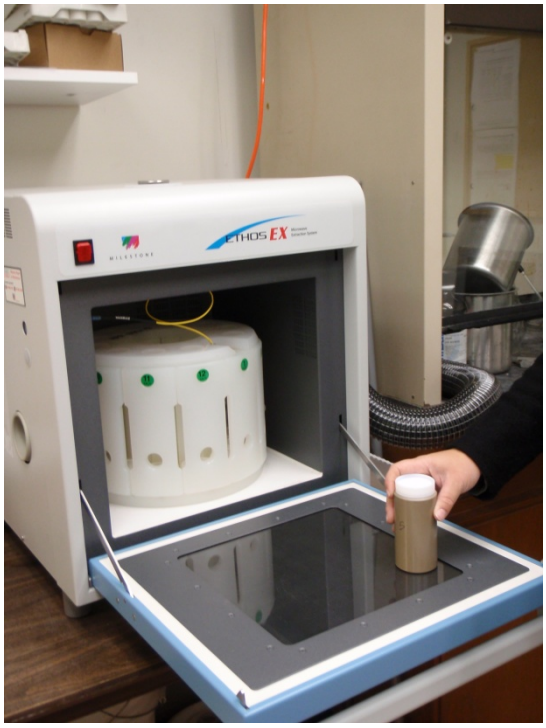
Workplan for CORE^{DFN} Matrix Diffusion Evaluation at the Foster Wheeler Energy Corporation/ Church Road TCE Site Mountain Top, Luzerne County, PA

Stone Project ID 102347-R

12/29/10, Revised 4/11/11



Prepared for:
Tetra Tech EC, Inc.
Robert Chozick
1000 The American Road, Morris Plains, NJ 07950
Tel. / 973.630.8337
Fax / 973.630.8577
E-Mail / Robert.Chozick@tetratech.com

Prepared by:
Stone Environmental, Inc.
535 Stone Cutters Way
Montpelier, VT 05602
Tel. / 802.229.4541
Fax / 802.229 5417
E-Mail / sei@stone-env.com

Table of Contents

1. INTRODUCTION

This workplan has been prepared by Stone Environmental (Stone) for Tetra Tech EC (TtEC), Inc. to describe the scope of matrix diffusion evaluation and processing, handling, preservation, analysis of rock samples, and related services Stone will perform at the Foster Wheeler Energy Corporation (FWEC)/Church Road TCE Site in Mountain Top, PA. The objective of this field program is to:

- Asses distribution of TCE in the bedrock at one coring location at the FWEC/Church Road TCE Site
- Evaluate the matrix diffusion potential of the bedrock at the Site

2. SCOPE OF WORK

Stone will mobilize/demobilize one data acquisition truck, three staff, and all necessary tools and materials from Montpelier, VT to the FWEC/Church Road TCE Site in Mountain Top, PA. Prior to commencement of work Stone staff will attend an on-site health and safety meeting conducted by TtEC. Stone staff will be equipped with Level D personal protective equipment (PPE) and will be prepared to upgrade to Level C PPE as required by TtEC. Upon completion of field work Stone will remove all materials, supplies, and equipment associated with the SOW Stone performs on the Site.

2.1. Roles and Responsibilities

TtEC will provide a Geologist whose main responsibility is to log each retrieved core run for lithology, color, hardness, weathering, texture, bedding characteristics, structure, solution and void conditions, and other features. The TtEC Geologist will be responsible for coordinating the drilling operation. Lee Rosberg of Stone will sample rock core for VOC and physical properties and will work closely with the TtEC Geologist to agree upon lithology and features of each core run retrieved.

Efficient processing and preservation of VOC samples by immersion of crushed rock into methanol is of primary importance during a CORE$^{DFN\ TM}$ investigation in order to minimize losses of VOCs. Stone field personnel can generally record sample information, collect samples, crush and preserve samples, and decontaminate crushing equipment from a core run in thirty minutes. Lee Rosberg will communicate with the TtEC Geologist if the drilling rate exceeds Stone's ability to process samples to avoid VOC losses. The TtEC Geologist and Lee will then advise the driller the amount of time they should wait before proceeding to core after retrieving a core run. This will minimize the time between when drilling of a core run begins and the time VOC samples are immersed in methanol. Collection of VOC samples takes priority over logging each core run, Stone's sampler will collect samples shortly after retrieval of each core run.

Key Stone personnel that will complete the scope of work are included in Table 1.

PROJECT OFFICER: **Seth Pitkin**	The Project Officer (PO) is ultimately responsible for project performance. The PO seeks and gets appropriate approvals for risk management decisions (e.g. from Regional/Practice Director(s), Legal Council, Corporate Health and Safety), and selects an effective and qualified project team. The PO supports the Project Manager or Deputy Project Manager with appropriate resources.
PROJECT MANAGER: **Lee Rosberg**	The Project Manager (PM) has the responsibility for executing the project in accordance with the scope of work and good engineering practice. The PM will supervise the allocation of resources and staff to implement specific aspects of this workplan and may delegate authority to expedite and facilitate any application of the program. The PM implements and executes an effective program of site-specific personnel protection and accident prevention. The Project Manager reports to the Project Officer.
QUALITY ASSURANCE MANAGER: **Kim Watson**	The Quality Assurance (QA) Manager is responsible for managing compliance with Good Laboratory Practices (GLP) Standards (40 CFR Part 160), the National Environmental Laboratory Accreditation Program (NELAC) quality system, and Corporate Quality Assurance (QA) programs. Her responsibilities include tracking regulatory updates, supervising QA/QC internal procedures and in the field, acting as the Quality Assurance Unit (QAU) for EPA related studies. She is responsible for developing and implementing quality systems for company processes both project and non-project related. Ms. Watson has over 21 years of experience in all phases of production and laboratory procedures, quality control and quality assurance, QA management and project management in an environmental analytical laboratory encompassing the EPA regulated environments (GLP, RCRA and CERCLA).
FIELD TEAM LEADER **Lee Rosberg**	The field team leader is responsible for managing Stone field personnel in daily field activities to implement the scope of work as defined in this workplan. The field team leader communicates project progress and needs to the TtEC field representative.

FIELD TEAM PERSONNEL: **Lee Rosberg** **Will Waterstrat** **Vincent DeLeone** **Andrew Klopfenstein**	Three of the four Stone staff listed as Field Team Personnel will collect, process, and preserve rock samples for VOC and physical properties analyses at the Site. Lee Rosberg is the "sampler" whose responsibilities include logging core features (such as fractures, staining, and precipitation), selecting portions of the core to be sampled, and describing the portion of the core from which the VOC and physical properties samples are collected. Will Watersrat or Vincent DeLeone will be the "crusher" whose main responsibility is to operate the hydraulic press, crushing and preserving the rock core VOC samples preparing sample vials and maintaining the sampling records and documentation. and preserve VOC samples. Andrew Klopfenstein will decontaminate all crushing equipment that comes in contact with samples during the crushing process.
LABORATORY MANAGER: **Mike Rossi**	The Laboratory Manager selects a qualified team of analysts to perform Microwave assisted Extraction (MAE) and determination of VOCs in the VOC rock samples collected by the field team. Responsibilites include compliance with QA/QC protocols outlined in laboratory SOPs.
LABORATORY ANALYSTS: **Mike Rossi** **Dave Crosby**	Laboratory analysts will perform Microwave assisted Extraction (MAE) and determination of VOCs in the VOC rock samples collected by the field team in accordance with QA/QC protocols outlined in laboratory SOPs.

Table 1: Key Stone personnel

2.2. VOC and Physical Properties Collection

Stone staff will collect, handle, and preserve up to forty (40) VOC and four (4) physical properties samples from one coring location. Sample locations will be selected for VOC analysis based on fracture distribution and lithology with a target frequency of approximately one sample every foot. Stone employs the discrete-fracture network (DFN) investigation approach developed by Beth Parker and associates at the Universities of Guelph and Waterloo. This approach places emphasis for data acquisition on data specific to individual fractures, fracture networks and rock matrix blocks between fractures so that the characteristics and interactions between these domains can be better understood Studies indicate that sample interval plays a significant role in the usefulness of data obtained. Porewater concentrations and mass loading calculations can vary significantly with increased sample intervals. Sample locations will be selected for physical property analyses based on litholgy. VOC samples are collected at fractures (i.e. one of the fracture faces), joints and bedding planes, at lithologic changes (both sides of the contact), and from matrix blocks between fractures. The sampler evaluates whether breaks in the rock are so-called "machine breakes (i.e., breaks induced by drilling activities) or whether they are openings present in-situ. In addition the sampler evaluates whether the openings are likely to be active flow conduits by evaluating weathering, coatings, staining etc.

Equipment blanks will be collected prior to processing VOC samples (every twentieth VOC sample) and at the completion of VOC sample collection. Field duplicates will be collected at a minimum of every twenty VOC samples collected. A methanol blank will be collected from each 1Liter (L) bottle of methanol used to prepare VOC sample vials. One trip blank will be placed with each cooler used to transport VOC samples to Stone's laboratory in Montpelier, VT. For specific methods of VOC and physical properties sample collection, handling, and preservation refer to Stone SOP 6.37.0, *Field Methods for Retrieval, Collection, Handling, and Preservation of Rock Samples to be Analyzed for VOCs and Physical Properties* (Appendix A). **NOTE: The methods used in this work are proprietary. SOPs should not be copied, reproduced or shared outside of the limited project staff that have a need to know the contents of these documents.** Upon completion of coring activities at the FWEC/Church Road TCE site Stone staff will transport all VOC and physical properties samples to Montpelier, VT.

NOTE: Stone SOP 6.37.0 contains proprietary information- DO NOT DISTRIBUTE or REPRODUCE. Circulation of this document should be limited to only those project team members that have a need to know the contents of the documents.

Stone will adhere to decontamination methods outlined in section 4.4 of SOP 6.37.0. Stone anticipates generating five to ten gallons of investigation derived waste (IDW). IDW will be comprised of methanol and water rinsate from decontaminating VOC sampling and crushing equipment and rock chips from trimming VOC subsamples. Drums or other appropriate storage for IDW will be provided by TtEC and left onsite.

2.3. VOC Sample Analysis

Microwave assisted extraction (MAE) will be performed on all VOC samples following Stone SOP 10.17.0, *Microwave Assisted Extraction of Volatile Organic Compounds from Rock Samples* (Appendix B). Following MAE VOC samples will be analyzed for target analytes following Stone SOP 10.18.0, *The Determination of Volatile Organic Compounds by Gas Chromatography/Dual ECD Detectors in Rock Samples (Using Cool on Column Injection and Split Method Injection)* (Appendix C). QA/QC requirements for MAE and determination of VOCs in rock samples are found in their respective SOPs.

