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Initial Calibration	As per ILM04.0, Exhibit E, Section V, part 1	As per ILM04.0, Exhibit E, section V, part 1	Recalibrate until initial calibration criteria are met.

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Initial Calibration Verifications (ICVs)	As per ILM04.0. Exhibit E. Section V. part 2. subpart a)	As per ILM04.0. Exhibit E. Section V. part 2	Initial calibration criteria must be met or the analysis terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.
Continuing Calibrations (CCVs)	As per ILM04.0. Exhibit E. Section V. part 2. subpart b)	90 to 110 % of true value for all metals	Continuing calibration criteria must be met or stop analysis. determine the source of the problem. perform corrective action. the calibration verified and reanalysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification. and begin again with initial calibration prior to sample analysis.
CRDL Standards (routine limits)	1 per 20 samples analyzed, at the beginning and end of each sample analysis run, preceding the ICS but not before the ICV.	As per ILM04.0. Exhibit E. Section V. part 3	If criteria are exceeded, the ICP standards will be reprepared and reanalyzed until the analysis is linear.
Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs)	As per ILM04.0. Exhibit E. Section V. part 4. subpart a)	The absolute value of the calibration blank must be less than or equal to the CRDL	If the absolute value of the blank result exceeds the IDL, the result shall be reported as specified in Exhibit B. If the absolute value blank result exceeds the CRDL, terminate analysis. correct the problem. recalibrate. verify the calibration. and reanalyze the preceding ten analytical samples or all samples analyzed since the last compliant calibration blank.
Preparation Blanks	At least one preparation blank per SDG	As per ILM04.0. Exhibit E. Section V. part 4. subpart b)	If the criteria are exceeded, all samples associated with the blank shall be redigested and reanalyzed for that analyte.
Interference Check Sample (ICS)	1 per 20 analytical samples. per analysis run: ILM04.0. Exhibit E. Section V. part 5	±20% of the established mean value for the analyte	If the criteria are not met. terminate the analysis. correct the problem. recalibrate the instrument. and reanalyze the analytical samples analyzed since the last acceptable ICS.

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Solid Matrix Laboratory Control Sample (LCS)	As per ILM04.0, Exhibit E, Section V, part 8	The required quantitation limits must be met. Recovery not to exceed 125%.	If the criteria are not met, terminate the analysis, correct the problem, and redigest and reanalyze the analytical samples associated with the noncompliant LCS.
Spike Sample Analysis	1 per SDG	75 to 125% recovery	If limits are not within the accepted criteria, note this in the narrative and all samples associated with that spike sample are flagged with the letter "N" on FORMS I-IN and V-IN. If the sample concentration exceeds the spike concentration by a factor of four, the data shall be reported unflagged, even if the percent recovery criteria are exceeded.
Duplicate Sample Analysis	1 per SDG	20% for RPD if duplicates are ≥ 5x CRDL; =CRDL if duplicates are <5x CRDL; ILM04.0, Exhibit E, Section V, part 7	If results are outside the control limits, flag all the data for samples associated with that duplicate sample with an "*" on FORMS I-IN and VI-IN.
Solid Matrix Laboratory Fortified Blank spiked at the quant limits in Attachment A	1 per SDG	50 to 150% recovery	If the recoveries are outside the acceptance limits, note this in the case narrative and flag the results reported on a FORM V.
Serial Dilution	1 per SDG	Within 10% of the original determination	If the limit is exceeded, the data for all affected analytes in the samples associated with that serial dilution shall be flagged with an "E" on FORM IX-IN and FORM I-IN.
Interelement Correction Factors	Prior to field sample analysis and reported annually	As specified in ILM04.0, Exhibit E, Section V, part 11	If the instrument is adjusted, the IEC for that instrument will be redetermined and established IDLs submitted. Data will be reported on FORM XI-IN.

QC Checks Required	Frequency of QC Checks	Acceptance Limits	Corrective Action
Instrument Detection Limit (IDL)	Prior to field sample analysis and reported quarterly	As specified in ILM04.0 in Exhibit E, Section V, part 10	If the instrument is adjusted, the IDL for that instrument will be redetermined and established IDLs submitted.
Linear Range Analysis (LRA)	Analyzed and reported quarterly	5% of the true value	If a sample exceeds the linear range it should be diluted and the results reported from the dilution
Performance Evaluation Sample	1 per SDG	USEPA will score the results	Actions will be applied on a case by case basis.

9. ANALYTICAL DELIVERABLES

All deliverables specified in Exhibit B of ILM04.0, including all of the data reporting forms and all of the raw or supporting data must be provided. The laboratory data package deliverables must resemble as closely as possible the ILM04.0 format. The data package must be of good readable copy quality and paginated.

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment C, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using these audit forms, the laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks and QC samples as well as any other documents required by ILM04.0 and this analytical specification are contained in the data package deliverable for each SDG. In addition, all telephone communication logs (telecons) between the laboratory and project personnel must be provided.

Resubmittals for missing, inaccurate, and/or questionable data from the laboratory will be requested by facsimile followed by a telephone call. The resubmittals must be provided under custody seal within 48 hours of the date of facsimile request at no additional cost and the resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

Data package deliverables for each SDG must include the following:

- A Case Narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the EPA assigned sample numbers must be cross-

referenced in the Case Narrative.

- A copy of this analytical specification must be provided.

- Results for all samples, QC analyses, Quarterly Verification of Instrument Parameters forms, raw and tabulated data, and copies of the digestion logs must be included with the Inorganic Analysis Data Reporting Forms. The sample results for blanks, MS/MSDs, and PE samples must be reported on Form Is that have been modified to include all target compounds. All sample results must be reported on a dry weight basis in mg/kg. ILM04.0 sample result qualifiers must be used on all Form Is. Additional sample result qualifiers may be utilized by the laboratory (to meet the requirements contained in Sections 7 and 9 of this analytical specification), however, they must be completely defined in the Case Narrative.

- The SOW-required header information must be supplied on all Forms.

- The MS recovery results must be reported on FORM V-IN. Values that exceed the QC limits must be flagged with a "N" on FORM I-IN.

- The LFB recoveries must be reported on a FORM V-IN modified to indicate that the results are LFB recoveries.

- The Method Blank(s) and corresponding samples must be reported on FORM III-IN.

- The initial calibration results for ICP and GFAA analyses must be reported on FORM II-IN.

- All raw data, including reports for all standards, blanks, field samples and QC samples must be provided.

- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.

- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, and any telephone logs referring to the samples, must be provided in the data package.

- Provide all sample logbook pages, which have recorded the results for all % solids determinations with pre/post sample weights, start/stop times for desiccator cooling and start/stop times for post-drying sample weighing, spikes concentrations and volumes added, all LCS preparation records, and pages from any other logbook that the laboratory generated in the processing of the samples.

- Include the concentration of the spikes, calibration standards, and matrix spike components on all relevant reporting Forms and raw data.

- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

In addition, the laboratory must provide with the laboratory's bid or with the final data package:

An MDL study to demonstrate that the element analyzed by ICP, cold vapor AA, GFAA, or ICP TRACE can achieve the required quantitation limits presented in Attachment A prior to sample analysis. The MDL study must follow 40 CFR, Part 136, Appendix B. The MDL study must be supplied in tabular form including the standard deviations and an example calculation. Initial and continuing calibration, method blank, and instrument print out data must be provided along with the MDL study.

or

The results of a laboratory fortified blank analyzed at the required quantitation limits or lower to demonstrate the laboratory is able to detect the analytes at the low limits. Initial and continuing calibration, method blank, and instrument print out data must be provided along with the laboratory fortified blank data.

10. EXCEPTIONS

If the laboratory has any questions or if the laboratory experiences problems during any time from sample scheduling/receipt through analysis contact M&E immediately.

Mr. Bruce Livingston
Metcalf & Eddy Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (781) 224-6437
FAX (781) 245-6293

ATTACHMENT A

Analytes and Required Quantitation Limits

Element	Required Quantitation Limit mg/kg on a dry weight basis
Aluminum	4.0
Antimony	0.30
Arsenic	0.20
Barium	2.0
Beryllium	0.040
Cadmium	0.010
Calcium	8.0
Chromium	1.0
Cobalt	2.0
Copper	1.0
Iron	4.0
Lead	0.40
Magnesium	10
Manganese	1.0
Mercury	0.010
Nickel	2.0
Potassium	80
Selenium	1.0
Silver	0.020
Sodium	50
Thallium	0.40
Vanadium	1.0
Zinc	2.0

ANALYTICAL SPECIFICATION

FOR THE ANALYSIS OF

INORGANIC ANIONS BY ION CHROMATOGRAPHY IN

AQUEOUS SAMPLES (METHOD 300.0)

Prepared by:

Metcalf & Eddy
Wakefield, Massachusetts
Revision 1
March 1999

1. SCOPE

This specification is for the analysis of aqueous matrices for the following inorganic anions using ion chromatography: chloride, nitrate, nitrite, and sulfate. The method is based upon Method 300.0: Determination of Inorganic Anions by Ion Chromatography, from *Methods for the Determination of Inorganic Substances in Environmental Samples* - EPA/600/R-93-100, August 1993. Aqueous samples are injected into a stream of carbonate/bicarbonate eluent, and passed through a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2. PURPOSE

The data derived from these analyses will be used to determine whether natural attenuation of groundwater contaminants is occurring, and the extent to which it is occurring at different locations in the contaminant plume.

3. DEFINITION OF WORK

Aqueous samples, most of which will be groundwater, will be analyzed for inorganic anions in accordance with Method 300.0 including the modifications presented within this specification. It is anticipated that some samples may require multiple analyses since dilution may be required to put some anions within calibration range. The laboratory is required to report results for all diluted and undiluted analyses performed. Although chloride concentrations may be elevated for samples from some sites, M&E requires that at least one analysis of the sample be undiluted, such that the practical quantitation limits are met for each anion. If elevated concentrations are anticipated, M&E will indicate this on the work order and/or chain-of-custody form.

The laboratory must provide with the bid package one of the following proofs of laboratory capability generated during the past year of operation:

- A Method Detection Limit (MDL) study conducted according to 40 CFR Part 136 Appendix B with practical quantitation limits (PQL) less than or equal to those specified in Attachment A for each of the anions listed.

- A laboratory fortified blank (LFB) analysis containing all anions listed above at a concentration equal to the practical quantitation limit reported with a recovery of 90 to 110 percent of the true value.

- An initial calibration (IC) meeting the criteria presented in Section 7, Item B of this specification.

Should one of these proofs of capability not be available for delivery with the bid, it may be submitted after the bid, but one of these will be required to be submitted and accepted by M&E prior to the analysis of any samples.

Performance evaluation (PE) samples may be provided with up to one in each sample delivery group (SDG) to be analyzed along with the field samples. An SDG is defined in Exhibit A, Section II G of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-Media, Multi-Concentration (ILM04.0).

4. SCHEDULE

Target sampling dates will be specified in each work order. Samples will be shipped at most one day after collection. Samples to be analyzed for nitrate and/or nitrite will be shipped the day of collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Mr. Bruce Livingston, Metcalf & Eddy Inc., (781) 224-6437, or the person identified in the work order.

Holding Time:

> Analysis for nitrate and nitrite are required to be performed within forty-eight (48) hours of sample collection for aqueous samples. Analysis for chloride and sulfate are required to be performed within twenty-eight (28) days of sample collection for aqueous samples. Sample preservation will be noted on the chain of custodies.

Delivery of Data:

> Data is required to be delivered to M&E or the person identified in the work order within thirty-five (35) days of laboratory receipt of the last sample of each SDG of twenty (20) samples or less. Data must be delivered under chain of custody. Data delivered to M&E must be sent to Mr. Bruce Livingston, Metcalf & Eddy, Inc., 30 Harvard Mill Square, Wakefield, MA 01880-5371.

5. ANALYTICAL REFERENCES

The reference method is Method 300.0: Determination of Inorganic Anions by Ion Chromatography, from *Methods for the Determination of Inorganic Substances in Environmental Samples* - EPA/600/R-93-100, August 1993. Reference is also made to the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-Media, Multi-Concentration (ILM04.0).

6. SAMPLE PRESERVATION

All samples will be preserved by chilling and maintaining them at 4±2°C and protecting them from light. No additional sample preservation is required. USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler exceeds 6°C upon sample receipt, the laboratory must contact M&E immediately regarding the temperature deviation.

7. ANALYTICAL PROCEDURES

Method 300.0: Determination of Inorganic Anions by Ion Chromatography will be followed as promulgated and will be modified as instructed in the following items:

A. One of the following must be supplied with the laboratory's bid or proposal or one of these must be conducted prior to the analysis of any samples using this specification:

An MDL study is required. This study must follow the requirements described in 40 CFR Part 136 Appendix B using at least seven replicate analyses of calibration standard at a concentration within three to five times the determined MDLs. The study must demonstrate MDLs and present reporting limits acceptable to M&E. MDL studies not meeting these requirements will not be considered. The MDL study may be a study performed within the last year.

or:

A Laboratory Fortified Blank (LFB) containing all anions listed above at a concentration equal to the practical quantitation limit reported. The percent recovery for each anion must be within 90 to 110 percent of the true value. The LFB must have been performed in the last six months.

or:

An initial calibration meeting the criteria presented under Item B. The initial calibration must have been performed in the last six months.

and:

In addition to one of the preceding choices, the laboratory must submit a successful analysis of a Quality Control Standard (QCS), a secondary source standard, as described in Section 9.2.3 of Method 300.0. The standard concentrations must be within ±10% of the actual concentration. Concentration of the standard will be equivalent to the midpoint of the calibration curve.

B. Initial calibration, as described in Section 9.2.2 of Method 300.0- Linear Calibration Range, must be determined initially, and re-established at a minimum of each working day. Initial calibration must also be performed whenever the anion eluent strength is changed, or whenever a significant change in instrument response is observed or expected. Sufficient number of standards must be used to establish linearity throughout the calibration range. At a minimum, three calibration standards and one blank will be used to determine linearity. At a minimum, the first standard concentration will be equivalent to the practical quantitation limit, the second standard concentration will be equivalent to the upper calibration limit, and the third standard concentration will be equivalent to the midpoint of the calibration range. The correlation coefficient must be ≥ 0.995 for each anion. Calibration standards should be prepared the day of analysis for nitrite.

C. Since initial calibration will be performed daily, as described under Item B, verification of linearity of the calibration range, as described in Section 9.2.2 of Method 300.0, need not be performed.

D. The Quality Control Sample (QCS), a secondary source standard, as described in Section 9.2.3 of Method 300.0, will be analyzed once when beginning the use of this method, and monthly thereafter. The standard concentrations must be within ±10% of actual concentration. Concentration of the standard will be equivalent to the midpoint of the calibration curve.

E. A Laboratory Reagent Blank (LRB), as described in Section 9.3.1 of Method 300.0 must be analyzed at the beginning of each sample batch, prior to sample analysis, and after all calibration standards and QC samples. Concentration of any target anion cannot exceed ½ of the practical quantitation limit for that anion.

F. A Laboratory Fortified Blank (LFB), as described in Section 9.3.3 of Method 300.0, must be performed once per analytical batch. Initially, LFB recoveries should be reported relative to the 90-110% recovery criteria. Once a minimum of 20 to 30 analyses have been performed, the laboratory may establish QC criteria based on control charts as defined in Section 9.3.3 of Method 300.0.

G. Instrument Performance Checks (IPC), Continuing Calibration Blanks (CCB), and samples will be analyzed as described in Section 9.3.4 of Method 300.0. In addition, samples for which the concentrations of a target anion exceeds the calibration range must be diluted and reanalyzed.

H. A Laboratory Fortified Matrix (LFM), discussed in Section 9.4.1 of Method 300.0, as well as an LFM duplicate (also known as a matrix spike/matrix spike duplicate), will be performed on a minimum of one per SDG. M&E will select the field sample for MS/MSD analysis, and indicate the selection on the chain-of-custody form.

Criteria for the recovery of each anion will be 80-120% of spiked concentrations. Criteria for percent difference (%D) is ≤ 15% for each anion.

8. QC REQUIREMENTS

QC Element Required	Frequency of Performance	Acceptance Limits	Corrective Action
QCS and an MDL Study, LFB, or Initial Calibration	Once, to be delivered with laboratory bid, or prior to analysis of samples	Must meet the requirements in Section 7, Item B	Laboratory not considered without QCS and MDL study, LFB or initial calibration proof of capability
Initial Calibration	Once per working day, or more frequently as needed	≥ 0.995 correlation coefficient for all target anions	Rerun until all criteria are met. Must meet criteria prior to analysis of samples
Quality Control Sample (Secondary Source)	Once initially, as noted above, and monthly thereafter	Percent recovery 90-110% of actual for all target anions	Determine source of problem and resolve prior to sample analysis.
Instrument Performance Checks (IPC) and Continuing Calibration Blank (CCB)	Every 10 samples, and once at the end of the batch	IPC %D≤10% for all target anions	Reanalyze the IPC; If the second analysis does not meet criteria, sample analysis must be discontinued. All samples analyzed after the last acceptable IPC must be reanalyzed. Initial calibration must be performed.
Laboratory Reagent (Method) Blanks	At the beginning of each sample batch	Contamination < ½ the practical quantitation limits for all target anions	Determine the source of contamination and rerun all affected samples

QC Element Required	Frequency of Performance	Acceptance Limits	Corrective Action
Laboratory Fortified Blank	One per sample batch	Percent recovery 90-110% for all target anions or within laboratory control chart criteria	Reanalyze LFB. LFB criteria must be met prior to sample analysis on a daily basis
Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate	One pair per SDG	Percent recovery 80-120% of actual; RPD$\leq$15%	The LFM/LFMD recovery criteria are advisory. No corrective action is necessary. Flag recoveries or RPDs outside QC criteria on the Form III.

9. ANALYTICAL DELIVERABLES

a. The laboratory deliverables must resemble as closely as possible the Contract Laboratory Program (CLP) RAS Inorganic SOW OLM04.0 format. Reference is made to data reporting forms provided in SOW OLM04.0. The data package must be of good readable copy quality and any missing deliverable must be provided within 48 hours from the time requested at no additional charge. The following items are required as documented deliverables as well as meeting the required quantitation limits presented in Attachment A:

- Results for all samples. MDL Study Analyses, Initial Calibration Standards, Quality Control Samples, Instrument Performance Checks, Laboratory Reagent Blanks, Laboratory Fortified Blanks, Continuing Calibration Blanks, Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate Samples, and PE sample, if submitted, must be reported on a Form 1 modified to include all target anions. All applicable header information must be retained and information supplied on the modified Form 1 and all other data reporting forms.

- MDL study raw data, including all calculations performed to arrive at the MDLs.

- The Laboratory Fortified Matrix / Laboratory Fortified Matrix Duplicate recoveries and RPD must be reported on a modified Form 5. Values that exceed the QC Limits should be flagged with a "*".

- The Laboratory Fortified Blank recoveries must be reported on a modified Form 5. Values that exceed the QC Limits should be flagged with a "*".

- The Laboratory Reagent Blank(s) must be reported on a modified Form 3.

- All raw data for the initial calibration standards must be reported. Initial calibration results, including correlation coefficients (r^2) for each target anion, must be reported on a modified Form 2.

- The Instrument Performance Check results must be reported on a modified Form 2, and should include the standard concentrations, the instrument quantitated concentration, and the RPD.

- Report the analytical sequence for all instruments on Form 14.

- All sample tracking reports, chain of custody forms, custody seals, and any telephone logs referring to the samples must be delivered under chain of custody with the data package.

- The laboratory must provide a copy of this Analytical Specification.

- Copies of sample log in sheets indicating the cooler temperature and the sample arrival time and date must be provided.

- Bench sheets for all standards preparation, including the volume and concentration of all standards analyzed and spikes performed, any sample dilutions, instrument run logs, quantitation dates and instrument run times, dates, and pH determination bench sheets must be provided.

- The Laboratory ID Numbers and concentrations of the calibration standards used for the initial calibration, instrument performance checks, blanks, samples. QC samples, and PE samples must be clearly defined in the data.

- The source of all standardizing materials must be documented. The concentrations of all standards must be indicated.

- An example of an actual calculation where a positive target compound result was found.

- A case narrative explaining the methodology used, including the following: make and model of the anion guard columns, separator columns, analytical columns, suppressor devices, detectors, eluent and regeneration solutions and strengths, sample loop volume, and nominal sample volume injected. The case narrative will also explain any deviations from the method as presented in this specification, any deviations from laboratory Standard Operating

Procedures for this analysis, any problems encountered, problem resolutions, and any factors affecting the validity of the data. The narrative must also show all laboratory sample ID numbers and their corresponding field sample numbers.

- All chromatograms (with peaks used for quantitation noted, chromatographic conditions, volume injected, and instrument number) for calibration verifications, samples, diluted samples, QC samples, PE samples, and spike recoveries must be provided.

b. Complete Sample Delivery Group File (CSF) Audit

Region I EPA requires that all analytical data and all tabulated raw or supporting data be delivered with each SDG. With each SDG the CSF Completeness Evidence Audit must be carried out. The CSF Completeness Evidence Audit Forms are included in Attachment B and must accompany each data package. The laboratory using these audit forms must show that each piece of sample data, raw data, calibration data, QC data and any other requirement of the statement of work or analytical specifications are included in the data package.

The forms included in Attachment B are for all types of data packages. For this analytical specification the laboratory will use the forms supplied to the best of their ability where deliverable items are applicable.

10. EXCEPTIONS

If QC requirements are not met or QC acceptance limits are exceeded; or if analytical samples are compromised, destroyed or lost; or if matrix interference is suspected; or there are any other problems immediately contact:

Bruce Livingston
Metcalf & Eddy Inc.
30 Harvard Mill Square
Wakefield, MA 01880-5371
Phone (978) 224-6437
FAX (978) 245-6293

ATTACHMENT A

Anion	Practical Quantitation Limit (mg/L)
Chloride	0.25
Nitrate	0.10
Nitrite	0.10
Sulfate	0.25

B-2. REFERENCE DOCUMENTS

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Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique

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Abstract

The measurement of dissolved gases such as methane, ethane, and ethylene in ground water is important in determining whether intrinsic bioremediation is occurring in a fuel- or solvent-contaminated aquifer. A simple procedure is described for the collection and subsequent analysis of ground water samples for these analytes. A helium headspace is generated above a water-filled bottle. Gases that are dissolved in the water partition between the gas and liquid phases and equilibrate rapidly. An aliquot of this headspace is analyzed by gas chromatography to determine the gases' concentration in this phase. The concentration of the gas dissolved in the water can then be calculated based on its partitioning properties, as indicated by its Henry's Law constant.

Introduction

Our involvement in ground water sampling and analyses at fuel and/or chlorinated solvent spill sites has required the determination of dissolved methane, ethane, and ethene. These constituents are frequently used to detect biodegradation processes in contaminated aquifers. Presence of the compounds is used to determine whether natural processes of contaminant attenuation and destruction are occurring at a spill site (1). Under anoxic conditions, the bioremediation processes for fuel hydrocarbons shift toward methanogenesis, which forms methane. Under similar conditions, chlorinated solvents such as trichloroethylene are subjected to reduction dechlorination; the final products are ethene and chloride (2).

Techniques for the analysis of dissolved gases in water have included direct aqueous injection into a GC equipped with a flame-ionization detector (FID) (3), membrane inlet mass spectrometry (4), and near-infrared Raman spectroscopy (5). Our need was for a simplified, rapid technique using readily available equipment to analyze ground water samples simultaneously for methane, ethane, and ethene. Previously, we reported on a gas chromatography (GC) headspace technique that emphasized dissolved oxygen (6). In recent years, the emphasis has been on methane and ethene analysis in water.

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Experimental

Materials

Gas standards in helium were obtained from Scott Specialty Gases (Plumsteadville, PA). "Scotty II" cylinders of methane, ethane, and ethene at 10, 100, and 1000 ppm were used in addition to standards of methane at 1, 10, and 20%. High-purity helium was used as the GC carrier and as a source to prepare headspace in the sample bottles.

Instrumentation

Samples were analyzed using a Hewlett-Packard (Palo Alto, CA) 5890 GC equipped with a packed column (6-ft × 1/8-in. Porapak Q, 80/100) and an FID. The carrier gas was high-purity helium at 20 mL/min. The oven was programmed with an initial temperature of 55°C for 1 min, increased at 20°C/min to 140°C, then held for 5 min. The injector was set at 200°C, and the FID was set at 250°C. The FID hydrogen was set at 40 mL/min. and the air flow was set at 400 mL/min. The FID range and attenuation were both at 0. An HP 3396 Series II integrator was used for signal acquisition and peak integration.

Sample collection and preparation

Water samples from field monitoring wells were collected into 60-mL serum bottles (Wheaton, Millville, NJ). Water was gently added down the side of the bottle so as not to agitate or create bubbles, which could strip gases dissolved in the water. The

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bottle was completely filled, and several drops of 1:1 sulfuric acid were then added as a preservative. The bottle was capped and sealed using a 20-mm gray butyl rubber. Teflon-faced septum (Wheaton, Millville, NJ) and 20 mm aluminum crimp seal (Wheaton). The samples were kept cold in an ice chest in transit to the laboratory. Samples were kept at 4°C and analyzed within 14 days of collection.

GC analysis

The GC was calibrated by injecting 300 µL of each of the gas standards as listed in the *Materials* section. The Scotty II cylinders were sampled at atmospheric pressure. This was accomplished by attaching a short piece of 1/4-in. stainless steel tubing with appropriate fittings to the cylinder outlet. At the cylinder outlet, a 1/4-in. "tee" was fitted with a GC septum allowing for insertion of a gas-tight syringe needle into the gas stream. The exit end of the tubing was inserted into a 500-mL beaker of water. As gas "bubbled" through the water, 300 µL of the gas standard was removed and injected into the GC. The retention times for methane, ethene, and ethane were near 0.6, 1.9, and 2.5 min, respectively. Peak area counts generated for each sample were compared with a calibration standard curve.