NOTE: Stone SOPs 10.17.0 and 10.18.0 contain proprietary information- DO NOT DISTRIBUTE or REPRODUCE. Circulation of this document should be limited to only those project team members that have a need to know the contents of the documents.

2.4. Physical Properties Sample Analysis

Physical properties samples will be shipped, under COC, to Golder Associates in Mississaugua, Ontario where they will be analyzed for specific gravity *via* ASTM D854-06, water content *via* D2216-05, density wax method *via* ASTM-86, and total organic carbon *via* Whalkley-Black method (1947, Appendix D).

3. DATA DELIVERABLES

3.1. Draft/Final Letter Reports

Stone will provide TtEC with a Draft Letter Report describing field methods and findings within four weeks of field work completion. A Final Letter Report will be provided to TtEC within one week of Stone receiving TtEC's comments on the Draft Letter Report.

3.2. Deviations from SOW

Documents identifying deviations and their acceptance from the SOW by the TtEC Project Manager or designated field representative will be provided to TtEC as soon as the deviation is accepted by the TtEC Representative.

4. SCHEDULE

Stone will mobilize one data acquisition truck, three staff, and all tools and materials necessary to complete the scope of work from Montpelier, VT to the Site upon request from TtEC to proceed.

5. MEASUREMENT AND PAYMENT

At the end of each day Stone's field team leader and a TtEC Representaive will agree and complete summary sheets detailing the day's activities, including samples collected, amounts of consumables utilized, hourly charges, etc.

At the end of each month Stone will compute the quantities of completed work for that month and submit a monthly invoice review for approval. A back-up package will be attached to the monthly invoice will be prepared by Stone in sufficient detail to allow TtEC to verify the value of completed work by comparing the invoice to the summary sheets.

Payment for each line item found on Exhibit B, Price Form of TtEC's Order Number: 1065699 will be made according to the unit indicated for the line item and the quantities of work performed for that line item. These unit costs shall include all costs to collect the specified data, decontamination of equipment and other ancillary activities described in the scope of work.

APPENDICES

APPENDIX A: STONE SOP 6.37.0, *FIELD METHODS FOR RETRIEVAL, COLLECTION, HANDLING, AND PRESERVATION OF ROCK SAMPLES TO BE ANALYZED FOR VOCS AND PHYSICAL PROPERTIES*

STANDARD OPERATING PROCEDURE

SEI-6.37.0

Field Methods for Retrieval, Collection, Handling, and Preservation of Rock Samples to be Analyzed for VOCs and Physical Properties

NOTE: This SOP contains proprietary information – Do Not Distribute

SOP Number: SEI-6.37.0
Revision Number: 0

Date Issued: 07/01/08
Date of Revision: NA

1.0 OBJECTIVE

The purpose of this procedure is to collect and process samples of bedrock aquifer material which can be subsequently analyzed to determine the concentration of analytes in the pore water within the rock matrix. This is important information in dual porosity bedrock environments where diffusion of contaminants into the rock matrix porosity can result in a large portion of the total contaminant mass residing in the relatively immobile matrix.

Samples need to be obtained, logged, and crushed into methanol with a minimal loss of volatile analytes.

Rock cores are retrieved by a drilling team from fractured bedrock aquifers and sampled for volatile organic compounds (VOCs) along with representative samples for physical property analyses including porosity, bulk density, organic carbon content, chloride diffusion coefficient and matrix permeability.

2.0 POLICIES

1. According to 40 CFR Part 160, Subpart E, Section 160.81 and the NELAC standards, a testing facility shall have standard operating procedures in writing setting forth study methods that management is satisfied are adequate to insure the quality and integrity of the data generated in the course of a study.
2. Personnel will legibly record data and observations in the field to enable others to reconstruct project events and provide sufficient evidence of activities conducted.

3.0 SAFETY ISSUES

1. If necessary and appropriate, a site-specific health and safety plan shall be created for each study site. A template for creating a proper health and safety plan is provided on the SEI network.
2. Care must always be taken when approaching a sampling location. Do not, under any circumstances, place yourself in danger to collect a sample.

3. If necessary and appropriate, all chemicals are required to be received with Material Safety Data Sheets (MSDS) or appropriate application label. These labels or MSDS shall be made available to all personnel involved in the sampling and testing.

4.0 PROCEDURES

4.1 Rock Core Sampling Equipment and Materials

1. Sharpies and Ball point pens
2. Several small coolers
3. Small Dry-Erase White Board (2)
4. Tough-book Field Computer (2)
5. USB Data Stick (flash drive)
6. Printer
7. Wash Tubs (4)
8. Folding Tables (4+)
9. Chairs (3)
10. Scissors
11. Scrub Brushes (several)
12. Squirt Bottles (4+)
13. Required field personnel protective equipment (PPE).
14. Paper towels
15. Teflon tape (heavy duty)
16. Duct tape
17. Rubber bands
18. Aluminum foil
19. Saran wrap
20. Parafilm
21. Phosphate free detergent
22. Distilled Water
23. Bubble wrap
24. Ziploc bags (large and small)
25. Ice Packs
26. Kim-wipes
27. Crack Hammer (2 or more)
28. Steel Chisel, 3" blade (3 or 4)
29. Pick – For removing o-rings
30. MeOH, Purge and Trap grade and Wash grade
31. Enerpac™ Hydraulic system
32. Rock Crushing Press
33. Sample Trimming Cells
34. Complete Sample Crushing Cells
35. Stainless Rods (for knocking out pucks)
36. O-rings for Pucks
37. Spare Bolts for Base
38. Wood Blocks for marking sampled portions of core
39. 6' Plank marked in 0.1 foot intervals.

4.2 Core Retrieval and Sample Collection

Core runs will be HQ-sized (2.5-inch diameter) in five-foot lengths, collected using a triple-tube core barrel system. Immediately upon retrieval by the driller of the cores at ground surface, they will be removed from the core barrel and placed in aluminum foil-lined PVC trays (6 ft long, 4-inch diameter PVC pipe split lengthwise) and covered with a continuous sheet of clean aluminum foil to minimize volatilization of VOCs. Aluminum foil will be used to keep most of the core covered while the geologist and hydrogeologist inspect the core and select sample locations based on presence of fractures, lithology, weathering and evidence of groundwater and/or DNAPL fluid flow. The hydrogeologist will flag the sections of the core to be subsampled for VOC analyses and physical property measurements (moisture content, porosity and bulk density, diffusion coefficient, matrix permeability, organic carbon content). The drilling pace should be controlled by the on-site hydrogeologist to ensure that core is not drilled or retrieved before the hydrogeologist and crusher are prepared to receive it (i.e. previous core run has been completely processed or nearly so).

4.2.1 VOC Sample Selection

Subsamples (i.e. core segments ~1 to 2-inches long) for determining CVOC concentrations will be taken from the cores immediately to minimize chemical losses due to volatilization. The initial core logging will be performed to identify key features for subsampling purposes and samples will be quickly broken from the core using a hammer and chisel, and then wrapped in aluminum foil for VOC and moisture preservation and given a unique field ID. The foil wrapped sample is then placed in a zip-lock bag and labeled with the same field ID as the wood block. After these samples have been collected, the core will be logged in more detail by the geologist. Additional sample types will then be selected and removed from the core. Wood blocks will be placed in the core boxes with a unique field ID where samples have been removed for future reference, indicating the sample ID, length and depth of the removed section and the type of sample.

Samples for CVOC analysis will typically be collected using the three criteria identified below unless the project work plan specifies another scheme:

- Samples will be taken immediately adjacent to (including fracture surface) and 6 to 12 inches away from identified fractures, either above and below these features. All breaks in core should be suspected as being fractures *in-situ*, however, emphasis will be made on features with additional lines of evidence for active fluid flow (i.e. secondary mineral coatings/staining, slickensides, report from drillers regarding fluid loss/gain at specific depths during coring). These samples are intended for measuring the extent of

diffusion into the matrix blocks away from fractures that may have once contained DNAPL or solute contamination.

- Additional subsamples will be collected at distinct changes in lithology /mineralogy. Samples will be collected from both sides of such boundaries, referred to as lithology pairs so that representative samples are collected from the different matrix materials.
- Field duplicate samples will be collected at a minimum frequency of 1 in 20, taken from the same length of core split lengthwise (along the core axis) to provide samples from the same depth interval and lithology.

The hydrogeologist will exercise judgment during sampling to provide an average sample frequency which adequately describes the system, or as specified in the work plan. A typical average sample spacing of one sample every 1 to 2 ft is recommended.

Photographs of the core will be taken showing the top/bottom and depth interval of the core run, core location and date shown on the erasable white board in the photo. The geologist then continues logging the core stratigraphically and the hydrogeologist selects the physical property samples.

4.2.2 Physical Properties Sample Selection

These samples will be collected approximately every 20 ft in the same manner as the CVOC samples described in Section 2.2.1. An effort will be made to obtain samples from different lithologies or where variations in lithology occur as assessed during core logging. Each sample will be a cylindrical disc of the same diameter as the HQ core retrieved from the core barrel, with a height of 2 to 6 inches. These sections of core will be obtained such that the *in-situ moisture* conditions are retained: working quickly, keeping the core covered and out of direct sunlight, and immediately wrapping and sealing the samples. After the sample is broken from the core, it will be immediately wrapped tightly in clean aluminum foil twice around the circumference for complete coverage of the sample, followed by plastic wrap and tape. Finally, the sample will be completely wrapped in parafilm, labeled and placed in a sealable plastic bag. Each sample will be clearly labeled with the sample ID, core location, depth, and date. Details and a full lithological description of each sample will be recorded in the field notebook.

4.3 VOC Sample Preservation

VOC samples will be collected in 40 mL clear glass VOA vials with Teflon-lined septa and screw caps. The rock core sampling requires both purge and trap grade methanol for rock sample extraction and preservation, and wash grade methanol for decontamination. Methanol should be

ordered beforehand and available prior to start of drilling. Each labeled sample container and lid will be weighed empty, and re-weighed once the purge and trap grade methanol has been added to accurately determine the weight and volume of methanol extract. Sample vials are prepared with methanol on the day of sample collection where possible; otherwise the weight of the vial with methanol should be re-checked prior to use. At the end of each drilling day, each of the days vials used for rock samples will be weighed so the exact weight of each rock sample is known and then prepared for shipping. There should be a minimum of 15 g of rock in each sample jar. Sample bottles will be stored in a cooler with ice or fridge set to 4°C until they are shipped to the laboratory.