Samples were allowed to reach room temperature prior to analysis. A headspace was prepared by replacing 10% of the bottled sample (in this case, 6 mL) with helium. To generate headspace in the sample bottle, the bottle was placed upside-down in a three-fingered clamp attached to a ring stand. Next, a 20-gauge needle attached to a 10-mL Luerlok glass syringe set for dead volume was inserted through the septum. Then an 8-cm 20-gauge needle attached to Teflon tubing and a needle valve was inserted through the septum up to the bottom of the bottle. The Teflon tubing was plumbed to a two-stage regulator on a cylinder of high-purity helium, and the helium was passed through the needle at 5 mL/min or less. The helium forced water out of the bottle and into the syringe. When the volume of water in the syringe reached 6 mL, the 8-cm needle was pulled out, followed by the syringe. The sample bottle was shaken on a rotary shaker at 1400 rpm for 5 min to allow the gases to equilibrate between the headspace and liquid phases.

A 500-µL gas-tight syringe with a sampling valve (Dynatech Precision Sampling, Baton Rouge, LA) and equipped with a side-port needle was used to withdraw 300 µL of headspace, which was subsequently injected into the GC. The temperature of the remaining sample was determined. The volume of the sample bottle was measured by filling the bottle with water and pouring the contents into a graduated cylinder.

For purposes of quality control, field trip blanks were included with samples, and 10% of samples were collected in duplicate and analyzed. Prior to analysis and at the end of the day, calibration of the GC was checked by analyzing at least one of the gas standards for each analyte. The GC was considered to be in calibration if the analyzed value was within 15% of that expected. Calibration standards for at least one of the gases were analyzed with a frequency of 10%. Control charts were maintained to monitor variability. In addition, a method blank consisting of a serum bottle of deionized, boiled water was analyzed on a daily basis. This was necessary to correct for background levels of methane. Quantitation limits for methane, ethane, and ethene were 0.001, 0.002, and 0.003 mg/L, respectively. Normally, two samples could be prepared and analyzed per hour.

Calculations

The concentrations of the gases dissolved in the water sample were calculated using the partial pressure of the gas, Henry's Law constant, the temperature of the sample, the volume of the sample bottle, and the molecular weight of the gas. Values for Henry's Law constant were obtained from Perry's *Chemical Engineer's Handbook* (7).

The linear regression equation of the standard curve was used to determine the partial pressure (p_g) of the gas. The concentrations of the gas standards should be converted to their decimal equivalent before generating the curve (i.e., 10 ppm is equivalent to 0.00001, as is 1% to .01). The sample's area count obtained from the chromatogram peak for the analyzed gas was "inserted" into the equation to determine its partial pressure. For methane, it was necessary to subtract the area count obtained from the analysis of a method blank. The following sequence of equations were used to determine the concentration of the dissolved gas.

For the equilibrium mole fraction of the dissolved gas:

$$x_g = p_g/H \qquad \text{Eq 1}$$

where H is Henry's Law constant for the gas. Let n_g represent the moles of gas and n_w the moles of water. Then:

$$x_g = n_g/(n_g + n_w) \text{ and } n_g = x_g(n_g + n_w) \qquad \text{Eq 2}$$

Because 1 L of water equals 55.5 g-moles:

$$n_g = x_g(n_g + 55.5) \qquad \text{Eq 3}$$

and because:

$$n_g x_g << n_g \qquad \text{Eq 4}$$

therefore:

$$n_g = x_g(55.5) \text{ or } n_g = 55.5(p_g/H) \qquad \text{Eq 5}$$

For the saturation concentration of the gas:

$$C = n_g(MW)(1000 \text{ mg/g}) \qquad \text{Eq 6}$$

where MW is the molecular weight of the gas. To correct gas density for temperature:

$$D = MW/(22.4 \text{ L/mole})(ST\ °\text{K}/273°\text{K}) \qquad \text{Eq 7}$$

where ST is the sample temperature. Then:

$$A_h = (\text{mL of headspace})(p_g) = 6(p_g) \qquad \text{Eq 8}$$

where A_h is the milliliters of analyte in the headspace. Then:

$$A_l = (A_h/V)(D)(1000 \text{ mg/g})(1 \text{ L}/1000 \text{ mL}) \qquad \text{Eq 9}$$

where A_l is the analyte in liquid phase and V is the volume of water (bottle volume–headspace volume) in L; using a 60-mL serum bottle with 6 mL of headspace, V equals 0.054 L. Then:

$$TC = A_l + C \quad \text{Eq 10}$$

where TC is the total concentration of analyte in the original sample, in milligrams of gas per liter of water.

Example calculation for methane

Methane will be used as an example of the calculations used for the analysis of dissolved gases. From the analysis of a sample, an area count was determined. This area count was used in the equation for the linear regression of the calibration curve to give its partial pressure (p_g). Parameters used for this example are as follows: the sample area count was 978264, the method blank area count was 2766, Henry's Law constant was 4.13E+4 (at 25°C), the sample temperature was 25°C (298°K), the bottle volume was 60 mL, and the headspace volume was 6 mL.

From the equation of a straight line ($y = mx + b$), the calibration standard responses generated the following curve:

$$p_g = (1.814E{-}9)x - 6.716E{-}6 \quad \text{Eq 11}$$

Therefore, for this sample:

$$p_g = (1.814E{-}9[978264 - 2766]) - 6.716E{-}6 \quad \text{Eq 12}$$

$$= 0.0018$$

Then, using the previous equations:

$$x_g = 0.0018/4.13E{+}4 = 4.269E{-}8 \quad \text{(from Eq 1)}$$

$$n_g = 55.5(4.269E{-}8) = 2.37E{-}6 \quad \text{(from Eq 5)}$$

$$C = (2.37E{-}6)(16)(1000) = 0.038 \text{ mg methane/L water} \quad \text{(from Eq 6)}$$

$$D = (16 g/mole)/([22.4 L/mole][298/273]) = 0.654 \text{ g methane/L} \quad \text{(from Eq 7)}$$

$$A_h = 6(0.0018) = 0.0108 \text{ mL methane} \quad \text{(from Eq 8)}$$

$$A_l = (0.0108 mL/0.054 L)(0.654 g/L)(1 L/1000 mL)(1000 mg/g) = 0.1308 \text{ mg methane/L} \quad \text{(from Eq 9)}$$

$$TC = 0.1308 + 0.038 = 0.169 \text{ mg methane/L water} \quad \text{(from Eq 10)}$$

Results and Discussion

Water samples collected at field sites have been analyzed by the described procedure for over eight years. The method is relatively simple and reliable for the analyses of water samples. A typical chromatogram of a ground water sample from a contaminated site is shown in Figure 1. Table I lists the analytical data for several water samples. Calibration curves were generated using linear regression on a calculator or computer; area counts of the standards were plotted versus their concentrations.

Saturated solutions of methane and ethene in water were prepared with expected concentrations of 22.7 and 131 mg/L, respectively. They were analyzed to determine precision and accuracy. For methane, an average recovery of 87% was obtained for six replicates, the standard deviation was 0.64 mg/L, and the relative standard deviation (RSD) was 3.25%. For ethene, the

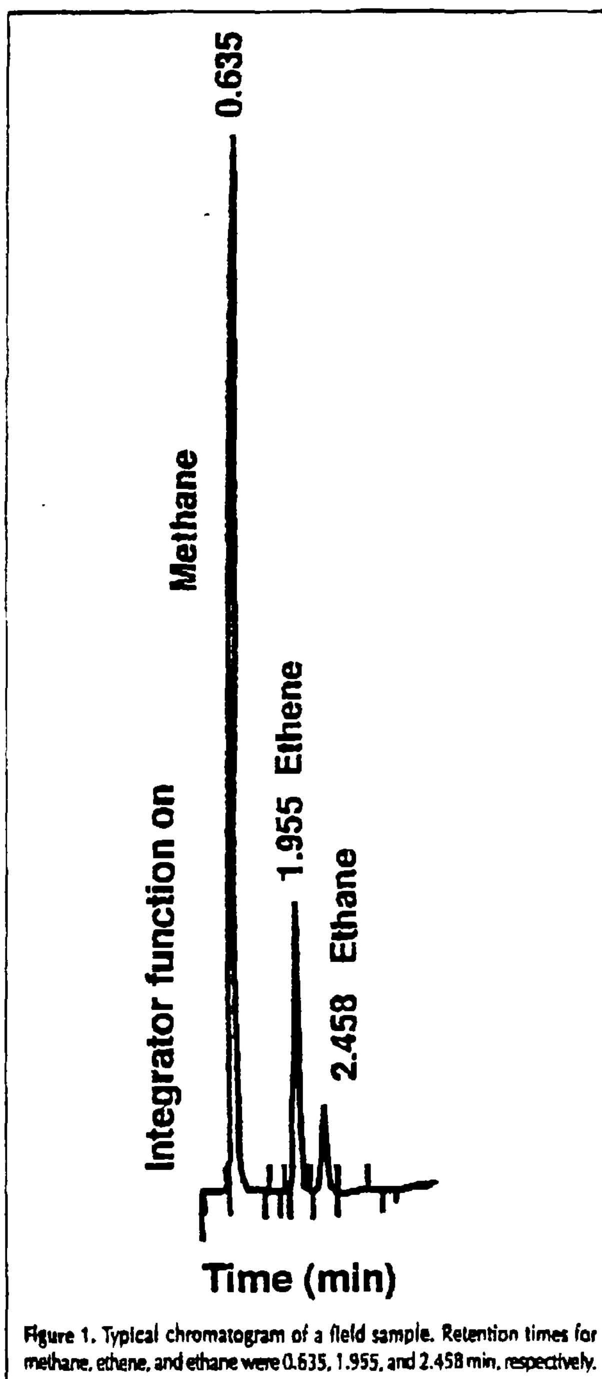

Figure 1. Typical chromatogram of a field sample. Retention times for methane, ethene, and ethane were 0.635, 1.955, and 2.458 min, respectively.

Table I. Analytical Data of Four Samples from a Field Site

Sample	Methane (mg/L)	Ethene (mg/L)	Ethane (mg/L)
RW-10	0.682	undetected	0.027
RW-11	4.753	undetected	0.219
RW-12	1.268	undetected	0.013
RW-12*	1.260	undetected	0.013
RW-13	3.074	0.268	0.112
RW-13†	3.143	0.258	0.107

* Lab duplicate (i.e., headspace of same sample analyzed twice).
† Field duplicate.

average recovery for three replicates was 90%, the standard deviation was 8.8 mg/L, and the RSD was 7.5%. Due to the unavailability of pure ethane in our lab, this exercise was not performed on ethane.

With appropriate GC detectors, this technique should be applicable to other volatile dissolved constituents in water such as carbon dioxide, nitrous oxide, nitrogen, and vinyl chloride. It should be noted that acid preservation should not be used for carbon dioxide analysis because inorganic carbon may be converted to carbon dioxide.

Conclusion

The sample preparation and analytical technique for dissolved methane, ethane, and ethene in ground water has been used successfully on a routine basis in our lab. We have analyzed thousands of ground water samples from numerous contaminated sites. The data from these analyses have been critical in determining the nature of the degradative processes in contaminated aquifers. This technique will continue to be used for routine analyses on water samples from both lab and field studies.

Acknowledgments

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DISSOLVED OXYGEN AND METHANE IN WATER BY A GC HEADSPACE EQUILIBRATION TECHNIQUE

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An analytical procedure is described for the determination of dissolved oxygen and methane in groundwater samples. The method consists of generating a helium gas headspace in a water filled bottle, and analysis of the headspace by gas chromatography. Other permanent gases such as nitrogen, and volatile aliphatic hydrocarbons such as ethane, propane, and butane could also be analyzed. BTX analyses could also be done on the sample. Detection limit for oxygen was 0.1 mg/l and 0.002 mg/l for methane. Good agreement was shown between Winkler titration and the GC-Headspace Equilibration Technique for oxygen analyses by a linear regression coefficient, $R^2 = 0.998$. Oxygen was greatly depleted in some field samples when they were stored for 30 days at 4°C without hydrochloric acid preservation.

KEY WORDS: Dissolved oxygen, GC, headspace, Henry's law, water, BTX.

INTRODUCTION

The concentration of dissolved oxygen, methane and aromatic hydrocarbons (BTXs) are important in evaluating biological activity with aquifers contaminated by petroleum fuels. Analytical methods are available for all three parameters, but each requires tedious separate sampling and analysis protocol.

The two methods most widely used for dissolved oxygen determination in water are Winkler titration and direct probe readings.[1] Both are reliable, but they require appreciable volumes of sample. Some gas chromatography methods for determining dissolved gases from solution are by inert gas purging,[2] *in situ* buried diffusion cells or probes,[3] direct injection into a heated column then separation from the vaporized liquid[4,5] or equilibrium of a solution in a closed bottle with an inert gas headspace.[6] The last approach has advantages of simplicity, reliability, and adaptability to routine analyses of samples.

Henry's law states that the equilibrium value of the mole fraction of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface, or $x_g = p_g/H$, where p_g = equilibrium partial pressure of gas, x_g = mole fraction of dissolved gas, H = Henry's law constant.[7] Henry's law is applicable at low concentrations and low partial pressures of a gas at or below one atmosphere pressure. Solubility data can be obtained from technical handbooks relating H values to temperature.[8,9]

Described is a technique for the analysis of dissolved oxygen and methane in water. The method is also applicable to nitrogen and other volatile aliphatic hydrocarbons. The aliquot of water removed during headpsace generation can be used for volatile organics analyses by EPA methods 601 or 602.[10]

EXPERIMENTAL

Sample Collection and Preparation

Water samples collected in the field or prepared in the lab were placed into 50 ml borosilicate glass Hypo-Vials (Pierce, Rockford, IL) and capped with aluminium seals and Teflon faced butyl rubber septa (Wheaton Scientific, Millville, NJ). Actual bottle volume was near 62 ml. Total volume for each bottle was measured by refilling with water and measuring the quantity. Water samples were added to the bottles down the side to prevent agitation and subsequent oxygen contamination. Also, care was taken to make sure that no air bubbles were entrapped in the sample. Initially, field samples were stored at 4 °C and analyzed by GC within four to eleven days after collection. In a later sample set, 0.15 ml of 1:1 of water:12 M HCl was added as a preservative. Winkler titrations were fixed and analyzed within 10 minutes of collection to conform to EPA guidelines.[10]

Headspace generation was done by placing the sample bottle upside down in a three finger clamp (Figure 1). A 20 gauge needle on a 10 ml Luerlock glass syringe, set for dead volume, was inserted into the sample by penetrating the septum about one centimeter. An 8 cm 22 gauge needle attached to Teflon tubing via a Mininert syringe valve was then inserted through the septa to the top of the water. A flow of five milliliters per minute of high purity helium was passed through the syringe valve. After six milliliters of water was forced from the bottle into the syringe, both needles were removed. The displaced water could then be used for BTX analysis. The sample bottles, which contained ten percent by volume helium headspace, were shaken five minutes at 1400 rpm on a rotary shaker (Tekmar VRX Vibrax, Thomas Scientific, Swedesboro, NJ) to allow gases to equilibrate between the liquid and gas phases. Samples for headspace analysis of both oxygen and methane were taken immediately after the five minute rotary shaking period.

Headspace Analysis

Oxygen GC Parameters—100 μl of the headspace was withdrawn with a 500 μl

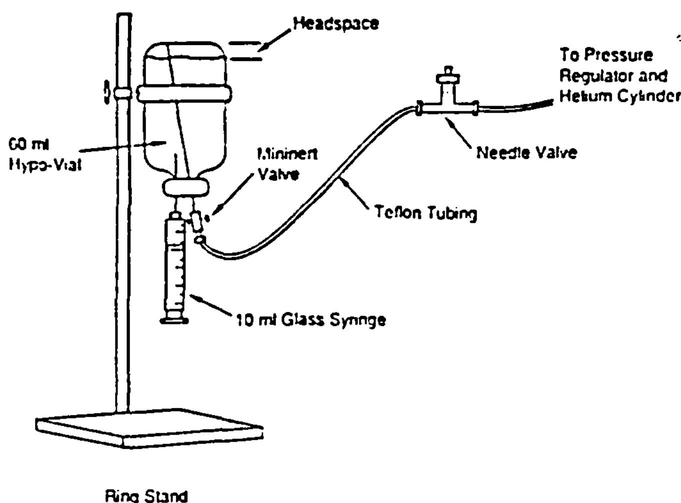

Figure 1 Headspace generation set-up for the headspace equilibration technique.

gas-tight syringe (Precision Scientific, Baton Rouge, LA), and injected into a Varian Vista 6000 GC for oxygen analysis. The column used was 6' × 1/8" stainless steel, 60/80 molecular sieve 5A (Supelco, Inc., Bellefonte, PA). Two columns were used with one each for the analytical and reference side. Carrier gas was high purity helium at 20 mL/min. The column oven was set at 50 °C, injector at 120°, TCD at 120°, and TCD filament at 140°. The TCD Attenuation = 1 and Range = 0.5 mV. Oxygen and argon chromatogram peaks were not resolved by the molecular sieve column at 50 °C oven temperature. Peak retention times in minutes were 0.98 for oxygen and 2.17 for nitrogen. Ambient air was used for calibration. It was assumed to be 21% oxygen. Detection limit for oxygen was 0.1 mg O_2/liter water.

Background Interference—Air equivalent to the syringe needle volume was unavoidably introduced into the GC during injection of the 100 μl headspace sample. Repeated analyses determined that about 2 μl oxygen + argon, which coelute, was introduced with each sample injection. This background may be reduced considerably by pumping the syringe several times into the 6 ml headspace. Confirmation of argon's contribution to the oxygen peak area was done by use of an activated charcoal packed postcolumn. This removed oxygen and left only argon to be measured. During routine analyses, argon was not determined for each sample since reconditioning of the charcoal + molesieve columns required a lengthy time period at elevated temperature. The background correction value for argon was determined by analyzing some water samples containing a slight excess of sodium sulfite, which consumed all the dissolved oxygen. Magnitude of the argon peak is shown in the example calculation.

Calculations—Pressure was assumed to be one atmosphere. Other variables needed for concentration are temperature and the actual volume of each sample bottle. Water samples were allowed to reach room temperature before generation

of headspace and subsequent analysis. Bottle volumes were determined by emptying refilled bottles into a graduated cylinder and recording the volume.

Example calculation from chromatogram peak areas obtained by analyzing air-saturated water at 20°C.

	Peak area
100 μl calibration standard, 21% oxygen	$126450 = A$
Air-saturated water, oxygen	$32759 = B$
2 μl syringe needle contribution	$2360 = C$
Background, argon	$3649 = D$

It is assumed that argon partitions the same as oxygen. Then response due to argon in ambient air is 3649/126450 or 2.88%. Then $E = 1 - 0.0288 = 0.971$.

$$\text{Partial pressure of oxygen, } Pg = \frac{(B-C) \times E}{A-D} \times 0.21 = 0.050.$$

$$\text{Equilibrium mole fraction of dissolved oxygen, } x_g = \frac{Pg}{H}$$

or

$$\frac{0.050}{4.01 \times 10^4} = 1.247 \times 10^{-6} \text{ moles } O_2.$$

Let

$$n_g = \text{moles gas and } n_w = \text{moles water.}$$

Then

$$x_g = n_g/(n_g + n_w) \quad \text{and} \quad n_g = x_g(n_g + n_w).$$

Since one liter of water is 55.51 g-moles,

$$n_g = (n_g + 55.5)(1.247 \times 10^{-6}) \text{ and since } n_g\ (1.247 \times 10^{-6}) \ll n_g,$$

$$n_g \approx 55.5\ (1.247 \times 10^{-6}) \text{ or } 6.92 \times 10^{-5} \text{ moles/liter oxygen.}$$

Saturation concentration of oxygen,

$$C = \frac{(n_g)(32\ \text{gm})(100\ \text{mg})}{(\text{mole } O_2)(g)}.$$

$$= (6.92 \times 10^{-5})(32)(1000) = 2.21 \text{ mg } O_2/\text{liter headspace oxygen.}$$

$$\text{Density} = 22.4\ \text{liter/mole} \times \frac{293\,^\circ\text{K}}{273\,^\circ\text{K}} = 24.04\ \text{liter at } 20\,^\circ\text{C}$$

or

$$\frac{32\ \text{gm/mole}}{24.04\ \text{liter/mole}} = 1.33\ \text{gm } O_2\text{/liter.}$$

Bottle volume = 62.5 ml and headspace volume = 6 ml.

So, 6 × 0.050 = 0.300 ml oxygen and liquid phase oxygen is

$$\frac{0.300\ \text{ml } O_2}{0.0565\ \text{liter } H_2O} \times 1.33 = 7.06\ \text{mg } O_2\text{/liter.}$$

Then liquid phase oxygen and headspace oxygen = 7.06 + 2.21 = 9.27 mg O_2/liter. Standard tables list 20 °C air-saturated water to contain 9.2 mg O_2/liter. This is in good agreement with the value of 9.27 mg O_2/liter shown above. Data listed in Table 2 was obtained from four sets of samples. New calibration units A and D were determined for each set to obtain a computer entry constant of $(E)(0.21)/(A-D)$. Partial pressure of oxygen Pg, for each sample in a set then was determined from $(B-C)$ × the constant.

Methane

GC Parameters—Immediately after oxygen analysis was completed on a sample, analysis for methane was done on the headspace by withdrawing another 100 μl and injecting into a Varian 3300 GC equipped with an FID. Column used was 5′ × 1/8″ stainless steel tubing containing Porapak N 80/100. Carrier gas was high purity helium at 25 mL/minute flow. Hydrogen and air flow for the detector was 30 and 300 mL/minute respectively. The column oven was 160 °C. The injector and detector were both 190 °C. Under these GC conditions, the following retention times in minutes were obtained using a 0.1% "Scotty" hydrocarbon gas standard (Scott Specialty Gases, Plumsteadville, PA): 0.31 for methane, 0.40 for ethane, 0.56 for propane, 0.92 for *n*-butane, 1.64 for pentane, and 3.10 for hexane. Detection limit for methane was 0.002 mg CH_4 per liter water. Since typical air is essentially methane free and good resolution of GC peaks was obtained, no correction was needed.

RESULTS AND DISCUSSION

Water samples prepared in the laboratory or collected at a Michigan field site were analyzed by our described procedure with emphasis placed on dissolved oxygen. Table 1 shows analytical data on a water sample that was saturated by purging with air ("oxygen") and natural gas ("methane").

Some chromatograms obtained for the analysis of water samples are shown in Figure 2. Table 2 lists the analytical results obtained from 26 water samples. The

Table 1 Replicate analyses of saturated water

	Oxygen	*Methane*
Expected	9.2	23.2
Rep A	9.17	19.2
Rep B	8.98	19.2
Rep C	9.22	19.7
Rep D	9.62	18.5
$\bar{x}$	9.25	19.16
Agreement ($\bar{x}$/Expected) × 100	100.5%	83%

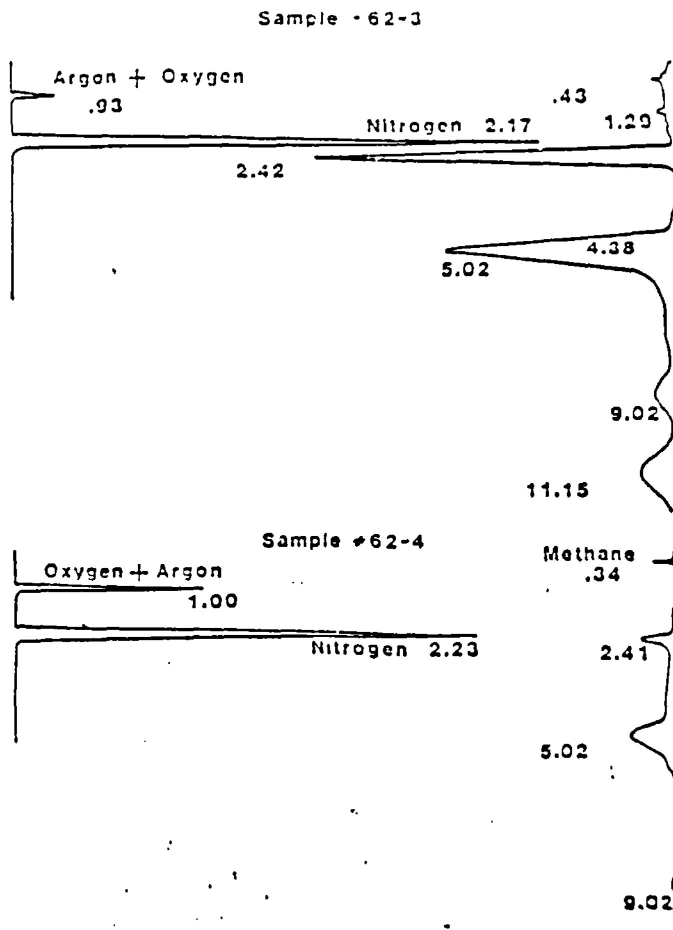

Figure 2 Example chromatograms for two water samples.