Following is a step-by-step outline of the process of rock core sampling for VOCs:

- Lay core in an aluminum foil-lined split PVC tray. Note top/bottom of core and depth interval, measure length and quickly identify features (fractures, breaks, lithology/mineralogy changes, evidence of fluid flow (i.e. secondary minerals, precipitates, slickensides, etc.) to select sample locations. Cover with aluminum foil to minimize CVOC volatilization and evaporation of pore water.

- Collect CVOC samples: break off a one to two-inch section of core using a rock hammer and chisel, inserting a wood spacer that specifies the sample ID, depth interval that was removed and the type of sample taken. If a field duplicate is planned, the disc length should be doubled and split lengthwise along the core axis to produce two samples from the same depth interval.

- Completely wrap each sample in a piece of clean aluminum foil to minimize volatilization loss and place in a zip-loc bag with a unique field ID, and place in a cooler with ice for storage prior to crushing. Record sample information including a lithology description, sample type (e.g. lithology pair, duplicate), depth, position relative to nearby fractures and other pertinent details.

Following collection of samples for each core run, transport samples to the crushing area.

- Trimming. Using a hammer and chisel and steel chipping tray, remove the outer rind of the sample exposed to drilling fluids.

- Place subsample in a clean, dry crushing cell and crush with the Enerpac™ system.

- Place stainless steel funnel and VOA vial with methanol below crushing cell. Empty crushed rock sample (minimum of 15 g) into 40 mL VOA sample vial containing a known volume (20 mL) of purge and trap grade methanol, taking care to avoid splashing of methanol out of the vial. Sample vials and screw caps with septum have been previously labeled and weighed both before and after filling with methanol so the mass/volume of methanol is accurately known. Bottle threads should be wiped clean with a kim-wipe prior to screwing on the cap to remove any rock fragments that prevent the cap from sealing properly.

- Decontaminate the rock crusher components using the procedure outlined in Section 4.4. Multiple crushing cells will be used (at least four or five sets) to allow processing of all samples from most core runs before decontamination is required.

- Equipment blanks and field duplicates will each be collected after every 20 samples.

After drilling is completed each day, weigh vials with the rock samples so the mass of rock is known. Wrap screw cap lid-bottle seam with Teflon tape, wrap vials with bubble wrap and place individually in zip-lock bags for shipping. Place in cooler with trip blanks, which remain with specific batches of samples until arrival at the laboratory, and keep on ice.

- Chain of custody (COC) forms will be filled out at the end of each day of sample collection and shipped with each cooler to the laboratory.

4.4 Decontamination of Drilling and Subsampling Equipment

Decontamination procedures are designed to remove all traces of contaminants from the equipment to prevent cross-contamination. Core barrels will be cleaned between runs using clean water and pressure washer. The sampling and trimming chisels will be sprayed off with wash grade methanol followed by distilled water, and dried with a clean cloth before re-use. Only those parts of the rock crusher that come into contact with the rock subsamples require cleaning, including the crushing cell with top/bottom plates (Pucks) and funnel used to direct the crushed rock sample into the VOA vial. Chipping trays will also be decontaminated between samples. At least four or five sets of crushing cells will be used, which in most cases should allow processing of all of the samples collected from a 5-ft core run. The procedure for cleaning these components consists of four steps:

Clean with a solution of water and a phosphate-free detergent (e.g. Alconox). Wash to get rid of obvious sediment.

1. Fully immerse in a clean water rinse,
2. Rinse with wash grade methanol using a squirt bottle to remove any traces of contaminants not removed previously.
3. Rinse with distilled (analyte-free) water using a squirt bottle to remove all traces of methanol.

Parts are then dried using clean paper towels. The soap and water baths will be changed on a regular basis, and equipment blanks will be collected after every twenty samples by wiping inside a clean crushing cell with a kim-wipe soaked in purge and trap grade methanol which is then placed in a 40 mL VOA vial to be submitted for analysis along with the rock samples. Decontamination fluids and remnant rock fragments will be contained and properly disposed.

4.5 Field QA/QC

Equipment blanks, collected as described above, will be taken after every 20 samples. Trip

blanks, consisting of purge and trap grade methanol in 40 mL vials will be placed with each batch of samples stored/shipped in coolers. These are filled with methanol at the same time as the sample vials, and handled with the prepared vials and methanol preserved VOC samples, and remain unopened until returned to the laboratory for analysis.

Field duplicate samples will be taken every 20 samples on core sections of double length split along core axis, so that the samples are taken from the same depth interval and lithology. Methanol blanks, used to identify contamination of the purge and trap grade methanol, are taken at the start and end of each methanol container (typically 1 L) while filling sample vials and stored/shipped separately from the samples. All QA/QC samples will be identified on the chain of custody forms and tracked throughout the sample handling and analysis process.

5.0 RESPONSIBILITIES

1. All personnel will legibly record data and observations (including phone conversations) in accordance with this SOP to enable others to reconstruct project events and provide sufficient evidence of activities conducted.

6.0 DEFINITIONS

1. *EPA* means the U.S. Environmental Protection Agency.

2. *Observations & Remarks Form (O&R):* A pre-printed form, which contains mostly blank space for general note taking. The form typically prompts the user for the study or project designation, the SEI project number, the client or sponsor name, the total number of pages (page *n* of n) and requires a signature and date. The form is generally used to capture notes of one person when another, more specific forms is not available.

3. *Raw data* means any worksheets, records, memoranda, notes, or exact copies thereof, that are the result of original observations and activities of a study and are necessary for the reconstruction and evaluation of the report of that study. In the event that exact transcripts of raw data have been prepared (e.g., tapes which have been transcribed verbatim, dated, and verified accurate by signature), the exact copy or exact transcript may be substituted for the original source as raw data. Raw data may include photographs, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments.

7.0 REFERENCES

40 CFR Part 160 Good Laboratory Practice Standards, August, 1989.

8.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

None

9.0 AUTHORIZATION

Written by:_____ Date:_____

Lee Rosberg, Staff Scientist

Approved by:_____ Date:_____

Seth Pitkin, Vice President

APPENDIX B: STONE SOP 10.17.0, *MICROWAVE ASSISTED EXTRACTION OF VOLATILE ORGANIC COMPOUNDS FROM ROCK SAMPLES*

STANDARD OPERATING PROCEDURE

SEI-10.17.0

MICROWAVE ASSISTED EXTRACTION OF VOLATILE ORGANIC COMPOUNDS FROM ROCK SAMPLES

NOTE: This SOP contains proprietary information – Do Not Distribute

SOP Number: SEI-10.17.0 Date Issued: 07/02/08
Revision Number: 0 Date of Revision: na

1.0 OBJECTIVE

The Microwave Assisted Extraction (MAE) method was designed at the University of Waterloo and is used to extract Volatile Organic Compounds (VOC) from rock samples.

2.0 SUMMARY OF METHOD

The microwave extraction is conducted in a microwave system model Ethos Sel Labstation, build by Milestone Srl, Italy. The main component of this system is the MPR-600/12S medium pressure segmented rotor which contains 12 vessels for solvent extraction.

Core samples are collected and the rock samples are immediately crushed using a new device that was designed by Parker's research team at the University of Waterloo. The crushed samples then undergo microwave assisted extraction (MAE). Typical solvent extractions using shaking or sonication require five weeks in order to extract all of the contaminant mass even following crushing. Using MAE this extraction time is reduced to less than an hour.

3.0 DEFINITIONS

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above-mentioned criteria.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

Instrument Blank: a blank matrix that is the same as the processed sample matrix (i.e. extract, digestate, condensate) and introduced onto the instrument for analysis.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Quality Control (QC): the overall system of technical activities, the purpose of which is to measure and control the quality of a product or service.

Spike: a known amount of an analyte added to a blank, sample or sub-sample.

Standard Operating Procedure (SOP): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

VOC – Volatile Organic Compounds

QA/QC – Quality Assurance/Quality Control

4.0 INTERFERENCES

When analyzing for VOCs, samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride), through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling must serve as a check on such interferences.
Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Whenever an unusually concentrated sample is encountered, it is recommended to prepare methanol blanks in the vessels used for the extraction of highly concentrated samples. Extraction vessels and syringes should be adequately cleaned and flushed prior to use. All glassware must be kept scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used or analyte-free water. Clean dry glassware should be stored in a clean environment.

5.0 SAFETY ISSUES

Laboratory personnel should take extra care when working with standards. When working with neat standards, make certain that there is adequate ventilation and that Nitrile or Latex gloves are worn and if necessary safety glasses.

If necessary and appropriate, a site-specific health and safety plan shall be created for each study site and followed. All samples as well as standards should be treated as a potential health hazard. Exposure to each

should be reduced to the lowest level possible using gloves and a hood. Material Safety Data Sheets (MSDS) should be available to all personnel.

Field visits may involve accessing remote areas. Health and safety concerns regarding these field visits are minimal, however, hazards such as slip, trip and falls, poisonous plant and dangerous animals, as well as getting vehicles stuck in remote areas, do present considerable health and safety issues. To help ensure field staff's health and safety in remote areas, all field staff are to have daily communication with the project manager or another appropriate SEI employee.
All chemicals are required to be received with a Material Safety Data Sheets (MSDS). MSDSs shall be made available to all personnel involved in the sampling and testing.

6.0 EQUIPMENT AND SUPPLIES

- The microwave system: model Ethos Sel Labstation, built by Milestone Srl. (Italy), equipped with the MPR-600/12S medium pressure segmented rotor containing 12 vessels for solvent extraction. The vessels are made of TFM Teflon, chemically inert to most organic solvents and combinations thereof, with very high stability to temperature extremes. It is microwave transparent; maximum working temperature for extended use is 260°C, and 300°C for brief use. Each vessel is protected by a safety shield, for which the maximum temperature for extended use is 250°C. The microwave system is controlled by a dedicated computer.
- Analytical balance
- Glass disposable pipettes
- 4 mL glass vials
- 1.5 mL GC vials
- Crimper
- Purge and trap grade methanol
- Wash grade methanol
- Nano (clean) water
- Spatulas
- Cleaning brushes
- Centrifuge

Oven®-lined septum

7.0 REAGENTS AND STANDARDS

Organic-free reagent water demonstrated to be free of compounds of interest (spring water, carbon filtered and/or deionized).

Purge and Trap Grade or equivalent grade methanol (demonstrated to be free of analytes and stored away from other solvents).

8.0 SAMPLE COLLECTION AND HANDLING

8.1 Sample Collection

Rock core samples are collected by trained geologist. Core samples are collected and the rock samples are immediately crushed using a new device that was designed by Parker's research team at the University of Waterloo. The core sample is placed in a closed stainless steel crushing cell fitted with "O"-rings and crushed with a stainless steel piston at pressures as high as 3000 psi. The crushed sample is then extruded from the cylinder directly into a **pre-weighed** 40 mL VOA vial containing a **known volume** of purge and trap grade methanol. The amount of air passing by the sample while being crushed is minimized as well as the time required to completely crush the rock fragments into the desired particle size. The stainless steel crushing vessels and associated tools are thoroughly decontaminated following each use. The samples are weighed upon receipt at the laboratory and recorded in the Log in summary sheet (Table 1.)

The crushed samples then undergo microwave assisted extraction (MAE). Typical solvent extractions using shaking or sonication require five weeks in order to extract all of the contaminant mass even following crushing.

8.2 Handling and Holding Times

Soil and rock samples collected in methanol are stored chilled at 4º C (<6 °C) from collection. Samples are allowed to come to room temperature just prior to analysis.

If necessary, a separate soil sample aliquot will be collected in a 40 mL vial or equivalent for percent moisture content so that results can be adjusted for %moisture and reported as dry weight rather than as received. Percent moisture is determined as follows: Percent Moisture Determination - Immediately after weighing the sample for analysis, weigh 5-10 g of the soil/sediment into a tared crucible. Determine the percent moisture by drying overnight at 105 ˚C. If available, allow to cool in a dessicator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

Percent moisture - %Moisture = gms of wet sample – gms of dry sample/gms of wet

9.0 PROCEDURE

Step 1: Sample Receipt

1. Unwrap samples carefully
2. Check all samples against the chain of custody forms
3. Sign all chains of custody and file them
4. Fill out the Stone Environmental sample login sheet (Table 1)
5. Assign unique SEI number to each sample received
6. Unwrap the teflon tape from each vial and weigh each sample in its vial
7. Record weight on login sheet
8. Rewrap the teflon tape around the vials

Step 2: Preparing Vials

1. Choose 12 samples for the current extraction batch and return the other samples to the refrigerator.
2. Each sample will require one 4-ml glass vial and two 1.5-ml glass autosampler vials. Each of these vials needs to be labeled with the sample's SEI number. When labeling the autosampler vials, make sure to label one with SEI # - A and the other with SEI # - B. The labeling process can be done while the microwave extraction (Step 3) is in progress.
3. Use the Dymo label software to print out labels for the vials. Attach the labels and organize the vials in racks for use later in the extraction process. NOTE: Make sure to affix labels as low as possible on the 1.5-ml autosampler vials so the autosampler does not encounter interference.

Step 3: Microwave Extraction

1. Assign a microwave vessel to each of the twelve samples in the batch and record that vessel number on the sample login sheet. NOTE: If there are both samples containing rock and samples not containing rock (e.g., trip blank) within the same extraction batch, make sure that the reference microwave vessel (Vessel #1) is used for a sample containing rock.
2. Turn on the microwave at the power switch. This also turns on the control screen. On the control screen, select Administrator and type in password (123456). Touch the PressPrep button and then go to the Method tab and the Param subtab. Make sure that the loaded method is rockcore.mpr and that the Twist and Start-Param buttons are checked. Also make sure that the Control for… dropdown menu is set to T1 and that Ventilation is set to 73 minutes. Use the vent button (looks like a fan) to rotate the rotor to access a certain vessel.
3. Prepare samples one at a time for microwave extraction via the following steps:.

a. Remove the appropriate segment from the rotor body

b. Place the workstation flat on the microwave door so that the ridge on the bottom edge is aligned with the base of the inside of the microwave for stability.

c. Using the torque wrench, unscrew the amber-colored cap of the microwave segment to release the vessel. Remove the vessel from the rotor segment by tilting it to the right and lifting it out.

d. Carry the vessel to the hood and open it by removing the brown spring and adapter plate, the teflon indicator ring, the teflon cover to expose the teflon vessel and the brown protection shield. Remove the vessel from the protection shield. There should be six separate pieces.

e. Empty the contents of the sample vial into the vessel.

f. Using the repipettor, introduce 5 ml methanol to the sample vial to rinse any remaining sample. Pour this rinse methanol into the vessel as well.

g. Weigh the teflon vessel with the sample in it and record the weight on the sample log in sheet.

h. Reassemble the entire vessel and return it to the segment. Use torque wrench to tighten down the cap until the wrench makes a loud click. Replace in the proper position within the rotor body and then move to the next vessel, using the vent button on the control screen to rotate the rotor if necessary.

i. After all vessels have been loaded with samples, put the round rotor cover on top of all the segments so they are locked into place. Install the temperature sensor by inserting the fiber optic sensor into the thermowell hole on the top of the reference vessel (vessel #1) until it is firmly set. Attach the other end of the temperature sensor (it is blue) to the microwave by plugging it into the top hole on the left inside wall of the microwave. Again, press in until it is firmly set.

j. To start the microwave extraction, press the green start button on the control screen. Before actually starting, the microwave will ask you two warning questions. The first asks you if you want to continue even if your pressure sensor is not monitoring. Say yes to continue. The second warning wants you to check your stirrer. We do not have this function enabled, so continue through this message too. At this point, the microwave program should begin, and proceed according to the rockcore.mpr method. The program should take two hours to complete. This includes a ventilation step that will cool the vessels down to approximately 30 degrees C. Turn the hood blower on.

k. Once the microwave program has completed, the ventilation fan will turn off. As long as the temperature is reading <30 degrees C, the vessels can be opened.

l. With the labeled 4-ml vials ready nearby, you can begin transferring the samples from the microwave vessels to the 4-ml vials. Start with the reference vessel and remove the temperature sensor from the reference vessel port and from the port inside the microwave. Place the temperature sensor on the shelf, out of harm's way. NOTE: Once you remove the sensor, the

temperature reading on the control screen will spike to a very high reading. This is ok. Now remove the round rotor cover so that you can access the vessels.

m. From here, prepare the samples for the centrifuge step. The centrifuge can only accept six samples at a time, so transfer the samples from the microwave to the 4-ml vials in two batches of six samples. Proceed to transfer the samples one at a time via the following steps:

   i. Use the workstation and torque wrench to unscrew the cap and remove the vessel from its segment.

   ii. Carry the vessel into the hood and carefully remove the spring and plate, indicator ring and teflon cover. Remove the vessel from the protection shield. NOTE: Use extra caution when removing the teflon cover from the reference vessel. Lift it straight up to prevent cracking the thermowell.

   iii. Weigh the sample in the teflon vessel. Record the weight on the login sheet.

   iv. Using a fresh glass transfer pipette, transfer approximately 3 ml of sample from the teflon vessel to an appropriately labeled 4-ml glass vial.

   v. Pour the remaining sample volume into the methanol waste container and rinse it 3x with 5ml methanol from the repipettor.

   vi. Make sure the vessel is dry before you seal it back up. You may want to set up a drying area in the hood, but make sure you keep all components for each vessel together without mixing them. Each component should be marked with a number corresponding to its vessel number.

Step 4: Centrifuge and Transfer Samples to Autosampler Vials

1. Load six 4-ml sample vials into the metal tubes of the centrifuge (the tubes are labeled 1-6).
2. Close the lid and turn on the centrifuge by setting the dial to 30 minutes.
3. While the first six samples are being centrifuged, prepare the second batch of six samples for the centrifuge step (i.e., transfer to labeled 4-ml vials).
4. After the first batch has centrifuged for 30 minutes, unload those vials and reload the centrifuge with the second batch of samples. Centrifuge for 30 minutes.
5. Once the centrifuge step is complete, transfer each sample from the 4-ml vial to two appropriately labeled 1.5-ml autosampler vials. Place a septum on top of the vial and crimp it securely with the hand crimper until the septum will not move/rotate on the vial. Until you are ready to run the samples on the GC, keep them in the freezer.

10.0 CALCULATIONS

None performed, See Analytical SOP

11.0 QUALITY CONTROL AND CORRECTIVE ACTION

Quality control samples are generated during sample preparation to determine if contamination or memory effects are occurring. Methanol blanks for all microwave vessels are prepared before new samples are extracted. The same procedure is followed when all the samples are prepared. Also, once a day, one microwave vessel blank is prepared. The vessel is chosen at random. It is also recommended to prepare microwave vessel blanks for the vessels used for the extraction of highly concentrated samples..

12.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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 United States Environmental Protection Agency (USEPA) has established a prevention 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.

The quantity of chemical 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.

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.

The USEPA requires that laboratory waste management practices conducted be 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 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.

13.0 REFERENCES

1. Yongdong Liu, “Microwave Assisted Rapid Extraction of VOCs from Low Permeability Media”, M.Sc. thesis, University of Waterloo, 2005.

2. Pawliszyn, Janusz, 1999, Applications of Solid Phase Microextraction, in RSC Chromatography Monographs; Smith, Roger S., Series Editor, Royal Society of Chemistry, Cambridge, UK, 655 p.

3. "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.