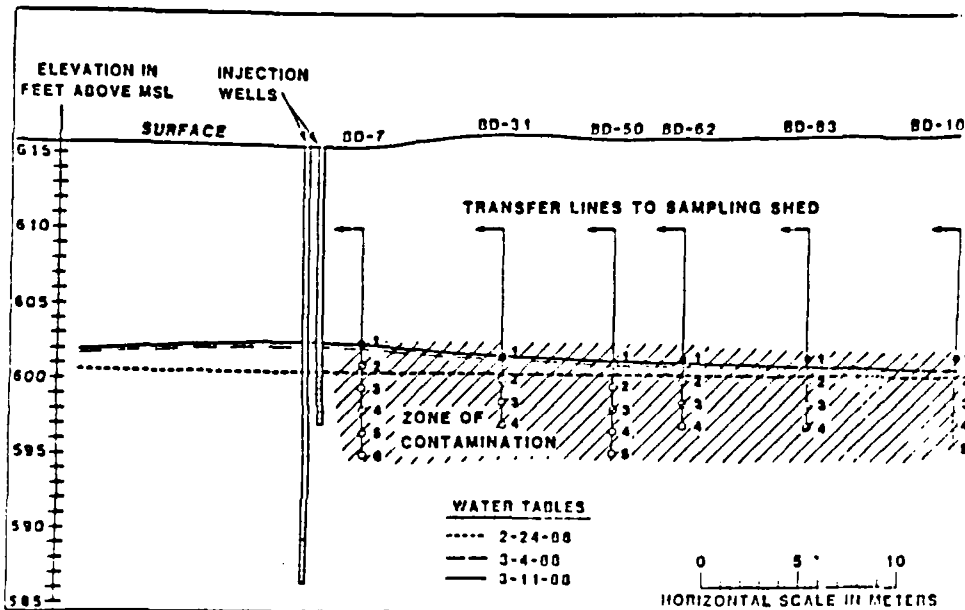

Figure 3 Cross section of pilot scale wells in plume containing gasoline at a remediation site.

first 13 were samples generated in the lab. The rest were collected from an aquifer contaminated with aviation gasoline which was being remediated by injection with water equilibrated with nutrients and pure oxygen. A cross section of the wells are shown in Figure 3. Levels ranged from <0.5 to 32 mg O_2/liter. Methane levels were low where detectable. Aromatic hydrocarbons (BTXs) were determined on the aliquot of headspace-displaced water using a Hewlett-Packard Headspace Sampler and 5890 GC/FID. The Winkler titrations were performed within minutes of collection. The samples labeled "w/HCl" were preserved by adding 0.15 ml of 1:1 water:12 M hydrochloric acid solution. Aquifer samples were taken on 3/11/88 and 5/26/88. Analysis by GC was done on 3/14/88 and 5/31/88.

Acid preservation both extended holding time and maintained integrity of samples. Large oxygen depletions occurred in a 30 day storage test for two of three samples not preserved with HCl (Table 3). A comparison by linear regression through the origin of the two dissolved oxygen methods is shown in Figure 4. A distinct correlation existed between the two methods as indicated by coefficient $R^2 = 0.998$ for 20 sets of real number data after exclusion of less than values.

CONCLUSION

The headspace equilibrium technique was successfully used for routine analyses of dissolved oxygen, methane, and indirectly BTXs. Liquid or solid matrix consti-

Table 2 Dissolved oxygen, methane, and aromatic hydrocarbons in water samples

Sample	Winkler-O_2 mg/l	GC-O_2 mg/l	Methane mg/l	Total[a] BTXs mg/l
1	2.1	2.54, 2.58	—	—
2	2.4	3.58	—	—
3	8.8	9.36, 9.32	—	—
11	<0.5	0.25	—	—
12 replicate of 11	<0.5	0.42	—	—
21	6.9	7.53	—	—
22 replicate of 21	6.9	7.44	—	—
31	7.6	8.00	—	—
32 replicate of 31	7.7	8.16	—	—
33 replicate of 31	7.7	7.87	—	—
41	8.2	8.52	—	—
42 replicate of 41	8.1	8.64	—	—
43 replicate of 41	8.0	8.15	—	—
48A-5	13.6	15.0	0.005	<0.006
48A-5 replicate	14.6	15.1	0.004	<0.006
31-2	<0.5	0.25	0.002	0.073
31-3 w/HCl	<0.5	0.61	0.004	0.045
31-4 w/HCl	31.9	33.1	<0.002	<0.006
48A-3	1.8	1.94	0.002	0.017
62-3	<0.5	0.49	<0.002	0.072
62-4	4.2	3.68	0.004	0.006
50B-2	<0.5	0.34	<0.002	0.0031
50C-2 w/HCl	<0.5	0.71	<0.002	0.038
7A-2-1	5.9	6.35	0.004	<0.006
7B-4-3	2.2	2.64	0.004	<0.006
7A-2-2	10.7	11.3	0.005	<0.006
7A-2-3	10.8	10.0	0.005	<0.006

[a]Includes summation of results for benzene, toluene, ethylbenzene, m,p, and o-xylenes, and 1,2,4-trimethylbenzene.

Table 3 Dissolved oxygen change in field samples after 30 days storage at 4 °C by GC-HET

Initial Winkler mg O_2/l	No HCl mg O_2/l	With HCl mg O_2/l
3.9	<0.1, 0.48	4.52, 4.50
12.2	0.63	11.6, 11.5
5.8	4.95, 5.15	5.74, 6.07

tuents should not interfere with the integrity of the headspace phase. Although the argon chromatogram peak was not separated from the oxygen peak, the additive introduction can be compensated for by reducing D.O. values by a constant. The technique will enable analysis of one bottle of water sample for three chemically different parameters. Because of its convenience and reliability, our headspace equilibrium technique with HCl preservation will be used for routine analysis of dissolved oxygen on samples from both field and lab studies.

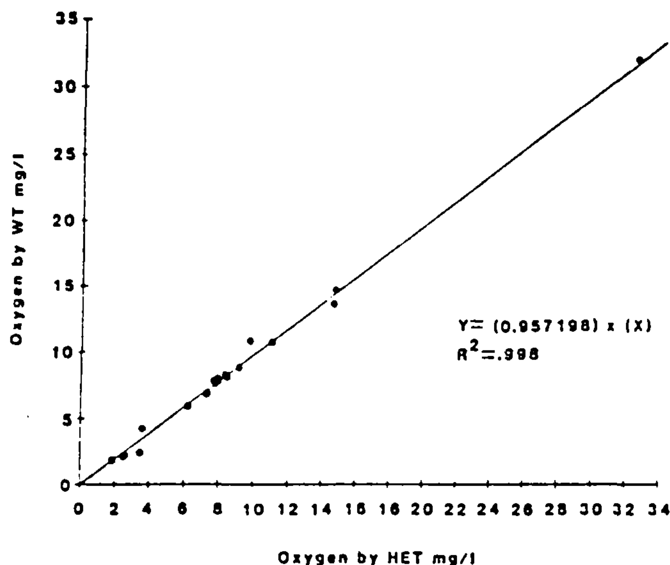

Figure 4 Comparison of dissolved oxygen measurements by Winkler titrations (WT) and headspace equilibrium technique (HET).

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STANDARD OPERATING PROCEDURE

SAMPLE PREPARATION AND CALCULATIONS FOR DISSOLVED GAS ANALYSIS IN WATER SAMPLES USING A GC HEADSPACE EQUILIBRATION TECHNIQUE

DISCLAIMER:

This standard operating procedure has been prepared for the use of the R.S. Kerr Environmental Research Laboratory of the United States Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

1. Purpose: (Scope and Application)

This method is applicable to the preparation of water samples for analysis of the headspace to quantify part-per-million levels of dissolved gases in the water sample. Although this method is specifically for determining methane, ethene, ethane, and nitrous oxide, it has also been used to determine vinyl chloride, nitrogen, oxygen and carbon dioxide in both laboratory and field samples. The number of analyses that can be performed in one eight hour day is approximately 30.

This method is restricted to use by or under the supervision of analysts experienced in sample preparation and in the use of gas chromatography and the interpretation of chromatograms.

2. Summary of Method:

A water sample is collected, in the field or in the laboratory, in a serum bottle and capped using a Teflon faced septum and crimp cap of the appropriate size to fit the bottle. A headspace is prepared using high purity helium. The bottle is shaken for 5 minutes and a sample is taken of the headspace and injected onto a gas chromatographic column where the gaseous components are separated and detected by flame ionization detector or electron capture detector. By using Henry's law, the concentration of the gas in the headspace, the bottle volume, and temperature of the sample, the concentration of dissolved gas in the original water sample can be determined.

3. References:

3.1 Kampbell, D. H., J. T. Wilson, S. A. Vandegrift, Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique, International Journal of Environmental Analytical Chemistry, Volume 36, pp. 249-257, 1991.

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3.4 Perry, J.H., *Chemical Engineer's Handbook*, (McGraw-Hill, New York, 1978), 5th ed.

4. Procedure:

Sample Collection and Preparation:

Water samples should be collected in the field or prepared in the lab by placing the water in a glass bottle. Typically, a 60 milliliter serum bottle is used. Add the water down the side of the bottle so as not to agitate or contaminate the sample. Fill to the top and cap using a butyl rubber Teflon faced septum and the appropriate size aluminum crimp cap. Care should be taken so there are no bubbles in the bottle. Field samples should be fixed with 1:1 hydrochloric acid to a pH less than 2 before they are capped. Do not add acid if carbon dioxide analysis is to be performed since it may convert inorganic carbon to carbon dioxide. Store samples at 4 C and analyze within 14 days of collection.

Remove samples from the refrigerator and allow them to come to room temperature. To generate headspace in the sample bottle, place the bottle upside down in a three finger clamp attached to a ring stand. Next, insert through the septum a 20 gauge needle attached to a 10 ml Luerlock glass syringe set for dead volume. Then insert an 8 cm 20 gauge needle attached to Teflon tubing with needle valve is inserted through the septum to the bottom of the bottle. Th Teflon tubing is attached to a two-stage regulator on a cylinder of high purity helium and the helium is passed through the needle at 5 ml per minute or less.

NOTE: Helium should be allowed to flow through the Teflon tubing and needle for 30 minutes prior to preparation of the first sample, and flow should continue throughout the day.

The helium forces water out of the bottle and into the glass syringe. The amount of water taken out of the bottle should be 10% of the volume of the sample bottle up to the 100 ml size. If a 160 ml serum bottle is used, remove only 10 ml of the water during sample preparation. After the appropriate amount of water has been removed, pull the 8 cm needle out of the septum. Next, pull the syringe from the septum. The sample bottle is then shaken at 1400 rpm on a rotary shaker for 5 minutes to allow the gases to equilibrate between the headspace and the liquid phase. A portion of the headspace is then taken immediately for analysis on the gas chromatograph. Use a 500 microliter gas tight syringe to take a 300 microliter sample of the headspace. This is done by inserting the syringe needle into the septum so that the side port of the needle is in the headspace. Pull the plunger up to the 300 microliter mark. Close the syringe and withdraw the needle from the septum. Inject the syringe's contents into a gas chromatograph for analysis.

The GC conditions for the analysis of methane, ethane, ethene, and nitrous oxide can be found in RSKSOP-147; for carbon dioxide, oxygen, and nitrogen the conditions for the GC are found in RSKSOP-114. After GC analysis is successfully completed, remove the cap from the bottle.

CAUTION: Excessive handling of the sample should be avoided, as this will raise the temperature of the sample.

Record the temperature of the remaining sample using a thermometer, then record the volume of the sample bottle by refilling the bottle and pouring its contents into a Class "A" calibrated to contain (TC) graduated cylinder. Along with the samples a method blank should also be analyzed. The method blank consists of deionized water prepared in the same type of bottle used for the samples. Area count for any detected analyte is subtracted from the area count for each sample. See example calculations.

5. Calculations:

5a. General Equations:

The calculations for dissolved gas concentration involve several steps. In this section, the general steps and equations will be given; in section 5b a specific example for methane will be shown. Parameters needed are partial pressure of the analyte(p_g)(the analyte is the gas in question), Henry's law constant (H), temperature of the sample, volume of the sample bottle, and molecular weight of the analyte.

1) From the analysis of the sample, an area count is obtained. Using this area count and the regression equation of the standard curve, the partial pressure is determined.

NOTE: To determine the regression equation, plot area count versus concentration of the standard gas in the decimal fraction i.e. 10 ppm would be 0.00001 on the curve.

NOTE: In these calculations total pressure is assumed to be equal to 1 atmosphere; therefore, $p_g/p_T = p_g$.

$p_g = m(\text{sample area count}) + b$ Eqn. 1
where p_g = partial pressure of the gas (decimal fraction)
m = slope of the line of the standard curve
b = y-intercept of the line.

2) The equilibrium mole fraction of the dissolved gas, $x_g = p_g/H$ Eqn. 2
where H = Henry's law constant for the gas.

3) Let n_g = moles analyte and n_w = moles water.
Then $x_g = n_g/(n_g + n_w)$ and $n_g = x_g(n_g + n_w)$. Eqn. 3
if $n_g \cdot x_g << n_g$,
then $n_g = x_g \cdot n_w$ or $n_g = n_w(p_g/H)$
therefore, $n_g/V = n_w/V(p_g/H)$ Eqn.4.

4) One liter of water is 55.5 g-moles,
$n_g/V = 55.5 \text{ moles/L}(p_g/H)$

5) Saturation concentration of the gas,
$C = (n_g/V)(MW)(1000 \text{ mg/g})$ Eqn. 5
where MW = molecular weight of the analyte.

6) Density calculation
p = (molecular weight of the analyte)/(22.4 l/mole)(ST in K/273° K)
where p = density
ST = sample temperature

7) $v = bv_{mls} - hv_{mls}(1L/1000mls)$ Eqn. 7
where bv = bottle volume
hv = headspace volume

Then,

8) $A_h = hv_{mls} * p_g$
where A_h = ml of analyte in headspace
then liquid phase analyte (A_l) is

$A_l = (A_h/(v))(p)(1000mg/g)(1l/1000ml)$ Eqn. 8.

Then $TC = A_l + C$
where TC = Total Concentration of analyte in the original sample
A_l = liquid phase analyte from Eqn. 8
C = saturation conc. from Eqn. 5.
The result will be in units of milligrams of gas per liter of water.

5b. Example Calculation

Methane will be used as the example of the calculation for dissolved gas concentration in water. From the analysis of the sample, an area count for methane is determined. This area count is used with the equation for the line of the standard curve, which is determined by analyzing a range (10 - 10,000 ppm CH_4) of methane standards, to obtain the partial pressure.

Parameters for this example calculation are as follows:
sample area count = 978264
method blank area count = 2766
Henry's law constant = 4.13E+4 (at 25 C)
sample temperature = 25 C
bottle volume = 60 ml
headspace volume = 6 ml.

1) For this sample the equation for the line of the standard curve is
pg = 1.814E-9x - 6.716E-6
$\therefore p_g$ = (1.814E-9(978264-2766))- 6.716E-6 Eqn. 1
so, p_g = 0.0018.

2) Using Eqn. 2, x_g = 0.0018/ 4.13E+4 or 4.269E-8 mole CH_4.

3 & 4) Using Eqn. 4 and the value above, n_g/V = (55.5)(4.269E-8) or 2.37E-6 moles CH_4 / liter CH_4.

5) Saturation concentration of CH_4, using Eqn. 5 and the value for n_g/V
C = (2.37E-6)(16)(1000) = 0.038 mg CH_4 / liter H_2O.

6) p = (16g/mole)/((22.4liters/mole)(298/273)) = 0.654 g CH_4 / liter.

7) bv = 60 ml and hv = 6 ml,
v =(60 ml- 6 ml)(1L/1000ml)= 0.054 L.

8) A_h = 6ml . 0.0018 = 0.0108 ml CH_4
A_l = (0.0108 ml/ 0.054 l)(0.654 g/l)(1l/1000ml)(1000mg/g)
A_l = 0.1308 mg CH_4 / l H_2O

9) then TC = A_l + C = 0.038mg/l + 0.131mg/l
TC = 0.169 mg CH_4/liter H_2O.

6. Quality Control:

The use of method blanks, field blanks, field replicates and laboratory duplicates are encouraged. See the SOPs used for the GC analysis for information on analytical quality control.

PRECAUTIONS: No special precautions are necessary aside from those used in good laboratory practice.

NOTE: See appendix for tables of Henry's law constants.

APPENDIX

Section 14

Gas Absorption

BY

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Portions of Section 14, "Chemical Engineers' Handbook," 4th ed., are used in this edition without substantial change. Acknowledgment is made of the authorship of that material by R. E. Emmert and R. L. Pigford.

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GAS ABSORPTION

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INTRODUCTION

Gas absorption is the unit operation in which one or more soluble components of a gas mixture are dissolved in a liquid. The absorption may be a purely physical phenomenon or may involve solution of the material in the liquid followed by reaction with one or more constituents in the liquid solution. The reverse operation called stripping or desorption is employed to transfer one or more volatile components from a liquid mixture into a gas. The following section is concerned primarily with the calculations and the fundamentals underlying those calculations that are necessary to design commercial equipment for carrying out these operations on a continuous basis.

Many materials are amenable to the gas-absorption process. Table 14-1 lists some absorption systems of commercial importance.

The equipment used for continuous contacting of a vapor and a liquid can be a tower filled with solid packing material, an empty tower into which the liquid is sprayed and through which the gas flows, or a tower that contains a number of bubble-cap, sieve, or valve-type plates. In general, the gas and liquid streams flow countercurrent to each other in order to obtain the greatest concentration driving force and therefore the greatest rate of absorption. Occasionally, absorption operations are carried out in spray columns, wetted-wall columns, stirred vessels, or other types of equipment.

There are three broad steps in the design of an absorption or stripping tower:

1. Data on the vapor-liquid equilibrium relations for the system are needed to determine the quantity of liquid necessary to absorb the required amount of the soluble components from the gas, or the quantity of gas necessary to strip the desired amount of the volatile components from the liquid. (Data of this nature are presented in Sec. 3. Additional sources of data specific to the absorption-stripping process are indicated in the text of this section.)

2. Data on the liquid and vapor capacity of equipment of the type being considered for use are needed to determine the necessary cross-sectional area and size of the equipment. (Data on the design of vapor-liquid equipment are included in Sec. 18. Specific problems peculiar to the absorption-stripping process will be covered in this section.)

3. Equilibrium data and material balances are used in combination with fundamental relations peculiar to the absorption-stripping process to calculate the number of equilibrium stages (theoretical plates or transfer units) required for the separation desired. Difficulty of the separation depends both on the degree of recovery required and the equilibrium for the system being considered.

Table 14-1. Gas-absorption Systems of Commercial Importance*

Solute	Solvent	Reagent	Degree of commercial importance		
			High	Moderate	Low
CO_2, H_2S	Water	. . . .	X		
CO_2, H_2S	Water	Monoethanolamine	X		
CO_2, H_2S	Water	Diethanolamine	X		
CO_2, H_2S	Water	Triethanolamine	. . .	. . .	X
CO_2, H_2S	Water	Diaminoisopropanol	. . .	. . .	X
CO_2, H_2S	Water	Methyl diethanolamine	. . .	. . .	X
CO_2, H_2S	Water	K_2CO_3, Na_2CO_3	X		
CO_2, H_2S	Water	NH_3	. . .	X	
CO_2, H_2S	Water	NaOH, KOH	. . .	X	
CO_2, H_2S	Water	K_3PO_4	. . .	X	
CO_2	Propylene carbonate	. . . .	. . .	X	
CO_2	Glycerol triacetate	. . . .	. . .	X	
CO_2	Butoxy diethylene glycol acetate	. . . .	. . .	X	
CO_2	Methoxy triethylene glycol acetate	. . . .	. . .	X	
HCl, HF	Water	. . . .	X		
HCl, HF	Water	NaOH	X		
Cl_2	Water	. . . .	X		
SO_2	Water	. . . .	. . .	. . .	X
SO_2	Water	NH_3	. . .	X	
SO_2	Water	Xylidine	. . .	X	
SO_2	Water	Dimethyl aniline	. . .	X	
SO_2	Water	$Ca(OH)_2$, oxygen	. . .	. . .	X
SO_2	Water	Aluminum hydroxide-sulfate	. . .	X	
NH_3	Water	. . . .	X		
NO_2	Water	. . . .	X		
HCN	Water	NaOH	X		
CO	Water	Copper ammonium salts	X		

* Kohl and Reisenfeld, *Chem. Eng.*, **66**(12), 127 (1959); Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.

Techniques will be presented for determining the necessary time of contact between the flowing streams or the required height of tower.

EQUILIBRIUM DATA*

Equilibrium data necessary for absorption calculations include the solubility of the solute gas in the solvent. In order to completely define the solubility, the data must generally state the temperature, the concentration of the solute gas in the liquid phase, the pressure of the solute gas in the gas phase, and the total pressure on the system. At low pressures the total pressure of the system is not so important, but as the total pressure increases, it can have a more significant effect on gas solubility. Equilibrium data will generally be found in one of three forms: solubility data expressed as either solubility in weight or mole per cent or as the Henry's law constant, pure component vapor pressures, or equilibrium distribution coefficients.

Solubility of Gases in Liquids. Where Henry's law holds, solubility is defined by giving the Henry's law constant and the temperature $H = p_a/x_a$ = atm./mole fraction of solute in solution. For many gases Henry's law holds quite well when the partial pressure of the solute gas is less than 1 atm. For partial pressures of solute gas greater than 1 atm., H is seldom independent of the partial pressure of the solute gas. In these instances H varies with partial pressure, and a given value of H can be used over only a narrow range of pressures. The use of Henry's law constants in obtaining liquid concentrations from gas solubility data is illustrated in the example below.

Example 1. We need to determine how much hydrogen from a gas mixture can be dissolved in 100 lb. of water when the total pressure on the gas is 760 mm. Hg. The partial pressure of hydrogen in the gas mixture is 200 mm. Hg, and the temperature is 20°C.

For partial pressures of hydrogen up to one atmosphere the value of H is 6.83×10^4 at 20°C. ("International Critical Tables," vol. 3, p. 256):

$$x_A = \frac{P_A}{H_A} \qquad (14\text{-}1)$$

$$P_A = 200 \text{ mm. Hg.} = 0.263 \text{ atm.}$$

$$x_A = \frac{0.263}{6.83 \times 10^4} = 0.385 \times 10^{-5}$$

where x_A is the mole fraction of hydrogen in the liquid phase. To calculate the pounds of hydrogen per hundred pounds of water we must convert from a molar to a weight basis. In a two-component system, the following formulation may be used:

$$\left(\frac{x_A}{1 - x_A}\right)\left(\frac{m_A}{m_S}\right)100 = \left(\frac{0.385 \times 10^{-5}}{1 - 0.385 \times 10^{-5}}\right)\left(\frac{2.02}{18.02}\right)100$$

$$= 0.431 \times 10^{-4}$$

Thus, 0.431×10^{-4} lb. (g.) of hydrogen is the maximum that can be dissolved in 100 lb. (g.) of water at 20°C. from a gas mixture under a hydrogen partial pressure of 200 mm. Hg.

Obtaining solubility data for the system under consideration can sometimes be a challenging problem. An idea of the range of solutes and solvents that the chemical engineer may encounter in his absorption problems can be gained by studying Table 14-2. The "International Critical Tables" are always an excellent starting point. Markham and Cobey [*Chem. Rev.*, **28**, 519 (1941)] summarized and critically reviewed gas solubility data available before 1941. Battino and Clever [*Chem. Rev.*, **66**, 395–463 (1966)] review more recent data with emphasis on solvents other than water. Osburn and Markovic (*Chem. Eng.*, pp. 105–108, Aug. 25, 1969) present monographs for determining H at 20°C. when surface tension and molar volume of the solvent are known.

Solubility data for hydrocarbons and oils are usually presented as pure component vapor pressures or as equilibrium constants ($K = y/x$, where y = mole fraction of the solute in the gas phase, and x = mole fraction of the solute in the liquid phase). Through the use of Raoult's law ($pp_A = P_A x_A$, where pp_A = partial pressure in gas phase, and P_A = pure component vapor pressure) vapor pressures can be used to predict solubilities. Extreme care must be taken, however, in attempting to use pure component vapor pressures to predict gas absorption behavior. Both liquid-phase and vapor-phase non-idealities can cause significant deviations from the behavior predicted from pure component vapor pressures combined with Raoult's law. Equilibrium distribution coefficients (K) vary with temperature, pressure, and composition, as discussed in Sec. 13. Assuming that data are available for a given system under similar conditions of temperature and pressure, the K value is a much more reliable tool for predicting vapor-liquid distribution.

*Equilibrium solubility data for specific systems are given in Sec. 3.

Table 14-2. Solutes and Non-aqueous Solvents for Gas Absorption

Solutes	Solvents
Acetylene, C_2H_2	Acetic acid (glacial), $C_2H_4O_2$
Air	Acetic anhydride, $C_4H_6O_3$
Ammonia, NH_3	Acetone, C_3H_6O
Bromine, Br_2	Amyl alcohol, $C_5H_{12}O$
Carbon dioxide, CO_2	Aniline, C_6H_7N
Carbon monoxide, CO	Benzene, C_6H_6
Chlorine, Cl_2	Bromobenzene, C_6H_5Br
Ethane, C_2H_6	Carbon disulfide, CS_2
Ethylene, C_2H_4	Carbon tetrachloride, CCl_4
Hydrogen, H_2	Chlorobenzene, C_6H_5Cl
Hydrogen chloride, HCl	Chloroform, $CHCl_3$
Hydrogen sulfide, H_2S	Ethyl acetate, $C_4H_8O_2$
Methane, CH_4	Ethyl alcohol, C_2H_6O
Methyl chloride, CH_3Cl	Ethylene chloride, C_2H_4Cl
Nitric oxide, NO	Ethyl ether, $C_4H_{10}O$
Nitrogen, N_2	Methyl acetate, $C_3H_6O_2$
Nitrous oxide, N_2O	Methyl alcohol, CH_4O
Oxygen, O_2	Nitrobenzene, $C_6H_5NO_2$
Sulfur dioxide, SO_2	Propyl alcohol, C_3H_8O
Etc.	Propylene, C_3H_6
	Toluene, C_7H_8
	Etc.