14.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Table 1. Example Sample Login Sheet

ROCK CORE LABORATORY SAMPLE LOGIN								
Sample ID	**SEI Number**	**Sample weight as received (sample + container)**	**Microwave Vessel ID**	**Pre-Sample Weight (Vessel and Lid)**	**Pre-Microwave Weight (sample + teflon vessel and lid)**	**Post-Microwave Weight (sample + teflon vessel and lid)**	**Analyst**	**Extraction Date**
		(g)		**(g)**	**(g)**	**(g)**		
			1					7/1/2008
			2					7/1/2008
			3					7/1/2008
			4					7/1/2008
			5					7/1/2008
			6					7/1/2008
			7					7/1/2008
			8					7/1/2008

15.0 AUTHORIZATION

Authored by: _____ Date: _____

Michael Rossi, Laboratory Manager

Approved by: _____ Date: _____

Seth Pitkin, Vice President

16.0 REVISIONS

APPENDIX C: STONE SOP 10.18.0, *THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/DUAL ECD DETECTORS IN ROCK SAMPLES (USING COOL ON COLUMN INJECTION AND SPLIT METHOD INJECTION)*

STANDARD OPERATING PROCEDURE

SEI-10.18.0

THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / DUAL ECD DETECTORS IN ROCK SAMPLES (USING COOL ON COLUMN INJECTION AND SPLIT METHOD INJECTION)

NOTE: This SOP contains proprietary information – Do Not Distribute

SOP Number: SEI-10.18.0 | Date Issued: 07/02/08
Revision Number: 0 | Date of Revision: na

1.0 OBJECTIVE

The method was developed at the University of Waterloo and is used to determine the concentration of volatile organic compounds (VOC) in soil and rock samples using an automated cool on-column injection and/or split method for highly sensitive determination of chlorinated solvents. The method was tested on chlorinated solvents presented in Table 1 and Table 2. For the automated cool on-column injection method, the calibration range is typically from 1.0 µg/L to 500 µg/L for the tri- and tetra-chlorinated compounds and 10 µg/L to 5000 µg/L for the dichlorinated compounds. For the split method, the calibration range is typically from 50 µg/L to 5,000 µg/L for the tri- and tetra-chlorinated compounds and 500 µg/L to 50,000 µg/L for the dichlorinated compounds. Higher values in the samples are measured by appropriate dilution of the samples.

2.0 SUMMARY OF METHOD

The analyses are performed on a Hewlett Packard model 6890 Gas Chromatograph with computer control. Methanolic extract is injected directly into a polar-deactivated pre-column connected to the analytical column. For the cool on-column method, the sample is injected using a cool on-column injector, set to ramped temperature mode. In the split method, the methanolic extract is injected using split-splitless injector (ratio 1:100) into the analytical column. A column coated with a thick film non-polar stationery phase (5 µm, HP-1, equivalent) is used in the method. Methanol is incompatible with this phase, and consequently elutes in dead time. The less polar analytes, refocused through the retention gap effect, are retained much more strongly and elute later, even when their boiling points are lower than that of MeOH. The use of non-polar stationary phase reduces the possibility of methanol coeluting with one or more of the analytes, which could adversely affect their chromatography and detection. Figure 1 presents a sample chromatogram obtained for a standard solution of the analytes obtained using the cool on-column injection

method and Figure 2 presents a sample chromatogram obtained for a standard solution of the analytes using the split method.

Core samples are collected and the rock samples are immediately crushed using a device that was designed by the University of Waterloo. For further details on the sampling and preservation technique associated with rock samples, see the Stone's SOP titled "*SEI-6.37.0 Field Methods for Retrieval, Collection, Handling, and Preservation of Rock Samples to be Analyzed for VOCs and Physical Properties"*.

The crushed samples then undergo microwave assisted extraction (MAE). For further details on the MAE procedure, see Stone's SOP titled *"SEI-10.17.0 Microwave Assisted Extraction of Volatile Organic Compounds from Rock Samples"*. Typical solvent extractions using shaking or sonication require five weeks in order to extract all of the contaminant mass even following crushing; using MAE this extraction time is reduced to less than an hour.

3.0 DEFINITIONS

Accuracy: the degree of agreement between a measurement and true or expected value, or between the average of a number of measurements and the true or expected value.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above-mentioned criteria.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

Instrument Blank: a blank matrix that is the same as the processed sample matrix (i.e. extract, digestate, condensate) and introduced onto the instrument for analysis.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Matrix: the substrate of a test sample.

Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Method Detection Limit: Method detection limits are determined according to the method described in "US EPA's Methods for Organic Chemical Analysis in Industrial Wastewater", EPA-600/4-82-057. For the purposes of this protocol, a sample of known concentration is analyzed 9 times. The results are

averaged, and the standard deviation of the results is calculated. The standard deviation multiplied by the value of Student's t for 8 degrees of freedom (n-1) at the 99% confidence level is considered to be equal to method detection limit. Limit of quantitation is defined as method detection limit multiplied by 3. Reporting limit is set equal to the lowest calibration standard.

Precision: an estimate of variability. It is an estimate of agreement among individual measurements of the same physical or chemical property, under prescribed similar conditions.

Quality Assurance (QA): an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Control (QC): the overall system of technical activities, the purpose of which is to measure and control the quality of a product or service.

Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

Quantitation Limit (QL): the minimum amount of a substance that can be quantitatively measured with a specified degree of confidence and within the accuracy and precision guidelines of a specific measurement system. The QL can be based on the method detection limit (MDL), and is generally calculated as 3-5 times the MDL, however, there are analytical techniques and methods where this relationship is not applicable. Also referred to as Practical Quantitation Level (PQL), Estimated Quantitation Level (EQL), Limit of Quantitation (LOQ).

Reporting Limit (RL): The level to which data is reported for a specific test method and/or sample. The RL is generally related to the QL. The RL must be minimally at or above the MDL.

Spike: a known amount of an analyte added to a blank, sample or sub-sample.

Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

Standard Operating Procedure (SOP): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

VOC – Volatile Organic Compounds

QA/QC – Quality Assurance/Quality Control

4.0 INTERFERENCES

When analyzing for VOCs, samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons, chloroform and methylene chloride), through the sample container septum during shipment and storage. A trip blank prepared from organic-free methanol and carried through sampling and subsequent storage and handling must serve as a check on such interferences.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be rinsed out between samples with an appropriate solvent. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a method blank to check for cross contamination. Extraction vessels and syringes should be adequately cleaned and flushed prior to use. All glassware must be kept scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used or analyte-free water. Clean, dry glassware should be stored in a clean environment.
There are some solvents, which cannot be separated in this method. On the non-polar column used as part of this method, bromodichloromethane always coelutes with trichloroethene and 1,1,1-Trichloroethane and 1,2-Dichloroethane can only be analyzed as a sum using the method. Also, VOC gases such as vinyl chloride and chloromethane can not be determined by this method.

5.0 SAFETY ISSUES

Laboratory personnel should take extra care when working with standards. When working with neat standards, make certain that there is adequate ventilation and that Nitrile or Latex gloves are worn and if necessary safety glasses.

If necessary and appropriate, a site-specific health and safety plan shall be created for each study site and followed. All samples as well as standards should be treated as a potential health hazard. Exposure to each should be reduced to the lowest level possible using gloves and a hood. Material Safety Data Sheets (MSDS) should be available to all personnel.

Field visits may involve accessing remote areas. Health and safety concerns regarding these field visits are minimal, however, hazards such as slip, trip and falls, poisonous plant and dangerous animals, as well as getting vehicles stuck in remote areas, do present considerable health and safety issues. To help ensure field staff's health and safety in remote areas, all field staff are to have daily communication with the project manager or another appropriate SEI employee.
All chemicals are required to be received with a Material Safety Data Sheets (MSDS). MSDSs shall be made available to all personnel involved in the sampling and testing.

6.0 EQUIPMENT AND SUPPLIES

1. Gas Chromatograph: Analytical system complete with gas chromatograph and all required accessories, column supplies, gases, syringes and data system to determine peak areas and perform integrations. Agilent (formerly Hewlett Packard) 6890 with computer control.
2. Cool on-column injector
3. Split-splitless injector
4. Dual ECD Detectors
5. Two auto sampler towers
6. Printer
7. Analytical Columns: Two capillary columns
8. Array of Microsyringes and glass disposable pipettes
9. Balance: Top loading, capable of weighing accurately to 0.01 grams
10. 1.5 mL glass GC vials and caps
11. Crimper
12. 4 mL glass vials
13. VOA vials: 40 mL collection containers with Teflon®-lined septum

7.0 REAGENTS AND STANDARDS

Organic-free reagent water demonstrated to be free of compounds of interest (spring water, carbon filtered and/or deionized).

Purge and Trap Grade or equivalent grade methanol (demonstrated to be free of analytes and stored away from other solvents).

Stock standards:
Stock standards may either be prepared from pure standard materials or purchased as certified solutions.

Secondary dilution standards are prepared using stock standard solutions, which contain the compounds of interest, either as single compounds or mixed together. Typically, for this method the stock standards are obtained from an approved vendor and mixed together. A certificate of analysis is retained by the laboratory and maintained on file or on file with the vendor.

Stone's SOP No. SEI-4.7.5 *Labeling, Preparation and Storage of Reagents, Solutions and Standards* provides procedures on properly labeling, preparing and storing of reagents and standards used in the

mobile laboratory for analytical methods. This SOP should be reviewed by the analyst before labeling, preparing and storing standards within the mobile laboratory.

8.0 SAMPLE COLLECTION AND HANDLING

8.1 Sample Collection

Rock core samples are collected by trained geologists. Core samples are collected and the rock samples are immediately crushed using a device that was designed at the University of Waterloo. The core sample is placed in a closed stainless steel crushing cell fitted with "O"-rings and crushed with a stainless steel piston at pressures as high as 3000 psi. The crushed sample is then extruded from the cylinder directly into a pre-weighed 40 mL VOA vial containing a known volume of purge and trap grade methanol. The amount of air passing by the sample while being crushed is minimized as well as the time required to completely crush the rock fragments into the desired particle size. The stainless steel crushing vessels and associated tools are thoroughly decontaminated following each use. The samples are weighed upon receipt at the laboratory and recorded in the Log in summary sheet.

The crushed samples then undergo microwave assisted extraction (MAE).

8.2 Handling and Holding Times

Rock samples collected in methanol are stored chilled at 4° C (<6 °C) from collection. Samples are allowed to come to room temperature just prior to analysis.

If necessary, a separate rock sample aliquot will be collected in a 40 mL vial or equivalent for percent moisture content so that results can be adjusted for %moisture and reported as dry weight rather than as received. Percent moisture is determined as follows: Percent Moisture Determination - Immediately after weighing the sample for analysis, weigh 5-10 g of the rock into a tared crucible. Determine the percent moisture by drying overnight at 105 ˚C. If available, allow to cool in a dessicator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of rock.

Percent moisture - %Moisture = gms of wet sample – gms of dry sample/gms of wet

9.0 PROCEDURES

Personnel Qualifications: The chemist performing these analyses should have substantial experience operating and troubleshooting gas chromatographs. Additionally, the analyst must be comfortable using microliter syringes and be familiar with basic analytical chemistry methodology and principles. The assessment of these qualifications is somewhat subjective but an analyst should normally be considered experienced after completing a B.Sc. in chemistry with one-year experience with gas chromatography in an analytical laboratory.