Vapor-pressure data are available in Sec. 3 of this handbook for a number of materials. Dreisbach ("Pressure-Volume-Temperature Relationships of Organic Compounds," Handbook Publishers, Sandusky, Ohio, 1952) presents an exhaustive compendium of vapor-pressure data for various families of hydrocarbons.

Values of the equilibrium distribution coefficient K are given by Katz and Hachmuth [*Ind. Eng. Chem.*, **29**, 1072 (1937)]. See also Sherwood and Pigford ("Absorption and Extraction," McGraw-Hill, New York, 1952) and an extensive series of articles by Sage et. al. (*Ind. Eng. Chem.*, 1934 to date). In addition, the "Engineering Data Book" of the Natural Gas Processors Association in both the 1957 and 1966 editions presents significant data, as do Winn [*Petrol. Refiner*, 33(4), 132 (1954)], Hadden and Grayson [*Hydrocarbon Process. Petrol. Refiner*, **40**(9), 207 (1961)], and Grayson and Streed (6th World Petroleum Congress, 1963). Chao and Seader [*A.I.Ch.E. J.*, **7**, 598–605 (1961)] have presented a wide-ranging correlation which takes into account both the vapor-phase and liquid-phase non-ideality effects up to pressures in the neighborhood of 1500 p.s.i.a.

In the case of absorption combined with chemical reaction, the engineer must be particularly careful that the data he uses include the effect of incomplete stripping on the absorption process. Burns and Maddox [*Oil Gas J.*, **65**, 112 (Sept. 18, 1967)] used data from Kohl and Reisenfeld ("Gas Purification," McGraw-Hill, New York, 1960) to solve in detail a problem illustrating the effect of mutual solubilities and incomplete stripping on absorption of H_2S and CO_2 in an amine-water solution.

MASS-TRANSFER FUNDAMENTALS

Homogeneous Diffusion. When a homogeneous material—either gas, liquid, or solid—contains two or more components whose concentrations vary from point to point, there is a tendency for

transfer of mass to take place in such a way as to cause the concentrations to become uniform. This phenomenon is associated with the thermal agitation of molecules; in a region where molecules of one kind are concentrated, there is a greater tendency for molecules of this kind to escape than to enter the region. The net rate of diffusion N_A of material A at a point in a stationary fluid is found from experiment as well as from theory to be proportional to the concentration gradient at the point,

$$N_A = -D_v \frac{\partial c}{\partial s} \tag{14-2}$$

where c = concentration, s = distance, and D_v = diffusivity. If c is expressed in g.-moles/cu. cm., s in cm., and D_v in sq. cm./sec., then the units of N_A are g.-moles/(sec.)(sq. cm.). The rate of diffusion is rapid in gases and much slower in liquids.

In the application of the theory of diffusion, it is often desirable to employ integrated forms of the diffusion equation, rather than Eq. (14-2), which is applicable only at a single point. Treatments of the use of Eq. (14-2) for steady-state diffusion are given by Treybal ("Mass-transfer Operations," McGraw-Hill, New York, 1955) and by Sherwood and Pigford ("Absorption and Extraction," McGraw-Hill, New York, 1952).

Several integrated forms of Eq. (14-2) are presented below, along with integrated expressions for the analogous equation for unsteady-state diffusion [Eq. (14-6)]. All these relationships are based on the assumption that diffusivity is not dependent on concentration. This assumption is good for gaseous systems (except at high pressure) and for dilute liquid solutions, but may not be true for concentrated solutions. Dependence on concentration is the result of (1) change of mobility of the solute with concentration because of a change in average molecule size of the medium, and (2) deviations of the mixture from ideal behavior [Wilke, *Chem. Eng. Progr.*, **45**, 218 (1949)].

Steady-state Equimolal Counterdiffusion. This case is typified by the mixing of two gases in a confined space and by counterdiffusion of two components in distillation. For this case, assuming D_v constant, Eq. (14-2) integrates to

$$N_A = \frac{D_v}{B_F}(c - c_i) = \frac{D_v}{RTB_F}(p - p_i) = \frac{D_v P}{RTB_F}(y - y_i) = k_G(y - y_i) \tag{14-3}$$

where concentration c can be expressed alternatively in terms of partial pressure p or mole fraction y. In c.g.s. units, N_A = g.-moles/(sec.)(sq. cm.); D_v = sq. cm./sec.; c = g.-moles/cc.; p = atm.; B_F = layer thickness, cm.; R = universal gas constant, 82.06 (cc.)(atm.)/(g.-mole)(°K.); T = temperature, °K.; P = absolute pressure, atm.; k_G = gas-phase mass-transfer coefficient, g.-moles/(sec.)(sq. cm.)(mole fraction). Subscript i refers to the interface. Other consistent sets of units may be used with suitable adjustments in the numerical value of R.

Steady-state Diffusion of One Component through a Second Stagnant Component. Examples are absorption of a soluble gas from a second insoluble gas and absorption of a slightly soluble gas into a non-volatile liquid. The integrated equation is

$$N_A = \frac{D_v P}{RTB_F}\frac{y - y_i}{(1 - y)_{lm}} = k_{G'}(y - y_i) \tag{14-4}$$

where $k_{G'}$ = gas-phase mass-transfer coefficient corrected for inert gas concentration = $k_G(p_{BM}/P)$; p_{BM} = partial pressure of inert gas; lm = logarithmic mean; other symbols as defined above.

Steady-state Diffusion of One Component through a Stagnant Multicomponent Mixture. According to Wilke [*Chem. Eng. Progr.*, **46**, 95 (1950)], Eq. (14-1) may be applied to this case provided an effective diffusivity of the diffusing species A is defined as

$$D_{vA'} = \frac{1 - y_A}{(y_B/D_{vAB}) + (y_C/D_{vAC}) + (y_D/D_{vAD}) + \cdots} \tag{14-5}$$

Unsteady-state Diffusion. Diffusion does not lead to conditions of constant concentration gradient unless a steady state is established. It is therefore often necessary to consider the change of concentration c with time t caused by diffusion as represented by the differential equation

$$\frac{\partial c}{\partial t} = D_v \frac{\partial^2 c}{\partial s^2} \tag{14-6}$$

where s = distance and D_v = diffusivity.

Solutions of this equation for a diversity of physical situations are given by Crank ("Mathematics of Diffusion," Oxford, New York, 1956) and by Jost ("Diffusion," Academic Press, New York, 1952). Figure 14-1 shows the change in average concentration $\bar{c}$ of a component in a slab, cylinder, or sphere as a function of time t when a constant surface concentration c_i is provided to permit that component to diffuse (*i.e.*, where the relative resistance to diffusion in the surrounding medium is negligible). The solution is analogous to that for the conduction of heat under the influence of a temperature gradient. Figure 14-1 is applicable only when the material in which the diffusing component is dispersed is not internally mixed and retains its shape during the period of time involved. This is not the case in packed or plate-column gas absorbers but may be so in some spray, descending-liquid-sheet, or falling-jet devices if the fluid is stagnant or in laminar flow.

Diffusion with Flow. If fluid motion is laminar, transfer of mass between adjacent layers of fluid takes place purely by *molecular diffusion*. If the velocity pattern of the flow is known, it is sometimes possible to calculate the over-all rate of mass transfer into the moving fluid by the use of the basic equations of molecular diffusion. If the flow is turbulent, however, such calculations are generally impossible, since the laws that govern the transport of matter by turbulent mixing of small volumes of fluid are not well enough understood. Prediction of mass-transfer rates under such conditions is based on empirical methods.

Laminar Flow, Uniform Velocity. If the velocity of a flowing stream is uniform over a very deep region (thickness $B_F >> \sqrt{D_v t}$) in which diffusion is taking place, Eq. (14-6) is applicable. It has

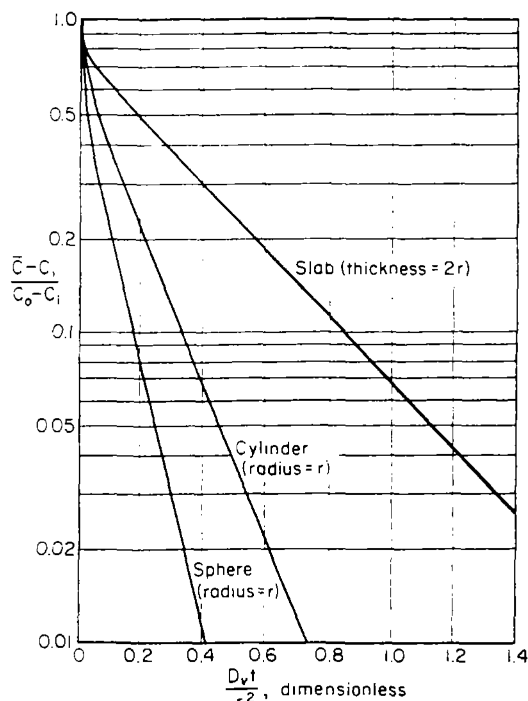


FIG. 14-1. Unsteady-state diffusion: c_0 = uniform initial concentration, c_i = constant surface concentration, $\bar{c}$ = average concentration. (*Crank, "Mathematics of Diffusion," Oxford, Clarendon, 1956.*)

FIG. 14
t = ti
transf
(1954)

been integrated by Higbie [*Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935)] to give

$$k_L = \frac{2}{\sqrt{\pi}}\sqrt{\frac{D}{t}} \qquad (14\text{-}7)$$

where k_L = liquid-phase mass-transfer coefficient, g.-moles/(sec)(sq. cm.)(g.-moles/cc.); D = diffusivity, sq. cm./sec.; t = time, sec.

This equation closely represents gas-absorption data taken with falling laminar jets of liquid [Cullen and Davidson, *Trans. Faraday Soc.*, **53**, 113 (1957); Nijsing and Kramers, *Chem. Eng. Sci.*, **10**, 88 (1959); Scriven and Pigford, *A.I.Ch.E. J.*, **4**, 439 (1958)], and with liquid layers descending in short wetted-wall columns when rippling is absent [Vivian and Peaceman, *A.I.Ch.E. J.*, **2**, 437 (1956)]. In the latter case, Eq. (14-7) predicts rates up to 15 per cent higher than those observed, possibly because of end effects [Lynn, Straatemeier, and Kramers, *Chem. Eng. Sci.*, **4**, 49, 58, 63 (1955)]. Equation (14-7) is applicable only when the diffusing molecules have not completely penetrated the fluid layer in question. It thus must be restricted to short contact times (less than about 1 sec. for freely descending water layers).

Laminar Flow, Parabolic Velocity Distribution. Gas absorption or desorption is frequently accomplished into or from liquid layers flowing down a solid surface, as in a wetted-wall column or over packing. The liquid layer in this case moves with maximum velocity at its free surface and zero velocity at the solid surface. The fully established velocity profile appears to be nearly parabolic between these limits as long as ripples are absent, according to the investigation of Grimley [*Trans. Inst. Chem. Engrs.* (*London*), **23**, 228 (1945)].

Pigford (Ph.D. Thesis, University of Illinois, 1941) solved the differential equation for this case with the result shown in Fig. 14-2. The dashed line on Fig. 14-2 represents Eq. (14-7) for a uniform velocity profile. Figure 14-2 has been shown to represent wetted-wall column data, as long as rippling is absent, by Emmert and Pigford [*Chem. Eng. Progr.*, **50**, 87 (1954)] and Lynn, Straatemeier, and Kramers (*loc. cit.*). Both investigations avoided rippling by using wetting agents in the liquid or by employing short wetted-wall columns (less than 4 in.).

Ripples are normally present on the surface when the Reynolds number for the liquid exceeds a critical value $(N_{Re})_c$ given by the relation (Grimley, *loc. cit.*)

$$\frac{\gamma^3\rho}{\mu^4 g} = 0.3(N_{Re})_c^{1.8} \qquad (14\text{-}8)$$

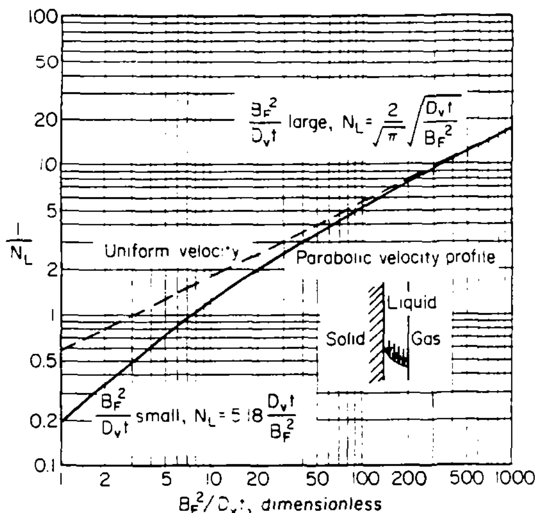


Fig. 14-2. Absorption or desorption to descending liquid: t = *time of surface exposure.* N_L = *number of liquid-phase transfer units.* [*Emmert and Pigford, Chem. Eng. Progr.*, **50**, 87 (1954).]

where γ = surface tension, ρ = density, μ = viscosity, g = gravitational constant, all in consistent units. For water, the critical Reynolds number is about 25. Turbulence within the liquid layer begins at a Reynolds number of about 1200 [Thomas and Portalski, *Ind. Eng. Chem.*, **50**, 108 (1958)]. Up to the Reynolds number at which actual turbulence sets in, surface rippling can be avoided by adding certain wetting agents or by employing such a short distance of flow that surface instability does not develop.

Two auxiliary relations are needed for using Fig. 14-2. Film thickness B_F can be calculated using the Nusselt equation,

$$B_F = \left(\frac{3\mu\Gamma}{g\rho^2}\right)^{1/3} \qquad (14\text{-}9)$$

which has been confirmed experimentally by Fallah, Hunter, and Nash [*J. Soc. Chem. Ind. London*, **53**, 368 (1934)] and others, even when rippling occurs. In Eq. (14-9), Γ = flow rate per unit of peripheral distance. Contact time t between gas and liquid is fixed by the velocity u of the free liquid interface, which is related to the average film velocity by the relation

$$u = \tfrac{3}{2}u_{avg} \qquad (14\text{-}10)$$

Turbulent Flow. When a fluid phase through which mass transfer is occurring is in turbulent motion, transfer takes place by the relatively fast process of eddy diffusion. Experimental measurements of eddy diffusivities at very high Reynolds numbers in ducts have revealed values in gases as high as 100 times the molecular diffusivities [Sherwood and Woertz, *Trans. Am. Inst. Chem. Engrs.*, **35**, 1034 (1939)], and in liquids as high as 100,000 times the molecular diffusivities [Kalinske and Pien, *Ind. Eng. Chem.*, **36**, 220 (1944)]. The following approximate equation can be fitted to the data of Sherwood and Woertz for gases in turbulent flow through ducts:

$$E\rho = 6.6 \times 10^{-5}N_{Re} + 0.2 \qquad (14\text{-}11)$$

where eddy diffusivity E is expressed in sq. ft./hr., and density of the medium ρ is in lb./cu.ft.

When a fluid moves over either a liquid or a solid surface, the eddy motion that causes mass transfer also causes heat transfer and fluid friction because of transfer of heat and momentum, respectively. The close similarity among the transfer of mass, heat, and momentum is brought out by the Reynolds analogy, which states that, when heat, mass, and momentum are supplied to the fluid in corresponding ways, the following ratios are equal:

$$\frac{\text{Rate at which mass is transferred from the solid surface}}{\text{Total rate at which the component, in excess of the interfacial concentration, flows past the surface}}$$

$$= \frac{\text{rate of heat transfer from the solid surface}}{\text{total rate at which heat, measured above the surface temperature, flows past the surface}}$$

$$= \frac{\text{rate of momentum loss due to friction}}{\text{total momentum of stream that flows past the surface}}$$

In terms of mathematical symbols, these statements may be written as

$$\frac{k_G(y - y_i)}{G_M(y - y_i)} = \frac{h(T - T_i)}{c_pG(T - T_i)} = \frac{g_c\tau_0}{\rho V^2} \qquad (14\text{-}12)$$

or

$$\frac{k_G}{G_M} = \frac{h}{c_pG} = \frac{f}{2} \qquad (14\text{-}13)$$

where k_G = gas-phase mass-transfer coefficient, lb.-moles/(hr.)(sq. ft.)(mole fraction); G_M = molar mass velocity, lb.-moles/(hr.)(sq. ft.); y = mole fraction; h = heat-transfer coefficient, B.t.u./(hr.)(sq. ft.)(°F.); c_p = specific heat, B.t.u./(lb.)(°F.); G = mass velocity, lb./(hr. sq. ft.); T = temperature; g_c = gravitational conversion factor, (lb. mass)(ft.)/(lb. force)(sec.^{2}); τ_0 = surface frictional stress, lb. force/sq. ft.; ρ = density, lb./cu. ft.; V = velocity, ft./sec.; f = friction factor.

Experimental data for mass transfer into gas streams agree approximately with Eq. (14-12) when the value of the Schmidt number $\mu/\rho D_v$ is near 1 and when the friction factor is calculated from the

"skin" friction. For flow through a straight tube, or along a flat plate that is parallel to the direction of flow, the pressure drop is due entirely to skin friction against the surface. On the other hand, the frictional force exerted on an immersed body, such as a sphere or a cylinder placed perpendicular to the direction of flow, is due in part to fluid pressure exerted on the front face of the body that is not counterbalanced by equal and opposite pressure on the rear face. Equation (14-11) does not apply in such cases if the friction factor is calculated from the total drag, including the "form" drag.

The limited conditions under which the Reynolds analogy can be expected to hold may be seen from the equations that govern the rate of transfer through a turbulent fluid [von Kármán, *Trans. Am. Soc. Mech. Engrs.*, **61**, 705 (1939)]. For mass transfer the assumption is that

$$N_A = N_m + N_t = -(D_v + E)\left(\frac{dc}{ds}\right) \qquad (14\text{-}14)$$

and for friction

$$\tau = \tau_m + \tau_t = -\left(\frac{\mu + \rho E_v}{g_c}\right)\left(\frac{du}{ds}\right) \qquad (14\text{-}15)$$

where N_m = rate of mass transfer due to molecular diffusion, and N_t = rate of mass transfer due to turbulent mixing, lb.-mole/(hr.)(sq. ft.); D_v = molecular diffusivity, and E = eddy diffusivity for mass transfer, sq. ft./hr.; c = concentration, lb.-moles/cu. ft.; s = distance, ft.; τ_m = shear stress due to molecular motion, and τ_t = shear stress due to turbulent mixing, lb. force/sq. ft.; μ = viscosity, lb./(ft.)(hr.); ρ = density, lb./cu. ft.; E_v = eddy kinematic viscosity, sq. ft./hr.; g_c = gravitational conversion factor, (lb. mass)(ft.)/(lb. force) (hr.^{2}); u = velocity, ft./hr.

In Eqs. (14-14) and (14-15) the first term in the parentheses gives the rate of transfer of mass or of momentum due to molecular diffusion, and the second term gives the rate due to turbulent mixing. The Reynolds analogy follows from these equations if one assumes that (1) either $\mu/\rho D_v = 1$ or both D_v and μ/ρ are much smaller than E and E_v, (2) $E = E_v$, and (3) N_A/τ is independent of position s. Under these conditions the concentration and velocity fields are similar and, just as Reynolds assumed, mass and momentum are transferred in the same way.

The Reynolds analogy thus fails to account for the mass-transfer resistance of the region of fluid near the solid (or liquid) boundary, in which transfer occurs principally by molecular motion. Colburn [*Trans. Am. Inst. Chem. Engrs.*, **29**, 174 (1933)] and Chilton and Colburn [*Ind. Eng. Chem.*, **26**, 1183 (1934)] showed empirically that the resistance of this laminar sublayer can be expressed by the following modification to the Reynolds analogy:

$$\frac{k_G}{G_M}\left(\frac{\mu}{\rho D_v}\right)^{2/3} = j_M = \frac{h}{c_p G}\left(\frac{c_p \mu}{k}\right)^{2/3} = j_H = \frac{f}{2} \qquad (14\text{-}16)$$

for turbulent flow through straight tubes and across plane surfaces, and

$$j_M = j_H \le \frac{f}{2} \qquad (14\text{-}17)$$

for turbulent flow around cylinders, where j_M = mass-transfer factor; j_H = heat-transfer factor; k = thermal conductivity, B.t.u./(hr.)(ft.)(°F.); other symbols as defined immediately above. Experimental data show Eqs. (14-16) and (14-17) to be approximately valid for values of $(\mu/\rho D_v)$ between 0.5 and 2, whereas the Reynolds analogy is substantially in error at these extremes.

Flow over Packings. Higbie [*Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935)] advanced the theory that, in a packed absorption tower, the liquid flows across each packing piece in laminar flow and is mixed with other liquid meeting it at the points of discontinuity between packing elements. Danckwerts [*Ind. Eng. Chem.*, **43**, 1460 (1951)] proposed a modification of this theory. It allows for eddy motion in the liquid that continually brings masses of fresh liquid from the interior to the surface, where they are exposed to the gas for a finite length of time before being replaced. Danckwerts assumed that any element has an equal chance of being replaced regardless of its age. The Higbie model leads to Eq. (14-7), where t is the time for flow across a single packing piece. The Danckwerts model gives

$$k_L = \sqrt{D s_r} \qquad (14\text{-}18)$$

where s_r is the fractional rate of surface renewal.

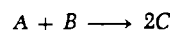
Note that both models predict a dependence on $\sqrt{D}$. Few data exist to confirm the validity of this effect of diffusivity. Sherwood and Holloway [*Trans. Am. Inst. Chem. Engrs.*, **36**, 39 (1940)] have compared absorption rates in a packed tower for CO_2, O_2, and H_2 and found them to vary nearly as $\sqrt{D}$. Danckwerts [*A.I.Ch.E. J.*, **1**, 456 (1955)] gives a more thorough treatment of the merits of these models as well as others. No theoretical model has yet proved adequate for predicting absorption rates in packed columns, and empirical correlations (see Sec. 18) are recommended.

Diffusion with Reaction. Gas absorptions are often conducted using a solvent which is reactive with the gas or which contains a solute that is reactive. When a chemical reaction takes place in the liquid with the absorbed molecules as they are diffusing, the concentration profiles are altered; hence, the rate of absorption is affected. For a liquid that is stagnant or undergoing rodlike laminar flow, unsteady-state diffusion equations akin to Eq. (14-6) can be written to represent diffusion with reaction of various types. Certain of these differential equations have been solved representing the following cases:

1. Absorption accompanied by first-order reaction [for irreversible reaction, see Danckwerts, *Trans. Faraday Soc.*, **46**, 300 (1950); for reversible case, see Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952]:

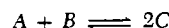
$$A \rightleftharpoons C$$

2. Absorption accompanied by very fast second-order reaction (Danckwerts, *loc. cit.*; Sherwood and Pigford, *op. cit.*):



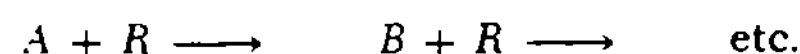
$$A + B \longrightarrow 2C$$

3. Absorption accompanied by finite-rate reversible second-order reaction [Perry and Pigford, *Ind. Eng. Chem.*, **45**, 1247 (1953); **49**, 1400 1957)]:



$$A + B \rightleftharpoons 2C$$

4. Simultaneous absorption of two or more gases which react rapidly with a component in the liquid [Roper, Hatch, and Pigford, *Ind. Eng. Chem., Fund. Quart.*, 1, 144 (1962)]:



$$A + R \longrightarrow \qquad B + R \longrightarrow \qquad \text{etc.}$$

5. Two gases that dissolve in an inert medium and then react with each other (Roper, Hatch, and Pigford, *loc. cit.*).

Absorption with First-order Reaction. Figure 14-3 shows the relation predicted for first-order reaction. The ordinate k_L/k_L^0 is the ratio of mass-transfer coefficients with and without reaction and thus represents the enhancement due to reaction. Both coefficients are averaged over time period t. The first-order reaction-rate constant is k_1 sec.$^{-1}$, and K is the equilibrium constant. Approximate experimental confirmation of the upper line of Fig. 14-3 has been

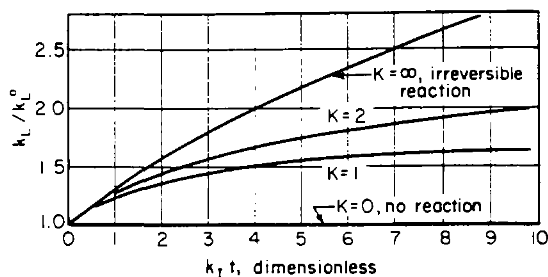


Fig. 14-3. Absorption with first-order reaction. (*Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.*)

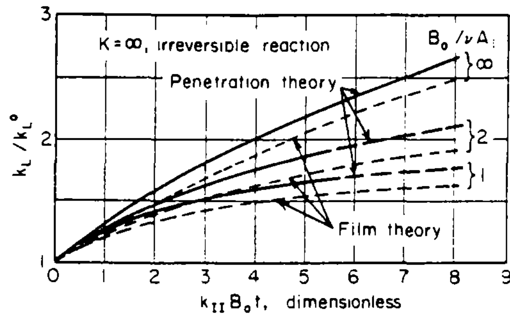


FIG. 14-4. Absorption with second-order irreversible reaction: k_{II} = second-order reaction-rate constant, liters/(g.)(mole-sec.); B_0 = initial concentration of dissolved reagent, g.-moles/liter; t = time, sec.; ν = stoichiometric coefficient; A_i = concentration of dissolving gas at liquid interface, g.-moles/liter. [*Perry and Pigford, Ind. Eng. Chem.*, **45**, 1247 (1953); **49**, 1400 (1957).]

obtained for absorption of CO_2 into alkaline buffer solutions by Danckwerts and Kennedy [*Trans. Inst. Chem. Engrs. London) Suppl.*, **32**, S49, S53 (1954)], using a rotating-drum apparatus, and by Nijsing and Kramers ("Chemical Reaction Engineering," pp. 81–89, Pergamon Press, London, 1958), using a short wetted-wall column. No adequate data are available to test the allowance the theory makes for effect of the reverse reaction.

Absorption with Second-order Reaction. Although the computational methods needed to provide a similar treatment for second-order reaction have been described by Perry and Pigford *loc. cit.*), solutions have been obtained only for a limited range of the variables of interest. Figure 14-4 shows the results of Perry and Pigford's computations for an irreversible reaction ($K = \infty$) and compares these with the predictions of the film (steady-state) theory of van Krevelen and Hoftijzer [*Rec. Trav. Chim.*, **67**, 563 (1948)]. The film theory, less representative of the actual physical behavior, nevertheless predicts only a slightly lesser degree of enhancement of the absorption coefficient because of reaction for the irreversible case. Until computations for the unsteady-state problem have been extended to cover wider ranges of the parameters, the theory of van Krevelen and Hoftijzer (modified to account for the effect of diffusivity as indicated by the unsteady-state theory) is recommended for use. Figure 14-5 shows the results of this theory so modified.

For very fast reactions, that is, when $k_{II}B_0t/(D_B/D_A)(B_0/\upsilon A_i) > 10$, the enhancement of the mass-transfer coefficient can be closely approximated by [Danckwerts, *Trans. Faraday Soc.*, **46**, 300 1950)]

$$\frac{k_L}{k_L^0} = \frac{1 + (D_B/D_A)(B_0/\upsilon A_i)}{(D_B/D_A)^{0.5}} \qquad (14\text{-}19)$$

where k_L/k_L^0 is the ratio of mass-transfer coefficients with and without reaction; k_{II} = second-order reaction-rate constant, liters/(g.-mole)(sec.); B_0 = initial concentration of dissolved reagent, g.-moles/liter; A_i = concentration of dissolving gas at liquid interface, g.-moles/liter; υ = stoichiometric coefficient relating the number of moles of B reacting with 1 mole of A; D_A = diffusivity of dissolving gas A, sq. cm./sec.; D_B = diffusivity of dissolved reagent, sq. cm./sec.

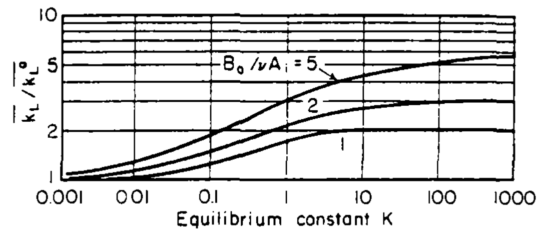
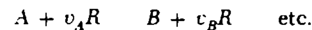


FIG. 14-6. Effect of reversibility on absorption with second-order reaction. (*Pigford, A.I.Ch.E. Meeting, Philadelphia, June* 24, 1958.)

When several soluble gases ($A, B, C, \ldots$) dissolve simultaneously and diffuse to a moving reaction boundary in the liquid, where they all react very quickly with a single reagent R by the simultaneous reactions,



$$A + \upsilon_A R \qquad B + \upsilon_B R \qquad \text{etc.}$$

Eq. (14-19) should be replaced by (Roper, Hatch, and Pigford, *loc. cit.*)

$$\frac{k_L a}{k_L^0 a} = \sqrt{\frac{D_A}{D_R}} \left[1 + \frac{1}{(\upsilon_A A_i/R_0)\left(\frac{D_A}{D_R}\right) + \left(\frac{\upsilon_B B_i}{R_0}\right)\left(\frac{D_B}{D_R}\right) + \cdots} \right] \qquad (14\text{-}20)$$

Symbols are analogous with those of Eq. (14-19). When $D_A > 2D_B$, a more exact solution is to be preferred, and reference to the original paper is recommended.

Both Eq. (14-19) and Fig. 14-5 apply only to irreversible reactions ($K = \infty$). The effect of reversibility can be accounted for by using Fig. 14-6, which, like Eq. (14-19), was derived for very fast reactions but which may also be used as an approximation for slower reactions. Equation (14-19) has been approximately confirmed by Emmert (Ph.D. Thesis, University of Delaware, 1954), who studied absorption of CO_2 in aqueous monoethanolamine in a short wetted-wall column, and more closely by Nijsing and Kramers (Dissertation, Delft, 1957), who studied the absorption of CO_2 in NaOH and KOH solutions in a wetted-wall column.

Absorption of Two Reacting Gases. Roper, Hatch, and Pigford (*loc. cit.*) have obtained a theoretical solution for the case where two absorbing gases react with each other. Their results are given in Fig. 14-7*A*, *B*, *C*. Figure 14-7*C* represents the case of a pseudo-first-order reaction ($B_0/\upsilon A_i = \infty$), where the interfacial concen-

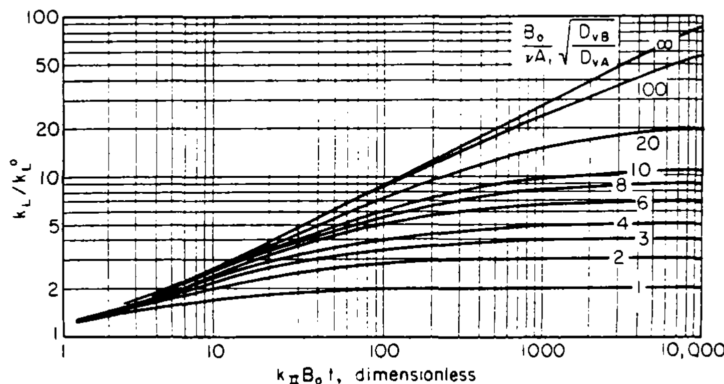


FIG. 14-5. Absorption with very fast second-order reaction.

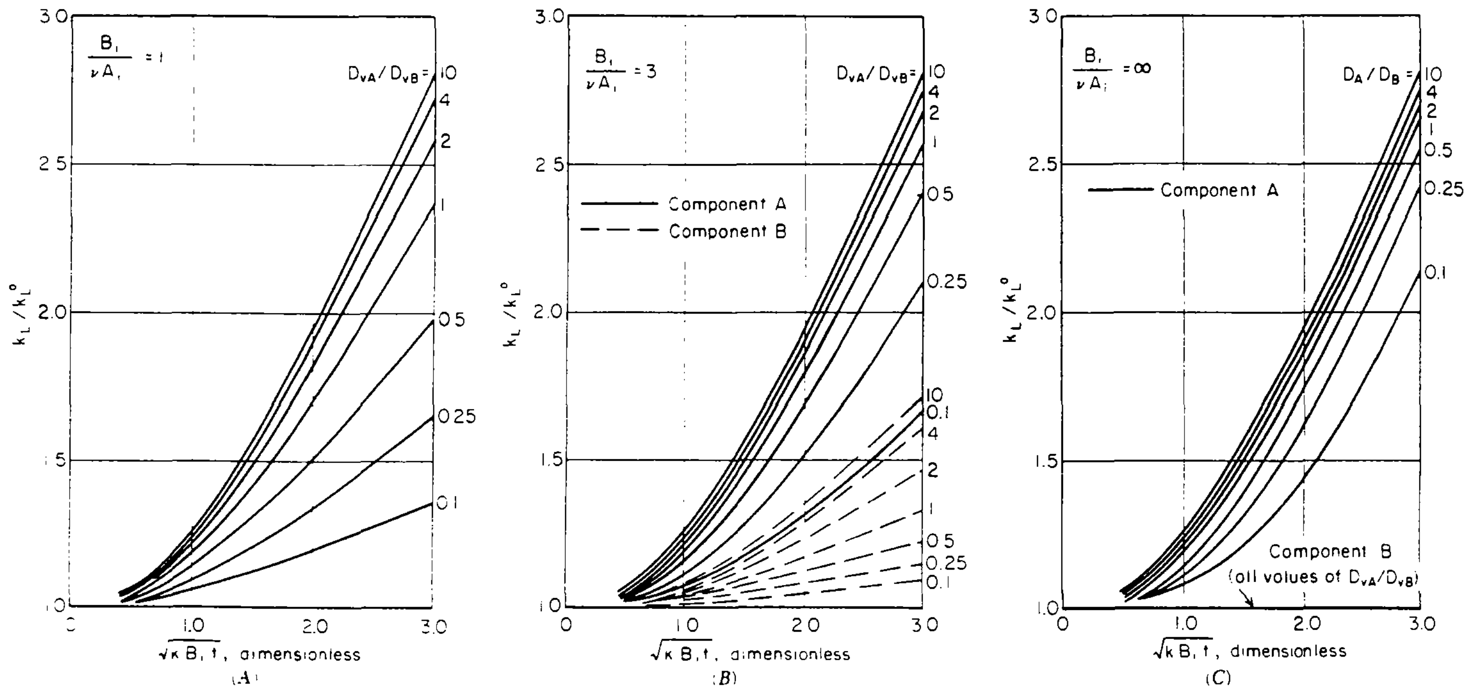


Fig. 14-7. Absorption of two reacting gases: k_L/k_L^0 applies to either *A* or *B*. [*Roper, Hatch, and Pigford. Ind. Eng. Chem., Fund. Quart.*, 1, 144 (1962).]

tration of component *B* far exceeds that of component *A*. In Fig. 14-7*A* the value of k_L/k_L^0 applies to both components *A* and *B*. In Fig. 14-7*B* separate curves are given for each component. In Fig. 14-7*C*, k_L/k_L^0 for component $B = 1$ for all values of time and diffusivity ratio.

Hatch and Pigford [*Ind. Eng. Chem., Fund. Quart.*, 1, 209 (1962)] describe an experimental study in which CO_2 and NH_3 simultaneously dissolve in water and react with each other. Their results confirm the aforementioned theory for the pseudo-first-order case.

Mass Transfer between Phases. When material is transferred from one phase to another across an interface that separates the two, the resistance to mass transfer in each phase causes a concentration gradient in each, as shown in Fig. 14-8. The concentrations of the diffusing material in the two phases immediately adjacent to the interface are generally unequal, even if expressed in the same units, but are usually assumed to be related to each other by the laws of thermodynamic equilibrium, as discussed previously.

Rate of transfer varies with time and may be expressed, at least for the laminar sublayer, by the Higbie or Danckwerts equations [Eqs. (14-7) and (14-18)] which predict that the rate of transfer is proportional to the difference between the bulk concentration and the concentration at the interface. Thus

$$N_A = k_L(x - x_i) = k_G(y_i - y) \qquad (14\text{-}21)$$

where N_A = mass-transfer rate, lb.-moles/(hr.)(sq. ft.); k_L = liquid-phase mass-transfer coefficient, and k_G = gas-phase mass-transfer coefficient, lb.-mole/(hr.)(sq. ft.)(mole fraction); x = mole fraction in bulk liquid phase; x_i = mole fraction in liquid at interface; y = mole fraction in bulk gas phase; y_i = mole fraction in gas at interface.

This equation may be used to find the interfacial concentrations corresponding to any set of values of x and y, provided that the ratio of the individual coefficients is known. Thus

$$\frac{y_i - y}{x - x_i} = \frac{k_L}{k_G} = \frac{L_M H_G}{G_M H_L} \qquad (14\text{-}22)$$

where L_M = molar liquid mass velocity, lb.-moles/(hr.)(sq. ft.); G_M = molar gas mass velocity, lb.-moles/(hr.)(sq. ft.); H_L = height of a transfer unit based on liquid-phase resistance, ft.; H_G = height of a transfer unit based on gas-phase resistance, ft.

Equation (14-22) may be solved graphically if a plot is made of the equilibrium vapor and liquid compositions, and a point is located representing the bulk concentrations x and y on this same diagram. A construction of this type is shown in Fig. 14-9.

In the design of equipment the rate of mass transfer must be estimated from known or predicted values of the transfer coefficients and the bulk concentrations. This may be done by solving

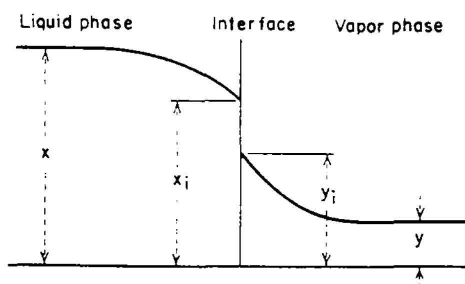


Fig. 14-8. Distribution of concentrations near an interface.

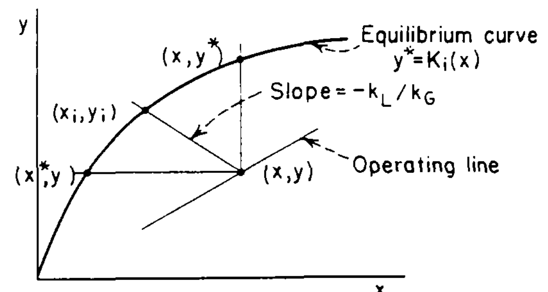


Fig. 14-9. Location of equilibrium concentrations for a point in a countercurrent tower.

Eq. (14-22) simultaneously with the equilibrium relation $y_i = K_i(x_i)$ to obtain y_i and x_i. The rate of transfer may then be calculated from Eq. (14-21).

If the equilibrium relation $y_i = K_i(x_i)$ is sufficiently simple, *i.e.*, if a plot of y_i vs. x_i is a straight line, not necessarily through the origin, the rate of transfer is proportional to the difference in the bulk concentration in one phase and the concentration in that same phase which would be in equilibrium with the bulk concentration in the other phase. One such difference is $y^* - y$, and another $x - x^*$. In this case there is no need to solve for the interfacial compositions, as may be seen from the following derivation: Since

$$N_A = k_G(y_i - y) = k_L(x - x_i) = K_G(y^* - y) \quad (14\text{-}23)$$

where K_G = over-all gas-phase mass-transfer coefficient and y^* = vapor composition in equilibrium with x.

$$\frac{1}{K_G} = \frac{1}{k_G}\left(\frac{y^* - y}{y_i - y}\right) = \frac{1}{k_G} + \frac{1}{k_G}\left(\frac{y^* - y_i}{y_i - y}\right)$$

$$= \frac{1}{k_G} + \frac{1}{k_L}\left(\frac{y^* - y_i}{x - x_i}\right) \quad (14\text{-}24)$$

in view of Eq. (14-22). If the equilibrium curve is a straight line, the term in parentheses is the slope m. Thus

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \quad (14\text{-}25)$$

If the units of driving force on which k_L is based are liquid-phase concentrations expressed in lb.-moles of solute/cu. ft. of liquid, and the units of k_G are partial pressures in atmospheres, rather than mole fractions, Eq. (14-25) becomes

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{m_c k_L} \quad (14\text{-}26)$$

where m_c is the Henry's law coefficient, lb.-moles/(cu. ft.)(atm.).

When the equilibrium curve is not straight, there is no logical basis for use of an over-all transfer coefficient. Calculation of the rate of transfer in such cases must be made by solving for the interfacial compositions, as described above. A true average value of m for use in Eq. (14-25) cannot be calculated, since the value used must represent the relation between concentrations in equilibrium at the interface and depends, therefore, on the ratio k_L/k_G.

If the rate of transfer from the over-all concentration difference based on liquid compositions $x^* - x$ is to be calculated, the appropriate over-all coefficient K_L is related to the individual coefficients by the equation

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G} \quad (14\text{-}27)$$

or

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{m}{k_G} \quad (14\text{-}28)$$

As in the case of Eq. (14-25), these equations apply only when the equilibrium line is straight.

Experimentally observed rates of mass transfer in diffusional operations equipment are often expressed in terms of over-all transfer coefficients, even when the equilibrium lines are curved. This procedure is purely empirical, since theory indicates that in such cases the rates of transfer may not vary in direct proportion to $x - x^*$ at all concentration levels, although the rates may be proportional to the concentration difference in each phase taken separately, $x - x_i$ and $y_i - y$.

In most types of diffusional operations equipment, such as packed or spray towers, just what interfacial area is available for mass transfer cannot be determined. For this reason experimentally observed rates of transfer are customarily reported in terms of transfer coefficients based on a unit volume of the apparatus rather than on a unit of interfacial area. Such volumetric coefficients are designated as K_Ga, k_La, etc., where a represents the interfacial area per unit of volume of the apparatus. Experimentally observed variations in the values of volumetric coefficients due to variations in flow rates, type of packing, etc., may be due as much to changes in the value of a as to changes in k. Calculation of the over-all coefficient from the individual coefficients is made by means of the equations

$$\frac{1}{K_Ga} = \frac{1}{k_Ga} + \frac{m}{k_La} \quad (14\text{-}29)$$

$$\frac{1}{K_Ga} = \frac{1}{k_Ga} + \frac{1}{m_ck_La} \quad (14\text{-}30)$$

$$\frac{1}{K_La} = \frac{1}{k_La} + \frac{1}{mk_Ga} \quad (14\text{-}31)$$

$$\frac{1}{K_La} = \frac{1}{k_La} + \frac{m_c}{k_Ga} \quad (14\text{-}32)$$

Because of the wide variation in the solubilities of gases in liquids, the variation in the value of m from one system to another sometimes has an important effect on the type of equipment that should be used for contacting. If, for example, an insoluble gas such as oxygen is to be dissolved in water, the large value of m for this system would cause the liquid-phase part of the over-all resistance to be extremely large in a spray tower, where the poor fluid mixing obtained in the liquid phase might result in a small value of k_L. On the other hand, this line of reasoning must be applied with caution, since gases with different solubilities are ordinarily absorbed under different conditions of operation; and the effect on the over-all resistance of changes in the solubility is therefore partly counterbalanced by changes in the specific resistance as the flow rates are changed.

Height Equivalent to a Transfer Unit (H.T.U.). Frequently the values of individual coefficients of mass transfer vary so rapidly with flow rates that the quantity obtained by dividing each coefficient by the flow rate of the phase to which it applies is more nearly constant than the coefficient itself. The quantity obtained by this division is called [Chilton and Colburn, *Ind. Eng. Chem.*, **27**, 255 (1935)] the height of one transfer unit, since it expresses in terms of a single length dimension the height of apparatus required to accomplish a separation of standard difficulty.

The number of over-all gas-phase transfer units N_{OG} required for changing the composition of the vapor stream from y_1 to y_2 is

$$N_{OG} = \int_{y_2}^{y_1} \frac{dy}{y^* - y} \quad (14\text{-}33)$$

for equimolal diffusion, and

$$N_{OG} = \int_{y_2}^{y_1} \frac{(1 - y)_f dy}{(1 - y)(y^* - y)} \quad (14\text{-}34)$$

for diffusion in one direction only, where y = mole fraction in gas and y^* = mole fraction in gas in equilibrium with liquid. Convenient solutions of these equations are given later.

The number of transfer units required for a given separation is closely related to the number of theoretical plates or stages required to carry out the same separation in plate-type or stagewise apparatus. In terms of H.T.U.'s the equations that express the addition of resistances become [Colburn, *Trans. Am. Inst. Chem. Engrs.*, **35**, 211 (1939)]

$$H_{OG} = H_G + H_L\left(\frac{mG_M}{L_M}\right)\frac{(1 - x)_f}{(1 - y)_f} \quad (14\text{-}35)$$

and

$$H_{OL} = H_L + H_G\left(\frac{L_M}{mG_M}\right)\frac{(1 - y)_f}{(1 - x)_f} \quad (14\text{-}36)$$

where H_{OG}, H_{OL}, H_G, and H_L = heights of transfer units, ft., based on, respectively, over-all gas-phase resistance, over-all liquid-phase resistance, gas-phase resistance, and liquid-phase resistance; $(1 - y)_f$ = logarithmic mean of $1 - y$ and $1 - y^*$; $(1 - x)_f$ = logarithmic mean of $1 - x$ and $1 - x^*$; x = mole fraction in liquid; x^* = mole fraction in liquid in equilibrium with gas; y, y^*, m, G_M, and L_M as defined earlier.

The following relations between the transfer coefficient and the values of H.T.U. apply, where the prime indicates that the coefficient is corrected for inert gas concentration by the factor p_{BM}/P

(p_{BM} = partial pressure of inert gas, P = total absolute pressure):

$$H_{OG} = \frac{G_M}{K'_G a(1 - y)_f} \tag{14-37}$$

$$H_G = \frac{G_M}{k'_G a(1 - y)_f} \tag{14-38}$$

$$H_{OL} = \frac{L_M}{K_L a(1 - x)_f} \tag{14-39}$$

$$H_L = \frac{L_M}{k_L a(1 - x)_f} \tag{14-40}$$

Presence of the factor $(1 - y)_f$ is due to the fact that, in the diffusion of one gas through a second stationary layer of insoluble gas, the resistance to diffusion varies with the concentration of the stationary gas, approaching zero as the concentration of this gas approaches zero. The factor $(1 - x)_f$ cannot be justified on the basis of kinetic theory for the liquid phase but is included in the equations on the assumption that diffusion through liquids is similar to that through gases. (In binary distillation, where both components diffuse simultaneously, both these factors should be omitted.)

H.E.T.P. (*height equivalent to one theoretical plate*) is another quantity that is used occasionally to express the efficiency of a packing material for carrying out a separation. Experimental data should be reported as H.T.U.'s rather than H.E.T.P.'s, since the former quantity is theoretically correct for equipment, such as packed columns, in which mass is transferred by a differential rather than a stepwise action. If equilibrium and operating lines are parallel, *i.e.*, $mG_M/L_M = 1$, H.E.T.P.'s and H.T.U.'s are equal. If the equilibrium and operating lines are straight, but not parallel,

$$\frac{H_{OG}}{\text{H.E.T.P.}} = \frac{(mG_M/L_M) - 1}{\ln (mG_M/L_M)} \tag{14-41}$$

DESIGN CALCULATIONS

Outline of General Design Procedure. For determination of the number of variables that must be specified in order to fix a unique solution for the design of an absorber, the engineer can use the same phase-rule-type approach discussed in Sec. 13 for distillation. The variables specified will normally include: (1) gas flow rate and composition; (2) operating pressure and pressure drop across the absorber; (3) desired degree of recovery of one or more solutes. In addition, the designer frequently has some degree of freedom concerning the solvent to be employed. Generally, the solvent must be recovered, and the recovery system ordinarily is considered an integral part of the absorption process design.

The designer ordinarily is required to determine (1) the best solvent; (2) the best gas velocity through the absorber (the vessel diameter); (3) the height of the vessel and its internal members, *e.g.*, the depth and type of packing or the number of trays; (4) the optimum rate of solvent circulation through the absorber; (5) temperatures of streams entering and leaving the absorber, and the quantity of heat to be removed to account for heat of solution and other heat effects; (6) the pressures at which the absorber and regenerator will operate; (7) the mechanical design of the absorption and regeneration towers. This section is concerned with all these choices, except the last which is discussed in Sec. 18.

Selection of Solvent. The ideal solvent is non-volatile, free, non-corrosive, stable, non-viscous, non-foaming, and non-flammable, and has infinite solubility for the solute. Unfortunately, ideal solvents seldom are found, and so choice is usually based on the most desirable of many alternatives. Where such a choice is possible, preference would be given to a liquid with very high solubility for the solute. The exit gas is usually saturated with solvent, and solvent loss may be costly; so low-cost solvents may be chosen over more expensive ones of higher solubility or lower volatility.

Selection of Vapor-Liquid Equilibrium or Solubility Data. Sources of solubility and vapor-liquid equilibrium data have been discussed earlier in this section. Accurate and correct data are very important because they determine the solvent circulation rate necessary to achieve the specified solute recovery. Experimental data on the particular system of interest are always best. In the absence of specified experimental data, generalized correlations must be referred to.

Calculation of Liquid-Gas Ratio. The minimum solvent rate is easily calculated, utilizing the entering-gas composition, and assuming saturation in the solute-rich solvent leaving the absorber. Estimation of the effect of heat of solution of the gas on exit solvent temperature may be necessary. Values of latent and specific heats and heat of solution (at infinite dilution) are given in Sec. 3.

The actual solvent circulation rate will be 25 to 100 per cent greater than the minimum. It will be arrived at on the basis of economic considerations, guided and corrected by judgment and experience.

In some packed-tower applications involving very soluble gases or vacuum operation, the minimum quantity of solvent required for absorption may not be sufficient to keep the packing surface thoroughly wet, leading to poor distribution of the liquid. There is no sharp dividing line of flow rate above which a packing material becomes thoroughly wet and below which flow distribution is poor. However, there is a minimum wetting rate described by Morris and Jackson ("Absorption Towers," Butterworth, London, 1953). The minimum wetting rate (M.W.R.) is computed as V_L/a, where V_L = volumetric liquid flow, cu. ft./(hr.)(sq. ft. of tower cross section); and a = packing surface area, sq. ft./cu. ft. When the net flow of solvent to the packed column is smaller than M.W.R., recirculation of liquid over the packing may be desirable, even at the expense of a reduced mean driving force.

Selection of Equipment. Usually packed columns are chosen for corrosive materials, for low pressure drop, for pilot-plant or small-scale operations (say less than 2 ft. in diameter), and for liquids that foam badly. Plate columns are preferred for large-scale operations (they are cheaper), for low liquor rates (where packing would be inadequately wetted), and where internal cooling is desired.