9.1 Typical GC Program for Back Inlet (Cool On-Column) and Front Inlet (split/splitless)

Oven Temp: 55°C (4.50 min), ramp: 10°C /min to 180°C, hold for 3 min.

Flow Rate: Cool on column, helium at 2.0 mL/min; Split/Splitless, helium at 2.3 mL/min.

Detector: uECD front and back detectors, detector temperature 350ºC

Injector: 1 uL injection on both front and rear inlets

Make-up gas: Nitrogen

Make-up gas flow: 60 mL/min

Cool on-column injector temperature: 55°C (0.0 min), ramp: 75°C /min to 220°C, hold for remainder of run.

9.2 GC Column

Column 1: Cool on column: Agilent HP-1 30.0 m x 0.320mm ID, 5 um film thickness, equivalent

Column 2: Split/splitless: Supelco SPB-1, 30 m x 0.250mm ID, 3 um film thickness, equivalent

9.3 Material Preparation:

Methanolic standards of the compounds of interest are prepared from a stock solution made by spiking pure chemicals of interest into purge and trap-grade methanol. Analyte concentrations for the standard solutions are calculated by mass. Methanolic standards should be kept in the refrigerator when not in use.

These standards are then diluted in methanol to obtain working (calibration) standards at the required concentrations. The working standards are analyzed in the same manner as the samples.

9.4 Calibration Criteria

Initial Calibration (ICAL):

Six to eight-point calibration for VOC compounds: For the automated cool on-column injection method, the calibration range is typically from 1.0 µg/L to 500 µg/L for the tri- and tetra-chlorinated compounds and 10 µg/L to 5000 µg/L for the dichlorinated compounds. For the split method, the calibration range is typically from 50 µg/L to 5,000 µg/L for the tri- and tetra-chlorinated compounds and 500 µg/L to 50,000 µg/L for the dichlorinated compounds.

The linearity of the calibration curves must be assessed and are used for all quantitation unless it is necessary to drop the high point or the low point. Linear regression is used for quantitation and the

correlation coefficient (r) of each compound must be greater than 0.995. Depending upon the on-site program acceptable correlation coefficient may be set at 0.99 in accordance with SW846 8000.

Initial Calibration Verification Standard (ICV):

A QC sample from a second (independent) source will be analyzed directly after the ICAL and after every 40 samples. The ICV sample will contain all the VOC compounds of interest at the mid-point. Recovery Limits for the ICV will be ±15%,

%Rec. = Actual Conc./Expected Conc.

Retention Time Windows and Pattern Recognition

Identification of the project- specific VOCs in the sample chromatogram is achieved by comparing the retention times generated by the calibration standards, continuing calibration standard and other fortified QC samples. Retention times must be within ± 0.04 minutes from the ICAL. If a retention time shift is observed in the CCV or daily ICV, then adjustments to the daily retention time windows will be made accordingly. Quantification of the VOCs is determined by comparison of the linear regression for that analyte from the initial calibration curve.

9.5 Sample Preparation, Analytical Sequence and Quality Assurance

Methanolic Sample: Using the Microwave Assisted Extraction (MAE) method (SOP SEI-10.17.n), the rock sample is transferred quantitatively from the vial into a 100 mL microwave vessel and prepared, following which a 5 mL aliquot of methanol is used to rinse the original sample vial. The vessel is weighed before and after addition of the sample and the rinse methanol. The vessel is then tightly sealed in the segment and is microwaved for 40 minutes at 120°C; with temperature ramp and cool down, the overall extraction time is usually one-hour and ten minutes. Twelve vessels can be microwaved at the same time. A 4 mL aliquot is taken from the 100 mL extraction vessel for the analysis. The remaining extract is then either stored or discarded, depending on project's needs. Only the MeOH aliquot is kept (no rock). A GC autosampler vial (about 1 mL of aliquot in each vial) is then prepared for the autosampler.

Analyze Samples on GC/ECD

1. In the Method & Run Control screen of the online method of the GC software, go to Sequence: Sequence Table to load your run sequence(s) for the front and/or back system.
2. Once the sequence has been established, go to Sequence: Sequence Parameters, to set up the data file structure for the run. Type in your initials for Operator Name, Under Data File, select Prefix/Counter and type in A and today's date under Prefix for Signal 1 (ex. A80606) and B and today's date under Prefix for Signal 2 (ex. B80606). The counter will update itself automatically to create a unique file name for each run.

3. Save sequence by going to Sequence Save Sequence As and typing in today's date (ex. 080606.S).
4. Print the sequence for the run log by going to Sequence Print Sequence. Once in this screen, check the Sequence Parameters box at the top. Under Sequence Table, check the Method and Injection Info Part box. Under Select Destination for Printout, select File and type the name of the sequence in the box (ex. 080606.TXT). Click Print and then go open the text file that was written. Print from there.
5. Load sample vials into the autosampler, making sure that the loading order matches that on the sequence printout.
6. When everything is ready, click Run Control, Run Sequence.

LCS or Second Source Preparation

Every 40 samples, a fortified blank, containing all of the targets and prepared from a source other than the material used for the calibration curve is analyzed. The QC limits are 80-120%.

Laboratory Duplicate:

Every 20 samples, a random sample is run in duplicate and the results are compared. The relative percent difference (RPD) should not exceed 15%.

Matrix Spike:

Every 40 samples, a matrix spike will be prepared and will contain only the VOC compounds of interest.

Methanol blanks

Every 20 samples. Methanol blanks should produce results lower than the lowest calibration standard

9.6 Data and Records Management

Samples are analyzed in sequences. The name of the sequence is set to be the date on which the analysis is performed. A chromatogram is printed for each analysis and stored in a binder. A sequence table is printed out and stored with the chromatograms of a given sequence. In addition, all chromatogram files are stored electronically. The file and the printed chromatogram can be easily accessed at any time because the analysis date is recorded in the report.

10.0 CALCULATIONS

All calculations are performed by the HP ChemStation software used to control the gas chromatograph. The calculations used to determine the concentration of a compound in an unknown sample are based on

the External Standard (ESTD) procedure, in which both calibration standards and unknown samples are analysed under the same conditions. The instrument is first calibrated using a set of seven to nine working standards, prepared according to the procedure described in paragraph 9. The software calculates the calibration curve, which is later used to convert analyte peak areas in the unknown samples into their concentrations. All calculations are performed automatically by choosing appropriate settings in the software.

Typical Reporting qualifiers are as follows:

B = Analyte is found in the associated method blank as well as the sample.

D = Compound is identified in an analysis at a secondary dilution factor.

E = Compound quantitation is above the instrument's calibration range for this analysis.

J = Indicates an estimated quantitation value.

U = Compound was analyzed for but not detected. Value reported is the method reporting imit.

11.0 QUALITY CONTROL AND CORRECTIVE ACTION

A new calibration curve is made at least once a week. A quality control (QC) sample set is analyzed every 20 samples. The QC set consists of a laboratory duplicate, methanol blank and one standard check. The laboratory duplicates and the standard checks should agree within 15% RPD and recovery, respectively. Methanol blanks should produce results lower than the lowest calibration standard. Second source standard or a laboratory control sample should be analyzed every 40 samples, and the results for all the analytes should fall within 20% of the expected values.

Quality Control Check	*Minimum Frequency*	*Acceptance Criteria*	*Corrective Action*
Initial Calibration (ICAL)	As necessary.	Minimum of 5 up to 8 points for VOCs. A correlation factor (r2) of 0.99 for linear regression.	Verify solution integrity and check instrument performance. Perform necessary maintenance and recalibrate instrument. Reanalyze all affected samples.
Initial Calibration Verification (ICV) and/or Laboratory Control Sample (LCS)	One per calibration (following acceptable ICAL) and every 40 samples	QC limits are 80-120% for target compounds. This same standard may be used as the daily LCS. Note: Limits may be adjusted based on the program should as required by DOD QMS.	Reanalyze once; if still out verify solution integrity or ICAL solution integrity, and instrument performance. Re-prepare and reanalyze all associated samples.
Retention Time (RT) Window Study	Every new column installation	All target compounds in all standards must fall within the established window of ± 0.04 minutes from ICAL	Perform system maintenance. Reanalyze affected samples.
Continuing Calibration Verification (CCV) or Standard checks	To be performed at the start of the analytical day and every 20 samples	± 15%D for VOCs	Verify solution integrity and instrument performance. Reanalyze standard once, if still out, recalibrate and reanalyze affected samples.
Matrix Spike (MS)	One per 40 samples of a similar matrix	QC limits are 70-130%D.	Reanalyze once; if still out, verify solution integrity and instrument performance. If necessary analyze a LCS or ICV and if acceptable, narrate as possible matrix effect.
Method Blanks	One per preparation batch	< the lowest calibration standard or reporting limit	Investigate source of contamination. Re-prepare and reanalyze all associated samples.
Laboratory duplicate	One set per 20 samples of a similar matrix	QC limits are 15 RPD for all detected compounds. .	Reanalyze once; if still out, verify solution integrity and instrument performance. If necessary analyze a LCS or ICV and if acceptable, narrate as possible matrix effect.

11.1 Data Review

The analyst is responsible for primary data review of data generated from the sample analysis. Analyses will be documented in the instrument run log. Maintenance is documented in the Instrument Maintenance Logbook. Instrument calibrations and recoveries of all QC samples must be within specified control limits. If instrument calibration or the recoveries of any QC sample exceed specified tolerances, then the affected sample results are evaluated and generally the samples are submitted for re-analysis. Manual integrations should be kept to a minimum and date and initialed by the analyst.

To determine if analytical results are acceptable, a qualified and independent QA/QC program shall conduct a secondary review on a weekly basis. If instrument calibration and recoveries of all QC samples are within the specified criteria, then the data reports will be submitted to the Project Manager as final results with no qualifiers. If recoveries of any QC samples exceed specified limits and re-analysis is not an option, then the samples will be qualified as estimated with a "J" qualifier (J= The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.). Data will not be reported if significant QC issues affect the batch analyses.

12.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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 United States Environmental Protection Agency (USEPA) has established a prevention 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.

The quantity of chemical 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.

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.

The USEPA requires that laboratory waste management practices conducted be 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 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.

13.0 REFERENCES

1. Maria Gorecka, T. Gorecki, B.L. Parker, "Automated Cool On-Column Injection for Highly Sensitive Determination of Chlorinated Solvents in Soils and Rocks", 24th International Symposium on Capillary Chromatography and Electrophoresis, Las Vegas, NV, May 20-24, 2001.
2. "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.

3. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8260b.pdf

14.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Table 1. Summary of the typical detection limits for the on-column method.

Compound	[1]Method Detection limit [3]µg/L]	[1]Method Detection Limit [4]µg/Kg]	Reporting Limit [3]µg/L]	Reporting limit [4]µg/Kg]
1,1-Dichloroethene	0.6	.6	10	10
trans-1,2-Dichloroethene	1.2	1.2	10	10
cis-1,2-Dichloroethene	.29	.29	10	10
Trichloroethene	[2]0.2	[2]0.2	1.0	1.0
Tetrachloroethene	[2]0.2	[2]0.2	1.0	1.0
Trichlorotrifluoroethane	[2]0.2	[2]0.2	1.0	1.0
Chloroform	[2]0.7	[2]0.7	1.0	1.0
1,1,1-Trichloroethane	[2]0.1	[2]0.1	1.0	1.0
Carbon Tetrachloride	[2]0.1	[2]0.1	1.0	1.0

1 = Method detection limits (MDLs) are determined according to the method described in "US EPA's Methods for Organic Chemical Analysis in Industrial Wastewater", EPA-600/4-82-057.
2 = MDLs for these compounds have been adjusted to ten times their statistically derived values so that they can be practically achieved by the method.
3 = Limit is given as mass per volume of methanol extract.
4 = Limit is given as mass per mass of wet rock – assumes 20 ml methanol is combined with 20 grams of wet rock.

Table 2. Summary of the typical detection limits for the split method.

Compound	[1]Method Detection limit [2]µg/L]	[1]Method Detection Limit [3]µg/Kg]	Reporting Limit [2]µg/L]	Reporting limit [3]µg/Kg]
1,1-Dichloroethene	200	200	500	500
trans-1,2-Dichloroethene	230	230	500	500
cis-1,2-Dichloroethene	190	190	500	500
Trichloroethene	19	19	50	50
Tetrachloroethene	17	17	50	50
Trichlorotrifluoroethane	25	25	50	50
Chloroform	18	18	50	50
1,1,1-Trichloroethane	22	22	50	50
Carbon Tetrachloride	22	22	50	50

1 = Method detection limits (MDLs) are determined according to the method described in "US EPA's Methods for Organic Chemical Analysis in Industrial Wastewater", EPA-600/4-82-057.
2 = Limit is given as mass per volume of methanol extract.
3 = Limit is given as mass per mass of wet rock – assumes 20 ml methanol is combined with 20 grams of wet rock.

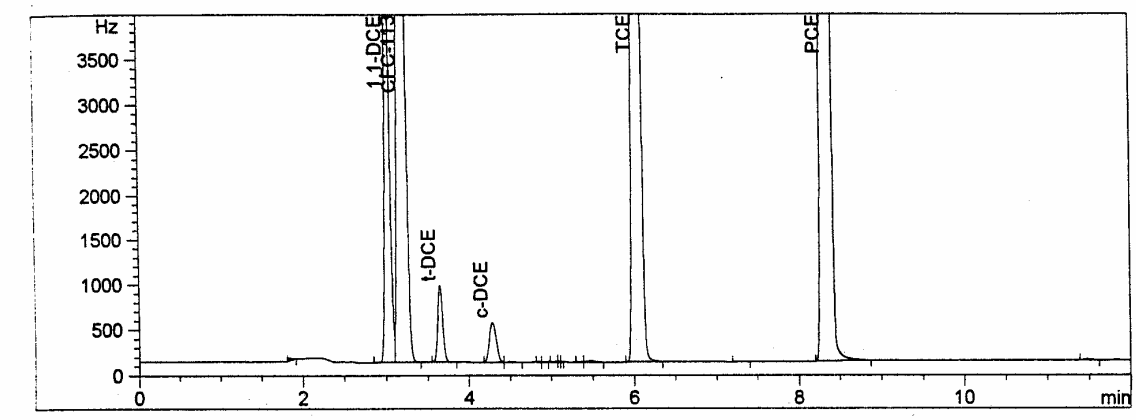


Figure 1. Example of a chromatogram obtained for a standard solution of the analytes using the cool on column method

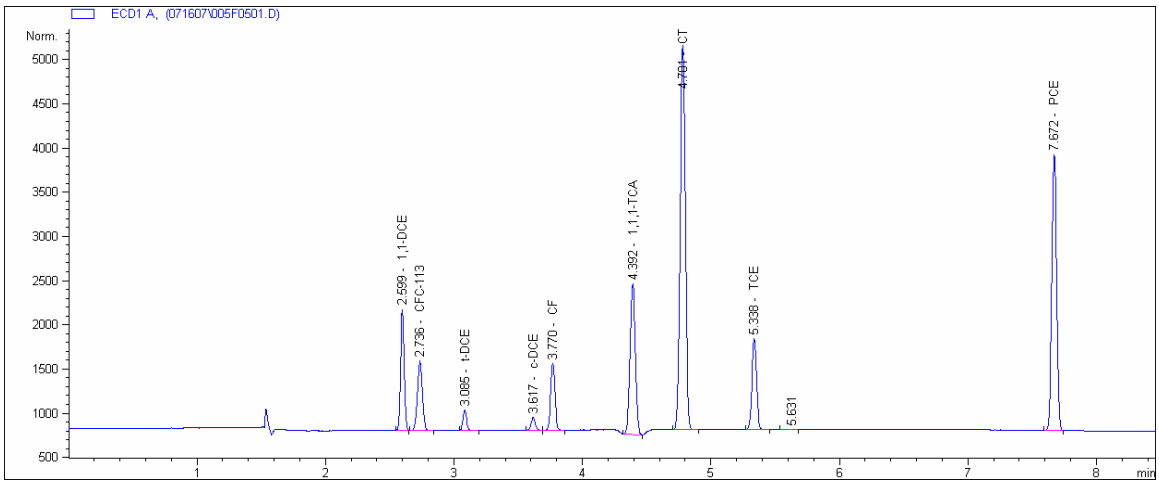


Figure 2. Example of a chromatogram obtained for a standard solution of the analytes using the split method.

AUTHORIZATION

Authored by: _____ Date: _____

Michael Rossi, Laboratory Manager

Approved by: _____ Date: _____

Seth Pitkin, Vice President

15.0 REVISIONS

APPENDIX D: WALKLEY, ALLEN, 1947, *A CRITICAL EXAMINATION OF A RAPID METHOD FOR DETERMINING ORGANIC CARBON IN SOILS-EFFECT OF VARIATIONS IN DIGESTION CONDITIONS AND OF INORGANIC SOIL CONSTIUENTS*, SOIL SCIENCE, VOL. 63

Soil Science (1947)
#63

A CRITICAL EXAMINATION OF A RAPID METHOD FOR DETERMINING ORGANIC CARBON IN SOILS—EFFECT OF VARIATIONS IN DIGESTION CONDITIONS AND OF INORGANIC SOIL CONSTITUENTS

ALLAN WALKLEY

The Waite Institute[1]

Received for publication September 3, 1946

The method discussed in this paper was tentatively suggested (30) in 1934 to meet the demand for a quick, simple, if approximate, means for determining organic carbon. The procedure was based on the well-known method of Schollenberger (21, 22), the chief difference being the manner in which the digestion was conducted. When concentrated H_2SO_4 was added to a mixture of soil and aqueous $K_2Cr_2O_7$, the heat of dilution raised the temperature sufficiently to induce a very substantial oxidation within a minute or so. Residual $K_2Cr_2O_7$ was titrated against ferrous ammonium sulphate as suggested by Schollenberger. Later the method was modified (31) in some of its details.

Trials conducted in 1935 by the International Society of Soil Science and reported by Crowther (5) showed that the method gave more variable results than those employing digestions at higher temperatures and of longer duration. In spite of this it is quite obvious from various publications on soil organic matter which have appeared in the last 10 years, that the method has been used a good deal. Evidently there are many who have rated convenience and speed more highly than accuracy, and who have at the same time demonstrated that the accuracy was sufficient for their purpose. During this period no other methods seem to have displaced the titrimetric ones.

The values obtained by the method were in most instances considerably lower than those obtained by orthodox dry combustion, and a multiplying factor was therefore proposed to bring them more into line with the latter. Some of the causes of the variation of this factor have been briefly mentioned elsewhere (5, 31). It is the purpose of this paper to deal more fully with some of these, and to present new data on other causes of variation, so that the method will have greater utility. Many relevant observations by other workers have also been incorporated.

It is perhaps debatable whether any attempt should ever be made to compare results obtained by an indirect method with those obtained by a direct one. Some prefer that the data be regarded as single values which should stand or fall on their own merits. There are many, however, who would rather think of the results of indirect methods in the units employed by the direct ones.

Some have sought to emphasize the use of the single-value concept in ti-

[1] Division of Soils, Council for Scientific and Industrial Research, The Waite Institute, Adelaide, South Australia. The author is now with the Division of Industrial Chemistry, of the Council, at Melbourne, Victoria. He wishes to thank G. S. Hart for assistance with some of the laboratory work in connection with this investigation.

trimetric methods on the score that the figure obtained is of value in showing the degree to which soil organic matter has already been oxidized. Such arguments cannot be pushed too far, since the substances easily oxidized by CrO_3 and other oxidizing agents are not necessarily those readily attacked by microorganisms. It has been found that lignin and cellulose are equally readily attacked in the CrO_3 digestion, so that the latter in no way simulates the action of organisms which discriminate so sharply between the two.

Whichever viewpoint is held, that is, whether the method is used with or without a multiplying factor, it is important to know the reasons for high or low results. The possible causes of variation have been arranged in three groups as follows:

1. Those due to differences in conditions of digestion and to differences in strength of reagents.
2. Those due to inorganic soil constituents.
3. Those due to variations in the composition of soil organic matter.

Many of the factors involved in group 3 (which are not discussed in this paper) are closely related to those of group 1, because certain types of organic matter are more susceptible than others to variations in oxidizing conditions. However, it is more convenient to separate them in this way.

It is apparent from the literature that a number of workers continue to follow the original procedure, being presumably unaware of the later modifications (5, 31). These, though slight, made for much greater convenience, especially in the handling of large numbers of samples. For this reason, and to serve as a basis for subsequent discussion, the method as it is used now is given below.

METHOD

Reagents

N Potassium dichromate. Dissolve 49.04 gm. reagent-grade $K_2Cr_2O_7$ in water and dilute to 1 liter.