In packed towers the type of packing is chosen for its mechanical strength, resistance to corrosion, cost, capacity, and efficiency. Packings found to be most economical and generally useful are 1- to 2-in. ceramic or carbon rings ($\frac{1}{2}$-in. size for columns under 4 in. in diameter), 1-in. saddles, 3-in. spiral or partition rings, drip-point tile, and wood grids.

Pressure Drop for Both Plate and Pipe Columns. Methods for estimating pressure drop are given in Sec. 18. Pressure drop at flooding for commonly used packing is around 2 in. of water per foot of packing height. For operation at about 50 per cent of flooding, the pressure drop is roughly $\frac{1}{2}$ in. water per foot of height. These values are convenient to keep in mind for operating control.

Height of Column. Height of the column is primarily dependent on the degree of removal of solute from the gas. To compute the economic recovery, as well as the eventual height, the designer must have values of plate efficiency (plate column) or height of a transfer unit (packed column). Data on plate efficiencies are given in Secs. 13 and 18. For packed columns, over-all values of H.T.U. are used if available for the conditions of the problem; otherwise, separate gas-liquid values of H.T.U. are estimated as shown in Sec. 18 and combined as shown below.

Computation of Tower Height. Methods for estimating the height of the active section of an absorber needed to effect a given separation are based on the use of rate expressions for representing mass transfer at a point on the interface, and on material balances to represent the changes in bulk composition in the two phases that flow past each other. Combination of such expressions leads to an integral expression for the number of transfer units, or to very closely related equations for numbers of theoretical plates. The paragraphs immediately below set forth convenient methods for using such equations.

Rate of Absorption for Packed Columns. Figure 14-10 shows a section of a packed absorption column, together with the nomenclature that will be used in developing the equations which follow. In the differential section dz we can equate the rate at which solute is lost from the gas phase to the rate at which it is transferred

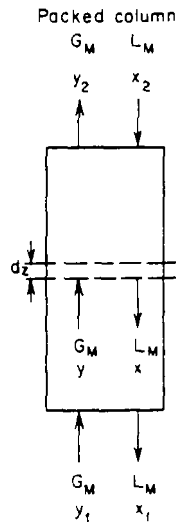


FIG. 14-10. Material balance, operating, and equilibrium lines.

through the gas phase to the interface.

$$-d(G_My) = -G_{M'}\frac{dy}{(1-y)^2} = k_GaP\frac{y-y_i}{(1-y)_{lm}}dz \quad (14\text{-}42)$$

where G_M = molar mass velocity of the gas stream, $G_{M'}$ = molar superficial mass velocity of the inert gas, k_G = gas-phase mass-transfer coefficient, a = interfacial area per unit of packed volume (smaller than the packing surface S), P = absolute pressure; y_i = mole fraction solute in the gas at the interface, and $(1-y)_{lm}$ = logarithmic mean of the mole fraction inert gas in the bulk stream $(1-y)$ and that at the interface $(1-y_i)$. The height of packing z needed to accomplish a specified change in gas composition is

$$Z = G_{M'}\int_{y_2}^{y_1}\frac{(1-y)_{lm}\,dy}{k_GaP(1-y)^2(y-y_i)} \quad (14\text{-}43)$$

This expression applies in the most general case and is more complex than normally required. It must be used when the mass-transfer coefficient varies from point to point, as may happen if the gas velocity varies through the absorber, or when the gas is concentrated with solute. Interfacial concentrations (y_i and x_i) are taken to be in equilibrium.

Equation (14-43) can sometimes be simplified by assuming that y_i equals zero, as would be the case when the solute reacts upon absorption to yield a reactant with negligible solute partial pressure. Frequently, changes in gas flow rate and mole fraction of inert gas are so small that terms such as $(1-y)$ and $(1-y)_{lm}$ can be neglected or included in only an approximate way. The following sections illustrate some of these simplified procedures.

Obtaining Driving Force by Material Balances. A steady-state material balance around the differential section of the packed column shown in Fig. 14-10 gives

$$d(G_My) = d(L_Mx) \quad (14\text{-}44)$$

$$G_{M'}\frac{dy}{(1-y)^2} = L_{M'}\frac{dx}{(1-x)^2} \quad (14\text{-}45)$$

where L_M = molar mass velocity of the liquid stream, $L_{M'}$ = molar mass velocity of the inert liquid component, and x = mole fraction in liquid. The reader should realize that x and y in Eqs. (14-42) to (14-45) are taken to be the average concentrations of solute in the liquid and vapor, respectively, within the differential packing height dz.

Integrating Eq. (14-45) around the upper section of packing gives

$$G_{M'}\left(\frac{y}{1-y}-\frac{y_2}{1-y_2}\right) = L_{M'}\left(\frac{x}{1-x}-\frac{x_2}{1-x_2}\right) \quad (14\text{-}46)$$

Equation (14-45) is the differential form and Eq. (14-46) is the integral form of the so-called operating line around the upper section of packing. When the mole fractions y and x are sufficiently small (dilute solutions), the total molar flows G_M and L_M will be very nearly constant. For this case the operating line equation is

$$G_M(y-y_2) = L_M(x-x_2) \quad (14\text{-}47)$$

Equation (14-47) is simply a material balance equation giving the relationship between the compositions of the gas and liquid streams at any point in the column. Figure 14-11 shows a plot of the equation in a typical case. Also shown in Fig. 14-11 is the typical equilibrium relationship between interfacial compositions y_i and x_i. Once y is known as a function of x along the operating line, y_i can be found at corresponding points from the equilibrium line. The operating line in Fig. 14-11 is straight only under the conditions for which Eq. (14-47) applies, *i.e.*, G_M and L_M constant. The case of curved operating lines has been treated by several authors including Mostafa [*Brit. Chem. Eng.*, **13**, 5 (May, 1968)].

Transfer Units. The local mass-transfer coefficient k_GaP in Eq. (14-43) has the units of length. It is called the height of a transfer unit for the gas phase and is symbolized by H_G. When the local coefficient is proportional to the first power of the point gas velocity G_M, the term $G_{M'}/k_GaP(1-y)$ may be taken as a constant. As pointed out in the development of Eq. (14-24), the driving force $y-y_i$ across the gas phase can be computed from the over-all driving force $y-y^*$ when the equilibrium line is straight. Since $(y-y_i)/(y-y^*)$ is equal to H_G/H_{OG}, the equation for the packed height of the column can be written in two ways:

$$Z = H_G\int_{y_2}^{y_1}\frac{(1-y)_{lm}\,dy}{(1-y)(y-y_i)} = H_GN_G \quad (14\text{-}48a)$$

where N_G = number of transfer units, based on gas-phase resistance, and

$$Z = H_{OG}\int_{y_2}^{y_1}\frac{(1-y)_{lm}\,dy}{(1-y)(y-y^*)} = H_{OG}N_{OG} \quad (14\text{-}48b)$$

where H_{OG} = height of a transfer unit, and N_{OG} = number of transfer units, based on over-all gas-phase resistance. Equation (14-48b) is the more useful equation in a practical sense; it requires either empirical knowledge of or computation of H_{OG} by adding estimated values of H_G and H_L; it does not, however, require knowledge of or estimation of interfacial compositions as does Eq. (14-48a).

A further convenient simplification of Eqs. (14-48a) and (14-48b) was suggested by Wiegand [*Trans. Am. Inst. Chem. Engrs.*, **35**, 679 (1939)], who pointed out that the logarithmic mean mole fraction

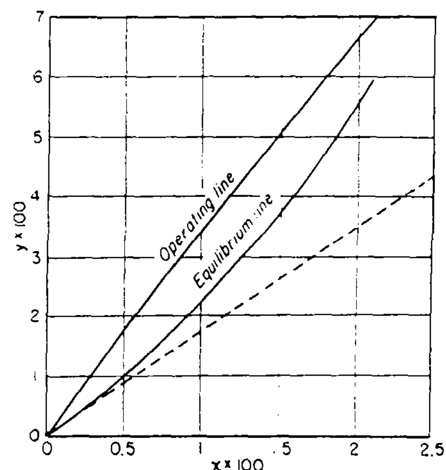


FIG. 14-11. Example of absorption of acetone, with a curved equilibrium line owing to heat of absorption. Dashed line is a tangent to the equilibrium curve at the origin.

of inert gas $(1 - y)_{lm}$ is often very nearly equal to the arithmetic mean. With this substitution the quotient of the first factors in the numerator and denominator of these equations becomes

$$\frac{(1 - y)_{lm}}{1 - y} \approx \frac{(1 - y^*) + (1 - y)}{2(1 - y)} = \frac{y - y^*}{2(1 - y)} + 1 \quad (14\text{-}49)$$

and so the equations may be simplified to

$$N_G = \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1} + \int_{y_2}^{y_1} \frac{dy}{y - y_i} \quad (14\text{-}50)$$

$$N_{OG} = \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1} + \int_{y_2}^{y_1} \frac{dy}{y - y^*} \quad (14\text{-}51)$$

The first terms, frequently amounting to only small corrections, give the effect of the finite level of gas concentration. The second terms give the number of transfer units for infinitely dilute gas. The procedure for applying Eqs. (14-50) and (14-51) involves two steps: evaluation of the integrals, and addition of the corrections corresponding to the first terms in the equations.

The simplest possible case occurs when (1) both the operating and the equilibrium line are straight (dilute solutions), (2) Henry's law is valid ($y^*/x = y_i/x_i = m$), and (3) absorption heat effects are negligible. Under these conditions the integral in Eq. (14-51) may be evaluated explicitly as

$$N_{OG} = \frac{1}{1 - (G_M/L_M)} \ln \left[\left(1 - \frac{mG_M}{L_M}\right) \left(\frac{y_1 - mx_2}{y_2 - mx_2}\right) + \frac{mG_M}{L_M} \right] \quad (14\text{-}52)$$

Equation (14-52) includes only the evaluation of the second (integral) term of Eq. (14-51) and does not include the correction for the first term on the right side of the equation. It does provide an approximate result even when solutions are concentrated or absorption heat effects are present if, as in many practical examples involving nearly complete cleanup of the gas, the driving forces in the upper part of the tower are much smaller than those at the bottom. In these cases the value of mG_M/L_M used in the equation should be the ratio of slopes of the equilibrium line m and the operating line G_M/L_M in the low-concentration range. Figure 14-12 is a plot of Eq. (14-52) from which the value of N_{OG} can be read directly as a function of the ratio of the slopes and the ratio of concentrations. This plot and Eq. (14-52) are equivalent to the use of a logarithmic mean of terminal driving forces but are more convenient because they avoid computation of the exit-liquid concentration. For stripping or desorption the change in concentration of the liquid stream is of principal concern. For this case the rate equation is more conveniently formulated in terms of liquid composition x. This leads to equations defining numbers of transfer units and heights of transfer units based on liquid-phase resistance:

$$Z = H_L \int_{x_2}^{x_1} \frac{(1 - x)_{lm} dx}{(1 - x)(x_i - x)} = H_L N_L \quad (14\text{-}53)$$

$$Z = H_{OL} \int_{x_2}^{x_1} \frac{(1 - x)_{lm} dx}{(1 - x)(x^* - x)} = H_{OL} N_{OL} \quad (14\text{-}54)$$

When the assumptions applicable are employed, an equation analogous to Eq. (14-52) is obtained.

Graphical Calculation of Transfer Units. The number of transfer units required for a given absorption can be obtained graphically. The technique involves the $x - y$ diagram in a manner similar to that for determination of theoretical stages. Baker [*Ind. Eng. Chem.*, **27**, 977 (1935)] presented a technique that involves locating a line vertically halfway between the operating and equilibrium lines, as shown by the dashed line in Fig. 14-13. Starting at point A on the operating line, a line is drawn toward the equilibrium line and extending to a point C such that AB equals BC. Point D on the operating line vertically above C is at a gas composition such that one transfer unit is required to go from A to D. If this procedure is applied successively from exit to inlet gas composition, the number of over-all gas transfer units (N_{OG}) results. If N_{OL} is sought, the dashed line must be located halfway horizontally between operating and equilibrium lines.

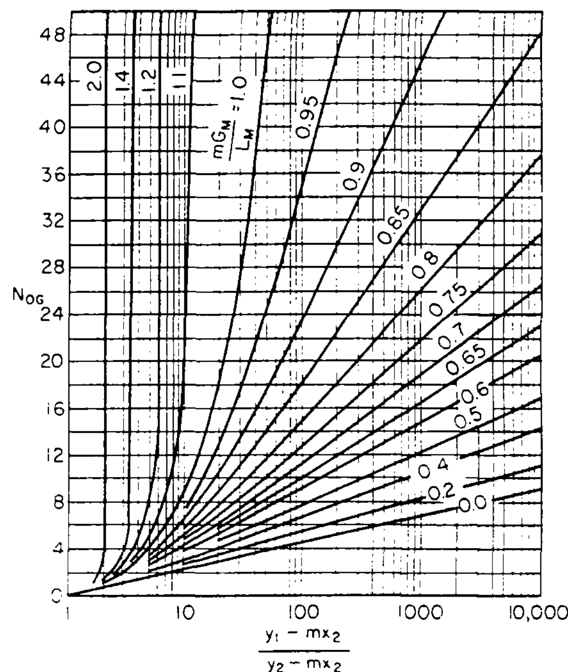


Fig. 14-12. Number of transfer units in an absorption column. Condition of constant mG_M/L_M, a plot of Eq. (14-52).

Multicomponent Systems. In cases where more than one soluble component is to be absorbed from an insoluble or slightly soluble gas, the method used by the designer will change. In general, a specified percentage of one solute will be recovered. Less volatile components will be recovered almost completely. Absorption of more volatile components will be incomplete, even though the rich solvent leaving the absorber becomes essentially saturated with respect to these components. In these cases calculation procedures derived from consideration of a theoretical plate (see Sec. 13) are generally used. All these procedures utilize, for convenience, an absorption factor $A = L/KV$, where A is the absorption factor for a given component, L is the total liquid molar flow rate, K is the equilibrium constant ($K = y/x$), and V is the total molar gas rate.

The simplest procedure utilizes equations based on analysis of a plate-type absorber by Kremser [*Natl. Petrol. News*, **22**, 48 (May 21, 1930)], as modified by Brown and Souders [*Ind. Eng. Chem.*, **24**, 519 (1932)]. Their equations are

$$\frac{Y_{n-1} - Y_1}{Y_{n+1} - Y_n} = \frac{A^{n+1} - A}{A^{n+1} - 1} \quad (14\text{-}55)$$

where Y is the moles of one component in the specified gas stream per mole of entering rich gas. A is the "average" absorption factor

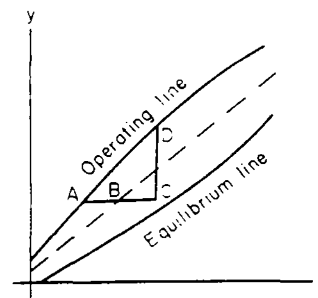


Fig. 14-13. Baker's construction for transfer units.

for that component, and n is the number of theoretical plates in the absorber.

Use of Eq. (14-55) to yield reliable numbers centers on proper selection of the average absorption factor. Brown and Souders recommend defining the average absorption factor as $A = L_0/KV_{n+1}$ where L_0 is the rate at which lean solvent flows through the column, and V_{n+1} is the rate of solute-rich gas flow. If the equilibrium constant is evaluated at a temperature about 15°F. above the average of the lean oil and rich gas temperatures, this will result in estimates of lean oil rates that tend to be slightly higher than those actually required.

In plate-type absorbers utilizing equations similar to (14-55) the number of theoretical plates will generally vary from approximately six to ten. Great caution should be used when estimates result in numbers of theoretical plates greater than ten.

Edmister [*Petrol. Eng.*, **18**, 130 (September, 1947)] suggested an "effective" absorption factor which is rigorous for a column with two theoretical plates and is defined as

$$A_e = \sqrt{A_n(A_1 + 1) + 0.25} - 0.5 \qquad (14\text{-}56)$$

where A_n and A_1 are the absorption factors on the bottom and top trays, respectively; and A_e is the effective absorption factor. A_e from Eq. (14-56) can be used in Eq. (14-55) to estimate the composition of the dry gas leaving the absorber. Estimation of A_e is more difficult because conditions on both the top and bottom trays of the absorber must be considered. If constant gas shrinkage per tray is assumed, and top and bottom tray temperatures are taken to be 10° to 25°F. higher than entering lean solvent and rich gas temperatures, respectively, estimates of component absorption and other column parameters will usually be reasonably accurate.

For convenience, plots relating the value of the right-hand side of Eq. (14-55) to the value of A are available (Natural Gas Processors Supplymen's Association, "Engineering Data Book," p. 151, 1966).

The analysis of a plate-type multicomponent absorber can be carried out plate-to-plate. When this is done, an equation similar to (14-57) is developed.

$$\frac{Y_{n+1} - Y_1}{Y_{n+1}} = \left(\frac{A_1A_2\cdots A_n + A_2\cdots A_n + \cdots + A_n}{A_1A_2\cdots A_n + A_2\cdots A_n + \cdots + A_{n+1}}\right) - \frac{L_0X_0}{V_{n+1}Y_{n+1}}\left(\frac{A_2A_3\cdots A_n + A_3\cdots A_n + \cdots + A_{n-1}}{A_1A_2\cdots A_n + A_2\cdots A_n + \cdots + A_{n+1}}\right) \qquad (14\text{-}57)$$

where X_0 is the moles of one component in the specified liquid stream per mole of entering lean oil. Analysis of an absorber utilizing Eq. (14-57) is difficult and time consuming. Prediction of the absorption factor on each tray requires knowledge of temperature, vapor-rate, and liquid-rate profiles that are known only after the column has been analyzed. Use of equations similar to (14-57) then are trial and error. One or more profiles for the column must be assumed, with calculations used to check the validity of the assumption. Obviously, procedures such as this are more ideally suited for computer solution. Approaches very similar to those discussed in Sec. 13 on distillation are used, though sometimes special convergence techniques must be employed in order to achieve a closed and unique solution to the absorption calculations.

Edmister [*A.I.Ch.E. J.*, **3**, 165 (1957)] presented a variation of the absorption factor analysis. He defined ϕ_A as the fraction of solute not recovered in the absorber,

$$\phi_A = \frac{1}{\Sigma_A + 1}$$

where

$$\Sigma_A = A_1A_2\cdots A_n + A_2\cdots A_n + \cdots + A_n$$

ψ_A, the fraction of a component in the lean solvent that is not lost with the off-gas, was defined as

$$\psi_A = 1 - \frac{\pi_A}{\Sigma_A + 1}$$

where $\quad \pi_A = A_1A_2\cdots A_n$

By using these two definitions the material balance equation for a simple absorber can be written as

$$\Sigma v_1 = \Sigma v_{n+1}\phi_A + \Sigma l_0\,\psi_A$$

Charts are provided for evaluating ψ_A and ϕ_A in terms of the average or effective absorption factor and the number of theoretical plates in the column. The real value of this kind of analysis is displayed when more complex towers, such as reboiled absorbers, are considered. Examples of the equations for several more complex column configurations are given in the original article.

All the absorption factor equations can be applied to stripping through use of the stripping factor

$$S = \frac{KV}{L} = \frac{1}{A}$$

The equations that result are:

$$\frac{X_{m+1} - X_1}{X_{m+1} - X_0} = \frac{S_{m+1} - S}{S_{m+1} - 1} \qquad (14\text{-}58)$$

$$S_e = \sqrt{S_m(S_1 + 1) + 0.25} - 0.5 \qquad (14\text{-}59)$$

$$\frac{X_{m+1} - X_1}{X_{m+1}} = \left(\frac{S_1S_2\cdots S_m + S_2\cdots S_m + \cdots + S_m}{S_1S_2\cdots S_m + S_2\cdots S_m + \cdots + S_{m+1}}\right) \times \frac{V_0Y_0}{L_{m+1}X_{m+1}}\left(\frac{S_2S_3\cdots S_m + S_3\cdots S_m + \cdots + S_{m+1}}{S_1S_2\cdots S_m + S_2\cdots S_m + \cdots + S_{m+1}}\right) \qquad (14\text{-}60)$$

In the case of a stripper, the bottom plate is number 1 and the top plate is m.

ECONOMIC DESIGN

Perhaps the most important variables and parameters to be considered in design of the absorption system are those that are most difficult to describe accurately by mathematical expression. Choice of the type of equipment to be used, the internals of that equipment, the liquid-gas ratio, column diameter, and column height are generally chosen on the basis of experience, judgment, and intuition. All these variables can have significant impact on the economics of the absorption-stripping operation and so are worthy of serious considerations and discussion.

Packed Towers. There are many instances in which packed towers have significant advantages. These would include:

1. Vacuum operations. The pressure drop through a packed tower can frequently be designed for a lower level than for a plate tower and still obtain adequate vapor-liquid contact.
2. Foaming liquids can frequently be handled more satisfactorily in a packed tower.
3. Liquid holdup is generally less, so that heat-sensitive materials, together with those absorption processes that may have undesirable side reactions may be better handled.
4. Construction is usually simpler and cheaper when the absorption system is corrosive to normal materials of construction.
5. For small columns (less than about 2 ft. in diameter) packed towers will usually be cheaper than plate towers.

Plate Towers. Plate-type towers show strong advantages in many areas.

1. Cooling coils are readily installed on plates, making them more desirable when heat of solution requires internal cooling.
2. With proper design for length of liquid cross flow, plate towers can handle higher liquid rates.
3. For extremely low liquid rates (*i.e.* dehydration of natural gas using a glycol) plate towers have an advantage because they can be designed to hold a given amount of liquid on the tray.
4. Certain types of plate towers may be preferred when there are deposits of solid material that must be periodically removed. Cleaning of plate towers can be accomplished through manholes, whereas packed towers require dumping of the packing to facilitate cleaning.
5. The total weight of a plate tower is usually less than that of a packed tower designed for the same duty. The limited crushing

strength of many packing materials may make use of multiple packing support plates mandatory, to bear the weight of the tall column of packing.

6. Plate columns are generally preferred for operations that require a large number of transfer units or theoretical plates. Packed towers tend to be subject to channeling of vapor and liquid streams, and proper distribution is difficult to maintain without rather elaborate redistribution schemes.

Liquid-Gas Ratio. mG_M/L_M is the design factor of prime importance. It helps to determine the height of a transfer unit, the number of transfer units, and the column diameter. If the solute gas is dilute, mG_M/L_M is apt to be nearly constant throughout the column. Where the solute gas is not dilute, heat of solution may cause a temperature rise, resulting in a larger value of m at the bottom of the column than at the top. Where mG_M/L_M is not constant, choice of the liquid-gas ratio is difficult. Frequently, however, conditions at the dilute end are of most importance. In the case of nearly complete absorption, most of the transfer units will be required in the dilute region.

Choice of the operating magnitude of mG_M/L_M is based on economic factors. The greater mG_M/L_M, the closer the solvent circulation is to the minimum value, and the more concentrated the solute-rich solvent leaving the absorber will be. This results in more economical operation because of lessened pumping costs and lowered costs of stripping the solute from the solvent. High values of mG_M/L_M result in more expensive absorption towers and lessened solute recovery in the absorber. Equation (14-61) represents a balance of the costs of absorption and subsequent stripping to recover the solute. Assumptions in deriving this equation were: the distillation column (stripping of solute from solvent by distillation) produces essentially pure solute overhead; denuded (no solute) solvent is withdrawn from the distillation column for recirculation to the absorber.

$$\left(\frac{L_M}{m_2G_M} - 1\right)^2 = \frac{BC_3H_{OG}(K_D - 1)}{C_5\theta rG_Mm_2} \tag{14-61}$$

where $$B = \left[1 + n\left(\frac{L_M}{m_2G_M} - 1\right)\right] \times 2.3\log_{10}\left[\left(\frac{y_1}{y_2}\right)\frac{(1 - m_2G_M/L_M)^2}{1 - K_1G_M/L_M}\right] - \frac{(1 - m_2G_M/L_M) - 2(K_1/m_2 - 1)}{1 - K_1G_M/L_M}$$

K_D = y^*/x, of the feed to the stripping column at its boiling point

m_2 = slope of equilibrium curve y^*/x at the temperature of the inlet liquid to the absorption column

C_3 = annual cost of apparatus and power for the absorption column, \$/(cu. ft.)(yr.) = $C_1[(G_{opt}/G) + 0.5(G/G_{opt})^2]$

C_5 = total cost of stripping operation, expressed as \$/lb.-mole of vapor supplied to the stripper; includes fixed charges, cost of cooling water, and cost of steam

y_1/y_2 = optimum ratio of solute mole fractions in gas stream flowing through absorber

θ = hr. operation/yr.

G_M = molal gas velocity through absorber, lb.-moles/(hr.)(sq. ft.)

r = (actual reflux ratio in distillation column) ÷ (minimum reflux ratio, defined as ratio of reflux to product)

n = exponent in the relation $H_{OG} \sim (G/L)^n$

Column Diameter. Gas velocity and column diameter are so closely related that they may be thought of interchangeably. The gas velocity for a column is selected by considering first the safe operating velocity with respect to flooding, and then the optimum velocity calculated by an economic balance between column costs and tower cost. Data on flooding velocities for various packings are given in Sec. 18. Design is usually for approximately 60 per cent of flooding to allow for flow fluctuations and a margin of safety to avoid shutdown of the column. An expression for the optimum gas velocity is

$$G_{opt} = 2680\phi\frac{4}{3}\left(\frac{C_1}{C_2\theta b}\right)^{1/3} \tag{14-62}$$

where C_1 = annual cost of packing in the shell, \$/(yr.)(cu. ft.); θ = hr./yr. operation; ρ = gas density; $\phi = (\rho/0.075)^{1/2}$; C_2 = cost of delivered energy, \$/kw.-hr.; and b = pressure drop, in H_2O/ft. height at G/ϕ = 1000 lb./(hr.)(sq. ft.). Note that b may be an extrapolated value.

At the economic velocity, according to Eq. (14-62), the annual cost of energy per cubic foot turns out to be approximately one-half the annual cost of the packing and shell (C_1), so that the total annual cost of column and energy in dollars per cubic foot becomes approximately equal to $1.5C_1$.

Column Height. Column height and solute concentration in the exit gas from the absorber are closely related and interdependent. The solute concentration in the exit gas may be determined by an economic balance between the cost of lost solute and the cost of additional column height,

$$(y_2 - mx_2)_{opt} = \frac{C_3H_{OG}}{C_4\theta G_M(1 - mG_M/L_M)} \tag{14-63}$$

for packed towers, where C_3 = annual cost of apparatus and energy for pressure drop, \$/(yr.)(cu. ft.); C_4 = value of solute at its concentration in the exit liquor, \$/lb.-mole of solute; θ = hr./yr. operation.

A similar result for the plate columns is

$$(y_2 - mx_2)_{opt} = \frac{C_6}{C_4\theta G_ME(2.3\log L_M/mG_M)} \tag{14-64}$$

where C_6 = annual cost of column and pressure drop, \$/(yr.)(plate)(sq. ft.); and E = over-all plate efficiency, fractional. Tiller [*Trans. Am. Inst. Chem. Engrs.*, **40**, 331 (1944)] gives an equivalent equation for the optimum number of plates in an absorber.

Optimum exit-liquor strength for a stripping column depends on a balance between the cost of lost solute in the exit liquor and the cost of additional tower height required for more stripping. Equations analogous to those for exit-gas strength in absorption are

$$\left(x_2 - \frac{y_2}{m}\right)_{opt} = \frac{C_3H_{OL}}{C_4L_M\theta(1 - L_M/mG_M)} \tag{14-65}$$

for a packed column, and

$$\left(x_2 - \frac{y_2}{m}\right)_{opt} = \frac{C_6}{C_4L_M\theta E\ln(mG_M/L_M)} \tag{14-66}$$

for a plate column. In these equations, C_3 = annual cost of apparatus (amortization and depreciation of column and packing) and power, \$/(yr.); C_6 = annual cost of apparatus and power, \$/(yr.)(plate)(sq. ft. of cross section); C_4 = value of solute at concentration of exit gas, \$/lb.-mole of pure solute; E = over-all plate efficiency, fractional; H_{OL} = over-all H.T.U. based on liquid-phase driving force, ft; θ = hr./yr. operation; L_M and G_M = molar velocities, lb.-moles/(hr.)(sq. ft.); and m = slope of equilibrium curve y^*/x at dilute end of stripper.

Column Pressure. The higher the column pressure, the greater the solubility of the solute in the solvent. In cases where gases must be compressed in order to achieve higher pressure, this is seldom economical. Frequently absorption pressure will be set by requirements of other processing steps and thus involve considerable detail in calculations at different absorber pressure levels. As a general rule, the absorber should be operated at the highest possible pressure consistent with other process requirements.

Lean Solvent Temperature to Absorber. In continuous operation of an absorber-stripper combination, the lean solvent must be cooled after leaving the bottom of the stripper. Frequently the solvent will be cooled further before entering the absorber or by intercoolers located at intermediate points in the absorber. Cooling the solvent increases the solubility of the solute and decreases the required liquid rate. The economic balance is between savings in stripper costs and lower liquid flows, and cost of additional heat-exchange

equipment and cooling media. Cooling of the solvent substantially below the solute-rich gas temperature is seldom justified.

Multicomponent Systems. The simplified equations (14-62) to (14-66) provide only rough guides to optimum design conditions for multicomponent systems. In such cases, detailed computations must be made for alternate designs and alternate operating parameters. Optimum gas velocity will be closely approximated by Eq. (14-62). In general, cooling of solute-rich gas and solvent can be justified to the range of 0°F. or lower for large, high-pressure natural-gas-absorption systems.

Non-isothermal Absorption. Computation of tower dimensions and required flows is straightforward when heat effects can be neglected, as indicated above. However, when temperature of the liquid stream varies from point to point in the absorber, owing to heat of solution of the solutes, heat of vaporization of the solvent, or to sensible heat exchange between gas and liquid phases, the problem is more difficult. Computations have to be made differentially from point to point through the absorber if they are to be precise, because solubility of the solute depends on the temperature, and the driving force cannot be found until the temperature profile is known. If the temperature changes are not large, however, approximate procedures may suffice.

Large Heat Effects. When the solute has a large heat of solution, or when feed gases containing high percentages of solute are treated, the effects of heat release during absorption may be pronounced. In such cases, heat-transfer surface may be supplied through cooling coils on the plates to remove the heat of absorption. In other cases, the partially saturated solvent will be withdrawn from a point intermediate in the tower and passed through an external heat exchanger for cooling. Provision of adequate heat-removal facilities may be as important in obtaining successful absorber operations as is provision for the absorption process itself.

Absorbers involving large heat effects are frequently operated adiabatically. Treybal [*Ind. Eng. Chem.*, **61**, 36 (1969)] presents a calculational procedure for designing adiabatic packed-tower gas absorbers and strippers. His procedure involves trial-and-error calculation of mass transfer and related heat release across the absorber in stepwise fashion. An example problem is solved in detail.

Mostafa (*op. cit.*) treats the graphical determination of number of transfer units when absorption heat release is considered. His procedure is also trial and error.

Mild Heat Effects. The principal object of considering heat effects is to fix the equilibrium line, which depends on liquid temperatures. Mild effects can be allowed for on the basis of estimated liquid temperatures at the top and bottom of the absorber. The former is fixed by external considerations (available cooling capacity applied to the liquid-feed circuit, for example), and the latter can be estimated from an energy balance around the whole absorber. These temperatures fix the gas solubilities at the ends of the absorber. Thus they determine the slope of the equilibrium curve at the inlet-liquid composition and a point on the curve at the proposed exit-liquid composition. If an approximate equilibrium line can be drawn through the end points without very much curvature, it may reasonably be assumed that driving forces are correct.

Example 2. Consider the absorption of acetone from air at atmospheric pressure in pure water fed to a packed absorber at 25°C. Inlet gas at 35°C. contains 2 per cent by volume acetone and is 70 per cent saturated with water vapor (4 per cent H_2O by volume). Mole fraction acetone in the exit gas is to be reduced to 1/400 the inlet value. Per 100 lb.-moles of feed-gas mixture, how many pound-moles of fresh water should be fed to provide a positive driving force throughout the packing? How many transfer units will be needed?

Differential heat of solution of acetone vapor in pure water = 2500 p.c.u./lb.-mole acetone, where p.c.u. = pound-Centigrade unit = 1.8 B.t.u. Latent heats at 25°C. are 7220 p.c.u./lb.-mole for acetone and 10,490 for water. Specific heat of air = 7.0 p.c.u./(lb.-mole)(°C.). Solubilities are given as a function of temperature by the following table:

t, °C.	25	30	35	40
γ_1, activity coefficient for acetone	6.7	7.1	7.5	7.8
P_1, vapor pressure of pure acetone, mm. Hg	229	283	346	421
$m = \dfrac{y^*}{x} = \gamma_1 \dfrac{P_1}{P}$	2.02	2.64	3.41	4.33

Solution. Relative to dry gas and liquid water at 25°C., the following enthalpies are computed for the inlet- and exit-gas streams (basis = 100 lb.-moles gas entering).

Entering gas:

$$\begin{aligned} \text{Acetone, } 2(2500 + 7200) &= 19{,}400 \text{ p.c.u.} \\ \text{Water vapor, } 4(10{,}490) &= 41{,}960 \\ \text{Sensible heat, } (100)(7.0)(35 - 25) &= \underline{7{,}000} \\ &\quad 68{,}360 \text{ p.c.u.} \end{aligned}$$

Exit gas (assumed saturated with water at 25°C.):

$$\begin{aligned} \text{Acetone, } (2/400)(94/100)(2500) &= 12 \text{ p.c.u.} \\ \text{Water vapor, } 94\left(\frac{23.7}{760 - 23.7}\right)(10{,}490) &= \underline{31{,}600} \\ &\quad 31{,}612 \text{ p.c.u.} \end{aligned}$$

$$\text{Enthalpy change of liquid} = 68{,}360 - 31{,}612 = 36{,}748 \text{ p.c.u.}$$

$$\Delta = \text{temperature rise of liquid} = \frac{36{,}748}{18L_M}$$

$$L_M = \frac{36{,}748}{18\,\Delta}$$

Δ, °C.	t_1, °C.	L_M	$m_1 = y_1^*/x_1$	m_1G_M/L_M	m_2G_M/L_M
0	25	....	2.02	0	0
2	27	1022	2.26	0.221	0.198
3	28	681	2.39	0.351	0.297
4	29	511	2.51	0.492	0.398
5	30	409	2.64	0.645	0.494
6	31	341	2.78	0.815	0.592
7	32	292	2.93	1.002	0.692

Evidently, Δ = 6°C. will give an operable absorber, *i.e.*, one having a positive driving force from gas to liquid at all points. Δ = 7°C. is a barely inoperable condition because the equilibrium line touches the operating line. Figure 14-14 shows operating and equilibrium lines for L_M = 341 lb.-mole.

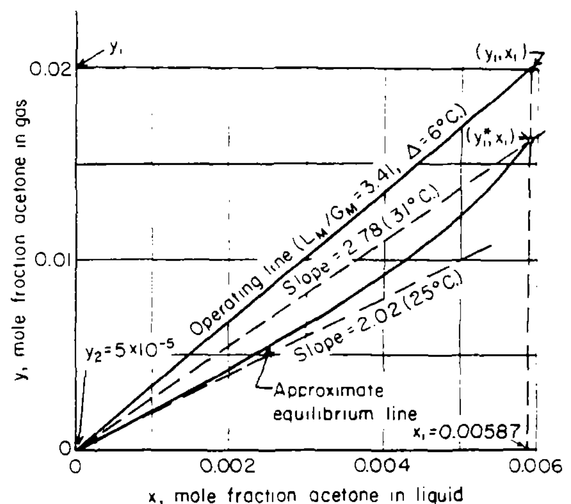


FIG. 14-14. Operating and equilibrium lines in adiabatic acetone absorber, Example 2.

the latter being drawn with a French curve so that it has the right slope at the origin and passes through a point corresponding to $x_1 = 0.02(100/341) = 0.00587$ mole fraction and $y_1 = 0.0163$.

The number of transfer units can be computed from the integral formula, but a quicker method is to use a formula derived by Colburn [*Trans. Am. Inst. Chem. Engrs.*, **35**, 211 (1939)] on the assumption that the equilibrium line is a parabolic arc having a slope m_2 at the bottom end and passing through the point $(x_1, m_1 x_1)$ at the upper end:

$$N_{OG} = \frac{1}{1 - m_2 G_M/L_M} \times \ln\left[\frac{(1 - m_2 G_M/L_M)^2 y_1 - m_2 x_2}{1 - (m_1 G_M/L_M) y_2 - m_2 x_2} + \frac{m_2 G_M}{L_M}\right] \quad (14.67)$$

In the present instance

$$N_{OG} = \frac{1}{1 - 9.592} \ln\left[\frac{(1 - 0.592)^2}{1 - 0.815}(400) + 0.592\right]$$

$$= 14.4$$

Note that Eq. (14-67) allows for curvature of the equilibrium line in the middle range of x. Erroneous use of the logarithmic mean of the terminal values of $y - y^*$, equal to 0.000543 mole fraction units, gives $N_{OG} = (y_1 - y_2)/\Delta y_{1m} = 23.8$ and leads to an overestimate of the packed height needed.

Absorption Accompanied by Chemical Reaction. There are many systems of industrial importance in which the solute reacts either reversibly or irreversibly with the material used as solvent. Most of these cases involve phenomena that can affect the rate of absorption of solute. Analytical treatment of these cases is not well understood, and for this reason design must be undertaken with particular caution. (See Sec. 18.)

If the reaction occurs in the liquid phase and is rapid and irreversible, the rate of absorption may be controlled primarily by the gas-phase resistance to mass transfer. In these cases the mass-transfer rate may be estimated by the methods outlined above for obtaining H_G. Absorption of ammonia into acid solution of SO_2 and H_2S into strong alkali illustrate this situation, so long as there is a stoichiometric excess of the reacting solvent. For the irreversible reaction, calculation of the tower height is also relatively simple because the back pressure of the gas over the solvent is zero. In cases where there is slight reversibility of reaction and therefore a small gas back pressure, the absorption may be gas-phase-controlled. In these cases the H_G for physical absorption would control the rate of absorption.

Frequently the reaction rate is slow enough that liquid-phase resistance must be considered. Generalized prediction methods for H_L are unsuitable for application when chemical reaction occurs in the liquid phase. In these cases operating data for the particular system in question must be utilized. Where liquid-phase resistance is important, extreme care must be taken in utilizing experimental data. Extrapolation to different concentration ranges must be made with care and caution. The mass-transfer coefficient may be affected by a reaction which changes concentration gradients near the interface. In many instances there may be competing or parallel reactions of varying rates and equilibrium concentrations. These variables may mask the influences of mass transfer to such an extent that even modest deviations from experimental conditions can lead to serious error.

MANTECH ENVIRONMENTAL RESEARCH SERVICES CORPORATION
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY

STANDARD OPERATING PROCEDURE CLEARANCE FORM

Number: RSKSOP-175

Title: Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique

Author(s): Bryan Newell

Kampbell wrote us to do paper on CH_4 in H_2O

CH_4 solubility in water?
20°C
.03303 ml/mL water
.002319 g/100g water
→ 2.32 mg/.1L = 23.2 mg/L

Author's Signature [signature] Date 12/21/94

ManTech Analytical Section Supervisory [signature] Date 12/21/94

ManTech QA Coordinator [signature] Date 12/27/94
Powell

25 → 24.1 mg/L

ManTech Program Manager [signature] Date 12/22/94
Seeley

EPA Technical Monitor [signature] Date 1-25-94
John Wilson

EPA Project Officer [signature] Date 1-25-95
Cosby

~~QA Project Leader~~ Date

EPA Quality Assurance Officer [signature] Date 4/4/95
D. Bertino

STANDARD OPERATING PROCEDURE

GAS CHROMATOGRAPHIC ANALYSIS OF GASEOUS SAMPLES FOR PART-PER-MILLION LEVELS OF NITROUS OXIDE, METHANE, ETHYLENE, AND ETHANE

Disclaimer:

This standard operating procedure has been prepared for the use of the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

1. Purpose: (Scope and Application)

This method is applicable to the analysis of gaseous samples for the quantitation of low part-per-million levels of nitrous oxide (0.3-1000ppm), methane (10ppm-40,000ppm), ethylene (10ppm-10,000ppm), and ethane (10ppm-10,000ppm). The number of analyses that can be performed on one eight hour day is approximately 32.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms.

2. Summary of Method :

A gas sample is injected onto a gas chromatographic column upon which its hydrocarbon components are separated and detected by a flame ionization detector. One minute after this injection, another sample is taken and injected onto a separate gas chromatographic column where nitrous oxide is separated and detected by an electron capture detector.

3. References :

3.1 Hewlett Packard 5890 Series II Gas Chromatograph Operator's Manual.

3.2 Hewlett Packard 3396 A Integrator Operator's Manual.

3.3 Hewlett Packard 3396 Series II Integrator Operator's Manual.

3.4 Vandegrift, S., RSKSOP-92, Rev. No. 1, Jan. 1991.

3.5 Vandegrift, S., RSKSOP-119, Rev. No. 0, Apr. 1991.

4. Procedure:

4.1 Gas Chromatographic Conditions

Hewlett Packard 5890 Series II w/ FID and ECD

Oven Temperature Program:

Initial Temperature:	55°C
Initial Time:	1 minute
Rate:	20°C/minute
Final Temperature:	140°C
Final Time:	5 minutes

Other Temperatures:

Injector (FID):	200°C
Detector (FID):	250°C
FID range:	0
FID attenuation:	0
Injector (ECD):	120°C

Detector (ECD): 275°C
ECD range: 3
ECD attenuation: 0

Column Type: Both columns are Porapak Q, 80/100, 6' X 1/8" stainless steel, (Supelco).

Carrier Gas (FID): High Purity Helium at 20 ml/min @ 55°C
Hydrogen: 40 ml/min
Air: 400 ml/min
Column Head Pressure: 14 psi
Carrier Gas (ECD): High Purity 95% Argon, 5% Methane at 27ml/min @ 40°C
w/ anode purge on: 39 ml/min
Column Head Pressure: 20 psi
Integrator (FID): Hewlett Packard 3396 Series II
Attenuation: 1
Threshold: 1
Chart Speed: 1.0 cm/min
Integrator (ECD): Hewlett Packard 3396A
Attenuation: 4
Threshold: 3
Chart Speed: 0.5 cm/min.
The HP 3396 Series II integrator is on the INET, and the HP 3396A integrator is interfaced to the GC using a signal cable on the SIG 2 output of the GC and a remote cable.

4.2 Gas Chromatograph Preparation

At the beginning of each day, replace the septa in each of the GC injectors.

-**CAUTION: BURN HAZARD!** Be sure to reduce the injector temperatures below 100 degrees C prior to touching the injector nut.

The septum which seems to work best for this application is the Hewlett Packard "red" septum (part no. 5181-1263).

The FID flame is ignited as follows: open the valves on the air and hydrogen cylinders. Open their respective valves for the FID on the GC (labeled detector A). Depress the FID Ignitor button on the GC. There should be a "pop" sound to indicate lighting of the hydrogen flame. Next turn the detector on by depressing the following key sequence: DET A ON. The FID should be ready for analysis in a few minutes.

To prepare the electron capture detector for analysis use the following procedure. Open the ECD Anode Purge valve on detector B. To turn the detector on, use the following key sequence: DET B ON. The ECD should be ready for analysis in a few minutes. The GC oven is kept at 120°C when the instrument is not in use.

4.3 Standards

Scotty standards are available "off the shelf" from Scott Specialty Gases for methane, ethylene, ethane, and nitrous oxide. Their availability is as follows: for methane 10ppm, 100ppm, 1000ppm, 1%, and 4%; for ethylene 10ppm, 100ppm, 1000ppm, and 1%; for ethane 10ppm, 100ppm, 1000ppm, and 1%; and for nitrous oxide 10, 100, and 1000ppm.

A 0.33 ppm nitrous oxide standard can be prepared as follows: immerse a 60 ml serum bottle in a water bath, filling the bottle with water. Displace the water with high purity helium and seal with a gray butyl rubber stopper and aluminum crimp cap. Inject 200ul of the 100 ppm nitrous oxide standard into the bottle. This standard can be used repeatedly, but should be prepared on a daily basis.

4.4 Analysis

A 500 ul gas-tight syringe (Precision Sampling Corporation) is used to withdraw samples and make injections into the GC. Sample volumes of 300 ul are analyzed. Samples are withdrawn without flushing the syringe.

Standards are sampled by "bubbling" the cylinders contents through water via tubing. A septum within a fitting in the tubing can be pierced to retrieve a sample of the standard. A cylinder of high purity helium is available in Lab # 208 to obtain samples for blank runs. The regulator and tubing should be purged for 15 minutes prior to analyzing a sample of the helium. The helium is also sampled by piercing a septa within a fitting in the tubing.

NOTE: Methane contamination can be a problem for this analysis; therefore, the syringe should be solvent rinsed after each injection with acetone. Make sure there is no residual solvent left in the syringe.

Retention times for each gas under the conditions listed are as follows: methane 0.6 minutes, ethylene 1.8 minutes, ethane 2.3 minutes, and nitrous oxide 2.2 minutes. (See attached chromatograms.)

4.5 Calibration/Quantitation

For each of the gases a calibration curve is generated on a weekly basis using the standards for each gas. The curve is generated by using linear regression on a calculator or computer. For methane the area count from the blank helium response is entered as the zero concentration. The area counts

for the unknowns can then be used to determine their concentrations. If the unknown's area count is outside of the range of the curve, the accuracy of the calculated concentration is not reliable. If the sample's area count is greater than the highest standard, and more sample is available, another injection using a smaller volume, e.g. 50-100 ul, may be used. The dilution factor, i.e. 300/ ul injected, must be used to correct for the smaller injection.

5. QUALITY CONTROL:

Calibration is checked each day prior to analyzing samples, by plotting standard area counts on control charts. For the FID; analyze high purity helium, 100 ppm methane, 100 ppm ethylene, and 100 ppm ethane. For the ECD, analyze high purity helium and 10 ppm nitrous oxide standard prior to analysis of samples. In addition, no fewer than one standard per every tenth sample analyzed should be analyzed.

When reporting results, any extenuating circumstances should be noted.

Control charts of the 100 ppm methane, ethylene, and ethane and of the 10 ppm nitrous oxide standards area counts are kept to monitor variability. If any analysis of these standards falls outside of the control limits, it should be determined why this has occurred, and corrective action should be taken. Some of the things that could be checked are the integrity of the GC septa, plunger "tightness" in the syringe barrel (it should be tight to provide a good seal), column fittings, carrier gas flow rate, air and hydrogen flow rates for the FID, and volume of gas in the standard container (at low pressures the area counts may vary considerably). This is not meant to be a comprehensive list as the analyst or supervisor should have

experience in troubleshooting gas chromatographs, as mentioned under "Purpose." A note should be made on the control chart itself as to the problem and action taken.

The 100 ppm methane standard was analyzed over a four week period on thirteen different occasions (n=13). This resulted in the following statistics:

mean = 60270
s = 859
= 1.43 ppm
CV = 1.43 %

The 100 ppm ethylene standard was analyzed over a four week period on six different occasions (n=6). This resulted in the following statistics:

mean = 106873
s = 1526
= 1.43 ppm
CV = 1.43 %

The 100 ppm ethane standard was analyzed over a four week period on six different occasions (n=6). This resulted in the following statistics:

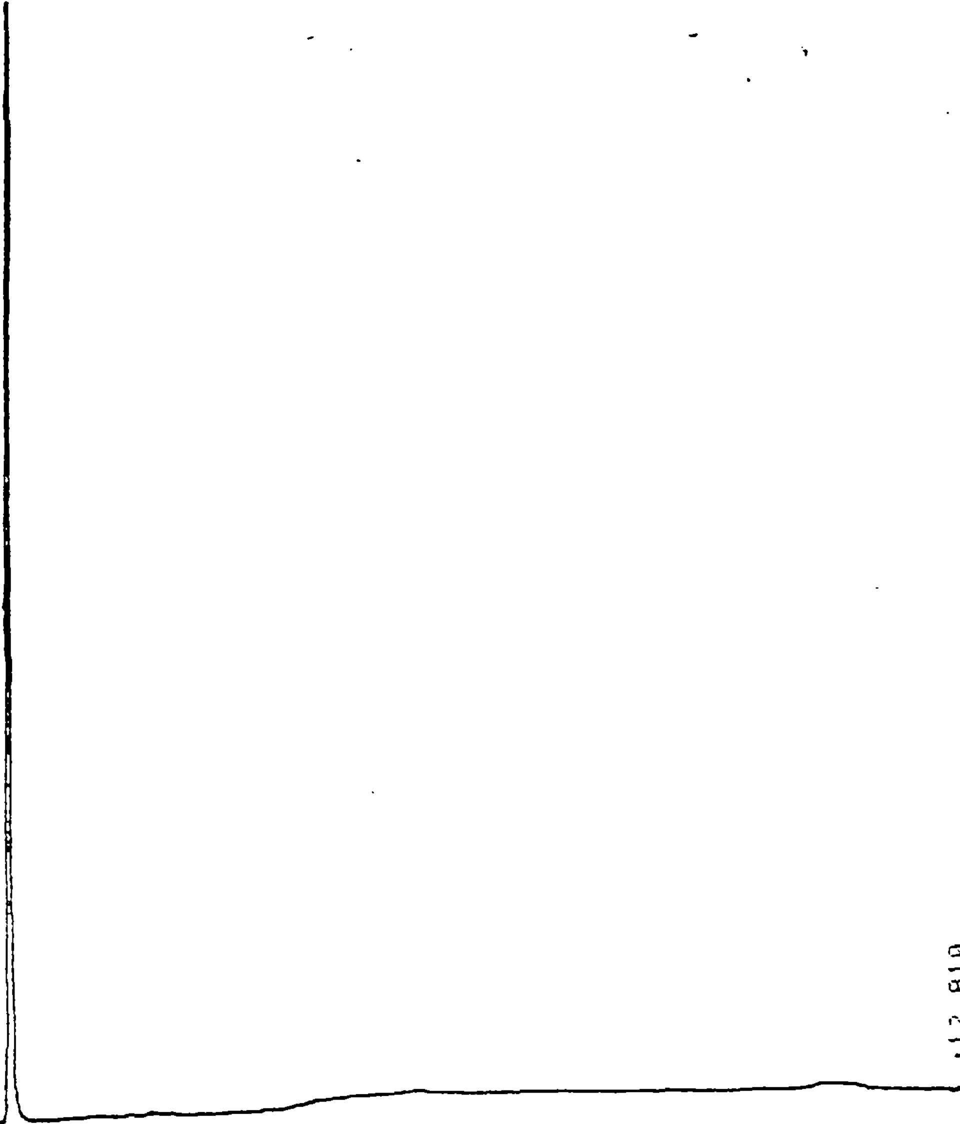
mean = 108020
s = 4067
= 3.77 ppm
CV = 3.77 %

The 10 ppm nitrous oxide standard was analyzed over a four week period on five different occasions (n=5). This resulted in the following statistics:

mean = 172446
s = 1568
= 0.09 ppm
CV = 0.91 %

PRECAUTIONS: Other than as noted, no special precautions are necessary aside from those used in good laboratory practice.

Example Chromatogram of 100 ppm Methane



RUN# 14 NOV 5, 1992 12:55:03

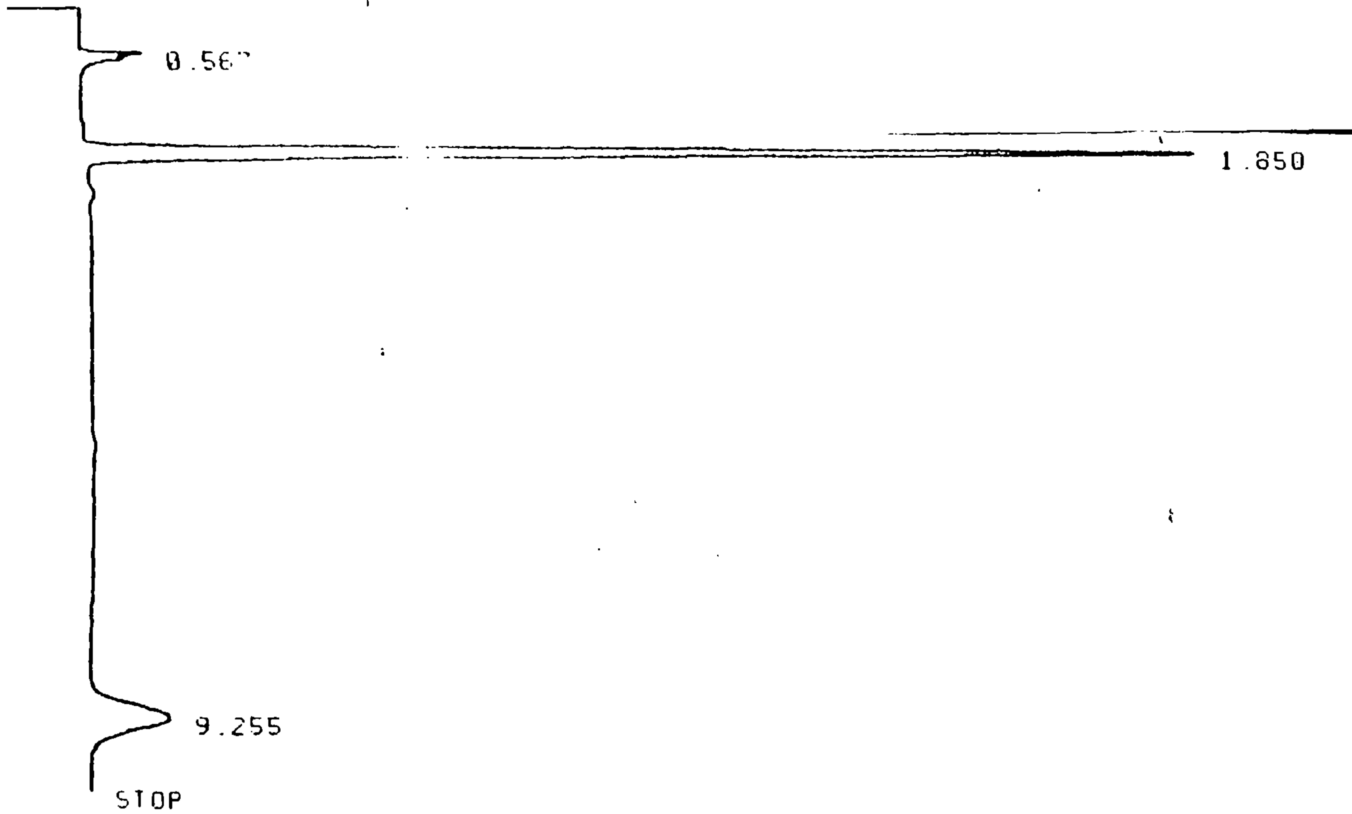
AREA%

RT	AREA	TYPE	WIDTH	AREA%
.601	61593	FB	.043	100.00000

TOTAL AREA= 61593
MUL FACTOR=1.0000E+00

Example Chromatogram of 100 ppm Ethylene

* RUN # 234 DEC 3, 1992 10:53:54
START

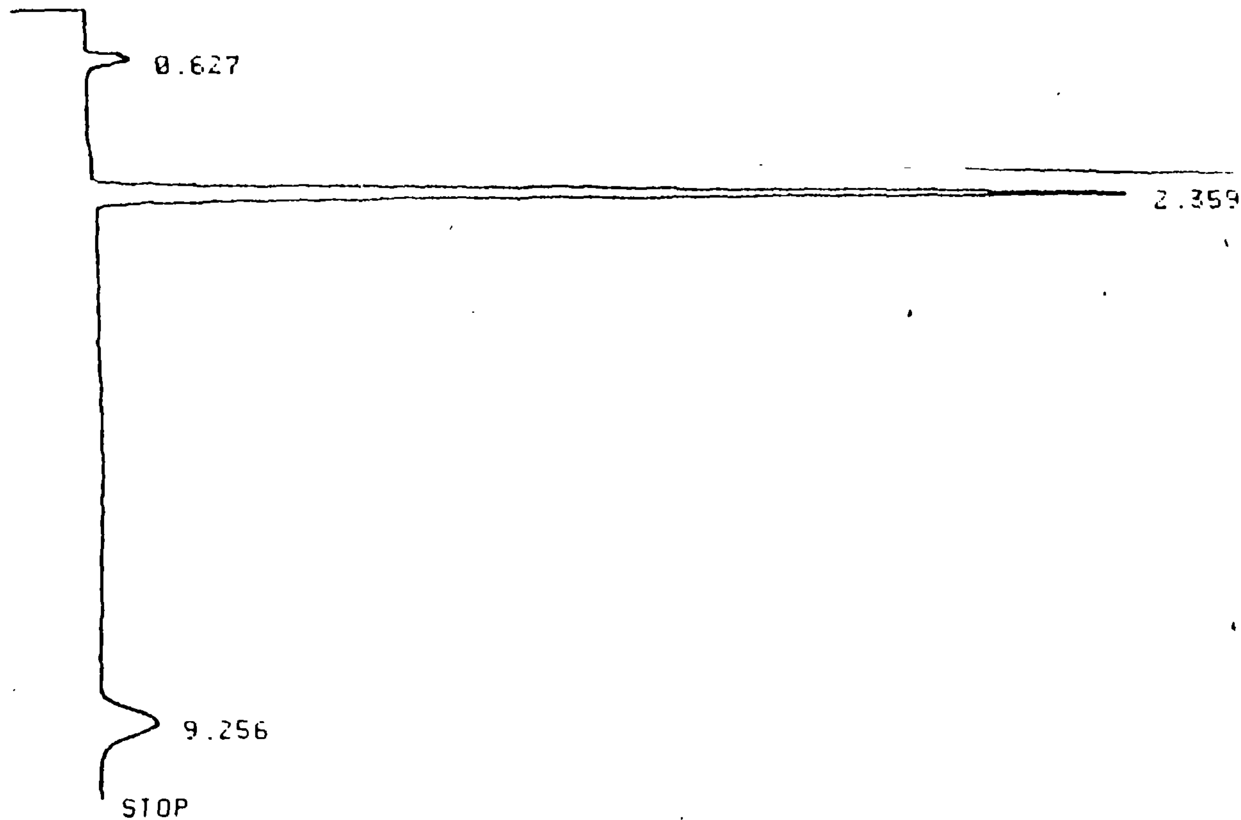


RUN# 234 DEC 3, 1992 10:53:54

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.567	2969	BV	.055	2.1359
1.850	109055	PB	.113	78.45741
9.255	26975	BP	.391	19.40662

TOTAL AREA= [illegible]



Example Chromatogram of 100 ppm Ethane

RUN# 235 DEC 3, 1992 11:07:56

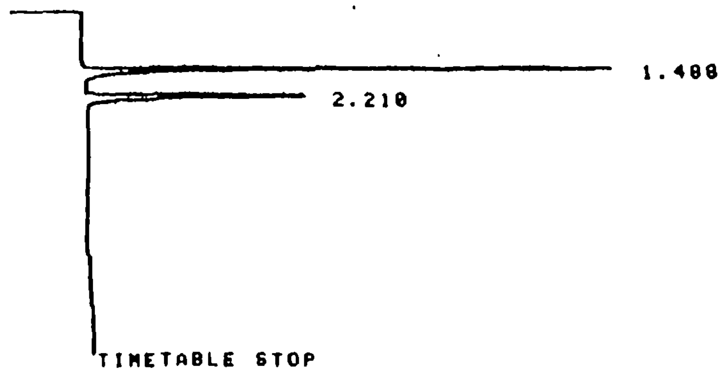
AREA%

RT	AREA	TYPE	WIDTH	AREA%
.627	5563	PV	.144	4.10787
2.359	110304	VB	.125	81.45146
9.256	19556	PP	.393	14.44068

TOTAL AREA= 135423
MUL FACTOR=1.0000E+00

Example Chromatogram of 10 ppm Nitrous Oxide

* RUN # 115 JAN 6, 1993 14:15:32



RUN# 115 JAN 6, 1993 14:15:32

AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.488	229462	PB	.063	57.38558
2.210	170398	PB	.112	42.61442

TOTAL AREA= 399860
MUL FACTOR=1.0000E+00

METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

John D. Pfaff
Inorganic Chemistry Branch
Chemistry Research Division

Revision 2.1
August 1993

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions:

PART A.

Bromide	Nitrite
Chloride	Ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.

Bromate	Chlorite
Chlorate	

1.2 The matrices applicable to each method are shown below:

1.2.1 Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7), leachates (when no acetic acid is used).

1.2.2 Drinking water and reagent waters

1.3 The single laboratory Method Detection Limit (MDL defined in Section 3.2) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 Method A is recommended for drinking and wastewaters. The multilaboratory ranges tested for each anion are as follows:

Analyte	mg/L
Bromide	0.63 - 21.0
Chloride	0.78 - 26.0
Fluoride	0.26 - 8.49
Nitrate-N	0.42 - 14.0
Nitrite-N	0.36 - 12.0
Otho-Phosphate-P	0.69 - 23.1
Sulfate	2.85 - 95.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.6.

1.7 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Section 9.0.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample, typically 2-3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.2 The main differences between Parts A and B are the separator columns and guard columns. Sections 6.0 and 7.0 will elicit the differences.

2.3 An extraction procedure must be performed to use this method for solids (See Section 11.7).

2.4 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, Quality Control.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Field Duplicates (FD)** -- Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 **Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.7 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.0 INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid (Section 7.4)

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2 Anion separator column: This column produces the separation shown in Figures 1 and 2.

6.2.2.1 Anion analytical column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met.

6.2.2.2 Anion analytical column (Method B): The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of Section 9.2 can be met.

6.2.3 Anion suppressor device: The data presented in this method were generated using a Dionex anion micro membrane suppressor (P/N 37106).

6.2.4 Detector -- Conductivity cell: Approximately 1.25 µL internal volume, (Dionex, or equivalent) capable of providing data as required in Section 9.2.

6.3 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 9.2.

7.0 REAGENTS AND STANDARDS

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CASRN 144-55-8) 1.7 mM, sodium carbonate (CASRN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water (Section 7.2) and dilute to 2 L.

7.4 Regeneration solution (micro membrane suppressor): Sulfuric acid (CASRN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 L with reagent water.

7.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 minutes) as listed below.

7.5.1 Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr, CASRN 7647-15-6) in reagent water and dilute to 1 L.

7.5.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 1.1798g of sodium bromate ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 1 L.

7.5.3 Chlorate ($Cl0_3^-$) 1000 mg/L: Dissolve 1.2753g of sodium chlorate ($NaCl0_3$, CASRN 7775-09-9) in reagent water and dilute to 1 L.

7.5.4 Chloride (Cl^-) 1000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl, CASRN 7647-14-5) in reagent water and dilute to 1 L.

7.5.5 Chlorite ($Cl0_2^-$) 1000 mg/L: Dissolve 1.3410g of sodium chlorite ($NaCl0_2$, CASRN 7758-19-2) in reagent water and dilute to 1 L.

7.5.6 Fluoride (F^-) 1000 mg/L: Dissolve 2.2100g sodium fluoride (NaF, CASRN 7681-49-4) in reagent water and dilute to 1 L.

7.5.7 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in reagent water and dilute to 1 L.

7.5.8 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$, CASRN 7632-00-0) in reagent water and dilute to 1 L.

7.5.9 Phosphate ($PO^{=}_4$-P) 1000 mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 1 L.

7.5.10 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 1 L.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Except for the chlorite standard which is only stable for two weeks. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

7.6 Ethylenediamine preservation solution: Dilute 10 mL of ethylenediamine (99%) (CASRN 107-15-3) to 200 mL with reagent water. Use 1 mL of this dilution to each 1 L of sample taken.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immediately
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Combined (Nitrate/Nitrite)	conc. H_2SO_4 to a pH <2	28 days
Nitrite-N	Cool to 4°C	48 hours
0-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Note: If the determined value for the combined nitrate/nitrite exceeds 0.5 mg/L as N^-, a resample must be analyzed for the individual concentrations of nitrate and nitrite.

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples

be cooled to 4°C and held for no longer than 28 days for Method A and analyzed immediately in Method B.

Note: If the sample cannot be analyzed for chlorite within ≤10 minutes, the sample may be preserved by adding 1 mL of the ethylenediamine (EDA) preservation solution (Section 7.6) to 1 L of sample. This will preserve the concentration of the chlorite for up to 14 days. This addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample (per Section 4.8) prior to the addition of EDA.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two

to three times the estimated instrument detection limit.[6] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t= 3.14 for seven replicates]

S = standard deviation of the replicate analyses

MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should

be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} x100$$

where,

R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

9.4.3 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits for Method A of 80-120% and 75-125% for Method B. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.6 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.

9.4.7 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. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

9.4.8 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.4.9 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B.

10.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Section 7.5) to a volumetric flask and diluting

to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3 Using injections of 0.1-1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

10.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.

10.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

11.0 PROCEDURE

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 10.0.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 μ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.

11.8 It has been reported that lower detection limits for bromate (≈7 μg/L) can be obtained using a borate based eluent[7]. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.

11.9 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg/L.

12.4 Report NO_2^- as N
NO_3^- as N
HPO_4 as P

13.0 METHODS PERFORMANCE

13.1 Tables 1A and 2A give the single laboratory (EMSL-Cincinnati) MDL for each anion included in the method under the conditions listed.

13.2 Tables 2A and 2B give the single laboratory (EMSL-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the listed conditions.

13.3 Multiple laboratory accuracy and bias data (S_t) and estimated single operator values (S_o) for reagent, drinking and waste water using Method A are given for each anion in Tables 3 through 9. Data from 19 laboratories were used for this data.

13.4 Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occurring concentrations of the same anion.

14.0 POLLUTION PREVENTION

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

14.2 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

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

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

16.0 REFERENCES

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2. Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

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4. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater", J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

5. American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

6. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART A)

Analyte	Peak #*	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns: as specified in Sesction 6.2.2.1
Detector: as specified in Section 6.2.4
Eluent: as specified in Section 7.3

Pump Rate: 2.0 mL/min.
Sample Loop: 50 µL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.
*See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART B)

Analyte	Peak #*	Retention Time (min)	MDL (mg/L)
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	4	7.1	0.003

Standard Conditions:

Column: as specified in Section 6.2.2.2
Detector: as specified in Section 6.2.4
Eluent: as specified in Section 7.3

Pump Rate: 1.0 mL/min.
Sample Loop: 50 µL
Attentuation - 1
y-axis - 500 ns

*See Figure 2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	GW	5.0	7	92	0.34
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Fluoride	RW	2.0	7	91	0.05
	DW	1.0	7	92	0.06
	SW	1.0	7	73	0.05
	WW	1.0	7	87	0.07
	GW	0.4	7	95	0.07
	SD	5.0	7	101	0.35
Nitrate-N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10.0	7	93	0.17
	WW	10.0	7	101	0.82
	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate-P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)

RW = Reagent Water
DW = Drinking Water
SW = Surface Water
WW = Mixed Domestic and Industrial Wastewater
GW = Groundwater
SD = USEPA QC Solid (shale)

TABLE 2B. SINGLE-OPERATOR ACCURACY AND BIAS OF BY-PRODUCT (PART B)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	0.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

TABLE 3. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR FLUORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.26	0.25	0.08	0.11	-3.8
	0.34	0.29	0.11		-14.7
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14		-2.7
	6.79	6.76	0.20	0.19	-0.4
	8.49	8.46	0.30		-0.4
Drinking	0.26	0.24	0.08	0.05	-7.7
	0.34	0.34	0.11		0.0
	2.12	2.09	0.18	0.06	-1.4
	2.55	2.55	0.16		0.0
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75		-1.4
Waste	0.26	0.25	0.15	0.06	-3.8
	0.34	0.32	0.08		-5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16		-2.7
	6.79	6.65	0.41	0.20	-2.1
	8.49	8.27	0.36		-2.6

TABLE 4. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR CHLORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46		+7.7
	6.50	6.31	0.27	0.14	-2.9
	7.80	7.76	0.39		-0.5
	20.8	20.7	0.54	0.62	-0.5
	26.0	25.9	0.58		-0.4
Drinking	0.78	0.54	0.35	0.20	-30.8
	1.04	0.51	0.38		-51.0
	6.50	5.24	1.35	1.48	-19.4
	7.80	6.02	1.90		-22.8
	20.8	20.0	2.26	1.14	-3.8
	26.0	24.0	2.65		-7.7
Waste	0.78	0.43	0.32	0.39	-44.9
	1.04	0.65	0.48		-37.5
	6.50	4.59	1.82	0.83	-29.4
	7.80	5.45	2.02		-30.1
	20.8	18.3	2.41	1.57	-11.8
	26.0	23.0	2.50		-11.5

TABLE 5. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRITE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06		0.0
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12		+6.4
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27		+0.6
Drinking	0.36	0.30	0.13	0.03	-16.7
	0.48	0.40	0.14		-16.7
	3.00	3.02	0.23	0.12	+0.7
	3.60	3.62	0.22		+0.6
	9.60	9.59	0.44	0.28	-0.1
	12.0	11.6	0.59		-3.1
Waste	0.36	0.34	0.06	0.04	-5.6
	0.48	0.46	0.07		-4.2
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18		+4.4
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56		+0.3

TABLE 6. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR BROMIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.63	0.69	0.11	0.05	+9.5
	0.84	0.85	0.12		+1.2
	5.24	5.21	0.22	0.21	-0.6
	6.29	6.17	0.35		-1.9
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93		+1.5
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13		-3.6
	5.24	5.11	0.23	0.13	-2.5
	6.29	6.18	0.30		-1.7
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65		-0.4
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15		+1.2
	5.24	5.23	0.36	0.11	-0.2
	6.29	6.27	0.46		-0.3
	16.8	16.6	0.69	0.43	-1.0
	21.0	21.1	0.63		+0.3

TABLE 7. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRATE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06		0.0
	3.51	3.34	0.15	0.08	-4.8
	4.21	4.05	0.28		-3.8
	11.2	11.1	0.47	0.34	-1.1
	14.0	14.4	0.61		+2.6
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09		+3.6
	3.51	3.45	0.27	0.10	-1.7
	4.21	4.21	0.38		0.0
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70		+1.6
Waste	0.42	0.36	0.07	0.06	-14.6
	0.56	0.40	0.16		-28.6
	3.51	3.19	0.31	0.07	-9.1
	4.21	3.84	0.28		-8.8
	11.2	10.9	0.35	0.51	-3.0
	14.0	14.1	0.74		+0.4

TABLE 8. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR ORTHO-PHOSPHATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15		+6.5
	5.77	5.72	0.36	0.18	-0.9
	6.92	6.78	0.42		-2.0
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35		+2.4
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20		+4.3
	5.77	5.43	0.52	0.40	-5.9
	6.92	6.29	0.72		-9.1
	18.4	18.0	0.68	0.59	-2.2
	23.1	22.6	1.07		-2.0
Waste	0.69	0.64	0.26	0.09	-7.2
	0.92	0.82	0.28		-10.9
	5.77	5.18	0.66	0.34	-10.2
	6.92	6.24	0.74		-9.8
	18.4	17.6	2.08	1.27	-4.1
	23.1	22.4	0.87		-3.0

TABLE 9. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR SULFATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	2.85	2.83	0.32	0.52	-0.7
	3.80	3.83	0.92		+0.8
	23.8	24.0	1.67	0.68	+0.8
	28.5	28.5	1.56		-0.1
	76.0	76.8	3.42	2.33	+1.1
	95.0	95.7	3.59		+0.7
Drinking	2.85	1.12	0.37	0.41	-60.7
	3.80	2.26	0.97		-40.3
	23.8	21.8	1.26	0.51	-8.4
	28.5	25.9	2.48		-9.1
	76.0	74.5	4.63	2.70	-2.0
	95.0	92.3	5.19		-2.8
Waste	2.85	1.89	0.37	0.24	-33.7
	3.80	2.10	1.25		-44.7
	23.8	20.3	3.19	0.58	-14.7
	28.5	24.5	3.24		-14.0
	76.0	71.4	5.65	3.39	-6.1
	95.0	90.3	6.80		-5.0

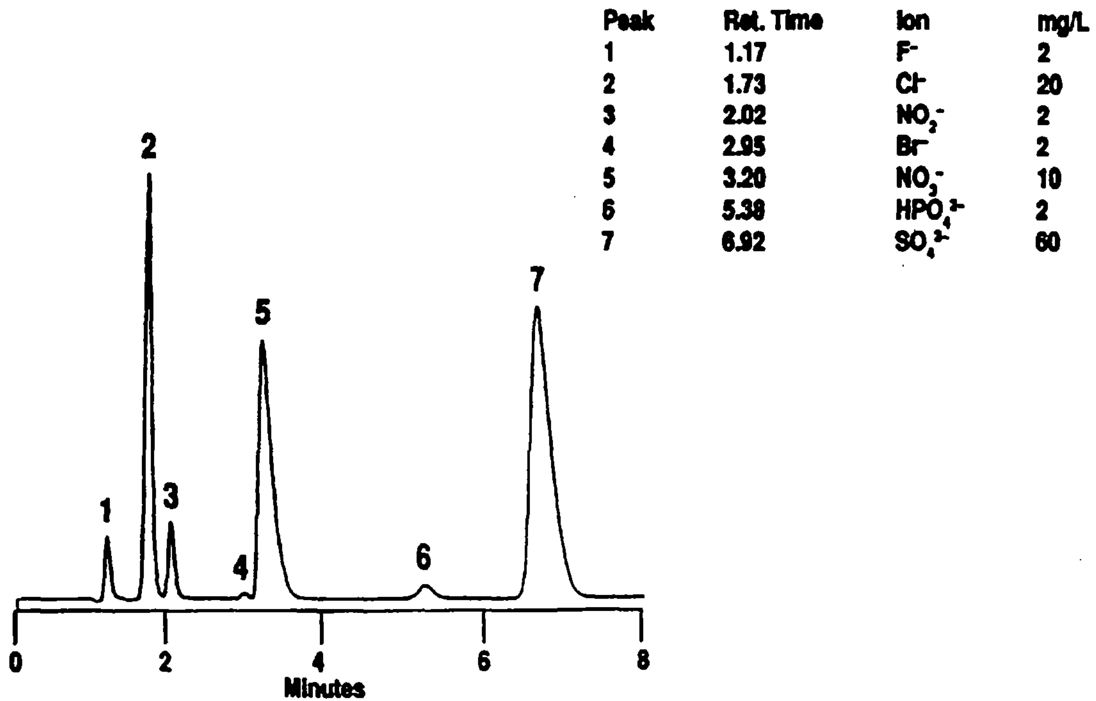

Figure 1. Chromatogram showing separation using the AS4A column

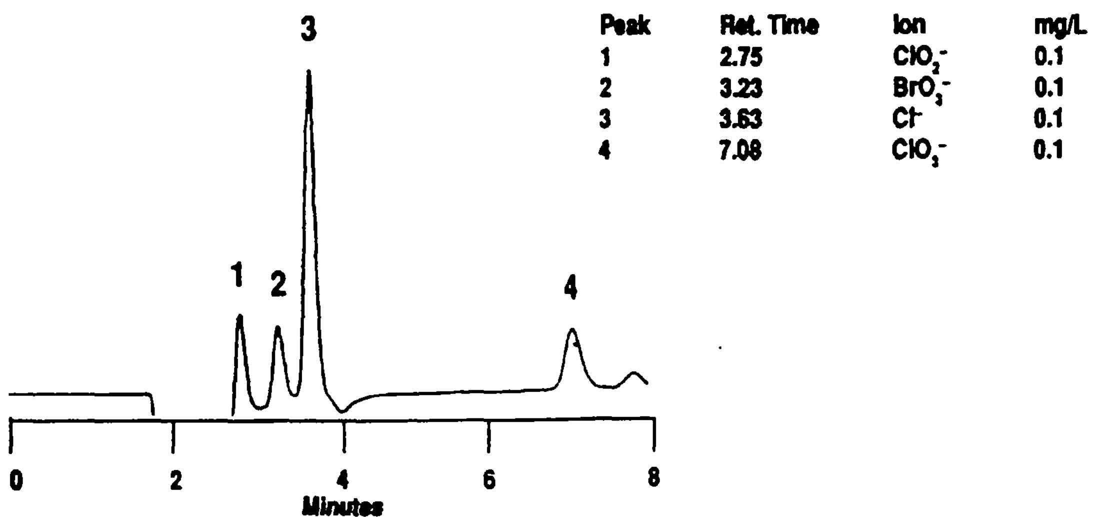

Figure 2. Chromatogram showing separation using the AS9 column