Sulfuric acid. Must be at least 96 per cent.

Phosphoric acid. Approximately 85 per cent.

Diphenylamine. To 0.5 gm. add 20 ml. water and 100 ml. concentrated H_2SO_4.

N Ferrous sulfate. Dissolve 278.0 gm. reagent-grade $FeSO_4 \cdot 7H_2O$ in water, add 15 ml. concentrated H_2SO_4, and dilute to 1 liter. Standardize by titration against the *N* $K_2Cr_2O_7$ solution above. A convenient piece of apparatus designed especially for routine titration, embodying a burette with self-adjusting zero which is filled from a reservoir containing $FeSO_4$ kept under hydrogen, is described by Piper (19, p. 225). An alternative method of keeping $FeSO_4$ employing a lead amalgam reductor has recently been given by Duke (7). The $K_2Cr_2O_7$ is delivered from a similar burette mounted over a storage vessel; the H_2SO_4 and H_3PO_4 are delivered from quick-delivery pipettes with self-adjusting zero fittings.

Procedure

Grind sufficient soil for convenient sampling to pass a 0.5-mm. screen, avoiding mortars of iron or steel. Transfer a weighed quantity, not exceeding 10 gm. and containing about 10 to 25 mgm. of organic carbon, to a 500-ml. Erlenmeyer flask. Add 10 ml. of $K_2Cr_2O_7$ followed by 20 ml.[2] of H_2SO_4. Shake the flask once or twice and allow it to stand for 20 to

[2] This amount is incorrectly given as 15 ml. in Tiruin, I. V. The Organic Matter of Soils, p. 159. Moscow, 1937.

30 minutes. Then add 200 to 300 ml. water, 10 ml. H_3PO_4, and 1 ml. diphenylamine solution. Run in $FeSO_4$ until the solution is purple or blue. Continue to add $FeSO_4$ in portions of about 0.5 ml. until the color flashes to green, which it does with little or no warning. Then add 0.5 ml. $K_2Cr_2O_7$ and complete the titration by adding $FeSO_4$ drop by drop until the last trace of blue disappears. If more than 8 of the 10 ml. $K_2Cr_2O_7$ originally taken has been reduced, repeat the determination with less soil.

The color is not always purple on adding the indicator at the beginning of the titration, but the color always appears just before the end point. Similarly the purple color often does not appear on the addition of 0.5 ml. excess $K_2Cr_2O_7$, but it soon develops with the first drop or two of $FeSO_4$. With more than 10 gm. soil present the color change may become difficult to follow. Large amounts of $CaSO_4$ (from calcareous soils) or AgCl (if Ag_2SO_4 is used to prevent chlorine interference in saline soils) alter the shades of the colors, but the change (now from lavender to pale green) is still just as sharp as before. It has been found convenient to have the flask illuminated brightly from the side by a bench light. The color change is then easily seen in a thin layer of liquid as the flask is shaken.

The percentage of carbon in the soil is given by the following formula:

$$\frac{V_1 - V_2}{W} \times 0.300 \times f$$

where V_1 = volume of N $FeSO_4$, in milliliters, required in blank titration
V_2 = volume of N $FeSO_4$ in milliliters, required in actual titration
W = weight of soil in grams
f = factor whose value is under discussion. The term "recovery" ($100/f$) is also used.

VARIATIONS DUE TO DIFFERENCES IN CONDITIONS OF DIGESTION AND TO DIFFERENCES IN STRENGTH OF REAGENTS

The oxidizing action of acidified dichromate can be represented by the half reaction:

$$Cr_2O_7^{--} + 14H^+ + 6e^- = 2Cr^{+++} + 7H_2O, E^\circ = 1.36.$$

Since the hydrogen-ion activity enters the E. M. F. equation at the high power of 14, increasing acidity will lead to a large increase in oxidizing power. Thus the redox potential of the system depends primarily on the concentration of the H_2SO_4, while the amount of material that can be oxidized depends on the concentration of the $K_2Cr_2O_7$. Up to a point at least, then, an increase in recovery of carbon would be expected from an increase in H_2SO_4 concentration. This is found to be so in practice. The recovery of carbon, however, also depends on the final temperature obtained during digestion, and obviously there will be some optimum ratio between the volumes of H_2SO_4 and aqueous solution yielding the maximum temperature rise. As a result of these two effects, the recovery of carbon first increases with increasing ratio of H_2SO_4 to $K_2Cr_2O_7$ solution, passes through a rather flat maximum, and then decreases. Figure 1 shows the mean recoveries for several soils.

Determinations conducted on some 20 soils using the 15:15 ratio gave consistently lower figures (about 25 per cent) than those on the same soils using the 20:10 ratio. The temperatures obtained were the same in each series, the effect being purely one of higher oxidation potential. The fact that the ratio 20:10 may be decreased to 20:15 without any appreciable fall off in recovery is of importance in determinations on highly calcareous soils low in organic carbon,

for the amount of H_2SO_4 neutralized is then appreciable. The 15:15 ratio is quite unsuitable for such soils. In this connection it is interesting to note that Snethlage (26) has shown that the rate of oxidation at 100°C. of a number of organic compounds has a definite maximum when the H_2SO_4 is about 80 per cent by weight. The strength of the acid in the 20:10 mixture is 75 per cent by weight.

The effect of increasing the dichromate concentration while maintaining the ratio of H_2SO_4 to aqueous solution at 20:10 is shown in figure 2.

In this trial the size of sample was, of course, appropriate to the strength of dichromate used. Sodium dichromate, being much more soluble than $K_2Cr_2O_7$,

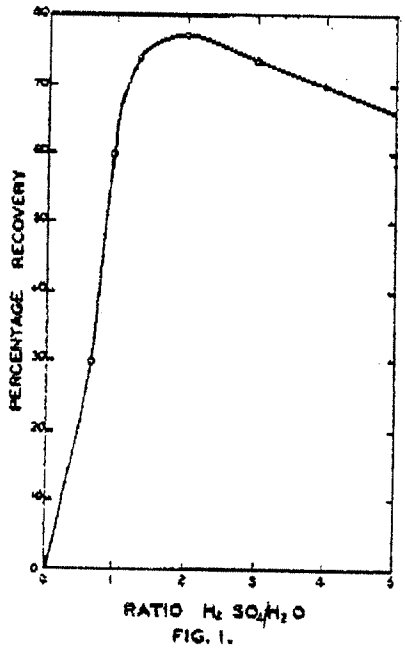


FIG. 1.

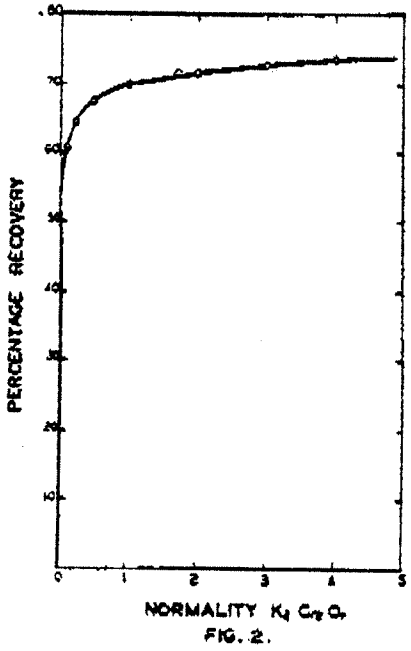


FIG. 2.

FIG. 1. EFFECT OF H_2SO_4 CONCENTRATION ON RECOVERY OF CARBON
FIG. 2. EFFECT OF $K_2Cr_2O_7$ CONCENTRATION ON RECOVERY OF CARBON

was used for the last three determinations. The results show that it is not worth while changing over to a stronger dichromate for general use, particularly as the volume required for the titration with *N* $FeSO_4$ then becomes greater and rather unwieldy for a rapid routine method. When dealing with organic soils, however, the use of stronger dichromate has decided advantages, because a correspondingly larger amount of soil can be taken, and sampling errors are thereby reduced. For the determination of organic matter in aqueous extracts it is sufficient to take 5 ml. of sample, add 5 ml. of one of the above solutions of appropriate strength, and then proceed as usual.

The unimportance of the concentration of dichromate is one of the factors

contributing to the success of all titrimetric methods employing it, for the constancy of the oxidation potential throughout the digestion ensures that the last fractions of the organic matter attacked are subjected to the same intensity of oxidation as the first fractions. If this were not so the recovery would depend on the size of sample taken, and a large excess of oxidant would be required to remove this source of error. In the method under discussion it has been found that at least 80 per cent of the $K_2Cr_2O_7$ can be reduced without affecting the results.

The final temperature reached in the reacting mass clearly depends upon the difference between the heat generated and that lost to the vessel, its contents and surroundings. The following factors are therefore of importance:

Acid strength. Experiments on a variety of soils, using acids of strengths varying between 90 and 99 per cent, showed an approximate linear increase of recovery of 1 per cent for every 1 per cent increase in acid strength. With H_2SO_4 containing dissolved P_2O_5, such as is sometimes used in the Kjeldahl method, further increases in recovery resulted, but these did not seem large enough to warrant departure from the use of a reagent available everywhere. The rate at which the acid is added is not critical. The automatic pipette used in this work delivers 20 ± 0.2 ml. in about 10 seconds.

Size of reacting vessel. Pyrex conical flasks of 500 ml. capacity resulted in lower recoveries (about 2 per cent) than when thin-walled 250-ml. flasks were used. The larger size, being more convenient for titration, was preferred, however, and a set of 24 was selected with weights varying between 100 and 130 gm.

Air temperature. A number of determinations on several soils with room and reagent temperatures varying from 15°C. to 30° C. showed that all recovery increased by about 1 per cent for every 5° C. rise in air temperature. Variations due to this and to changes in acid strength can be largely eliminated in any one laboratory by conducting one or two determinations on a standard soil with each large batch. This practice has been found useful in correlating results obtained over intervals of time.

Other methods of digestion such as Schollenberger's and Tiurin's (28) define the temperature much more precisely; for example, Schollenberger advises heating his digestion mixture to 175°C. in $1\frac{1}{2}$ to 2 minutes, whereas Tiurin recommends boiling (145°C.) for 5 minutes. Schollenberger (5, 23) has also shown that more consistent results are obtained if 10 ml. N $K_2Cr_2O_7$ and 10 ml. H_2SO_4 are used for the digestion and the temperature is held at 140°C. for 5 minutes than if 20 ml. H_2SO_4 is used with no external source of heat. In all chromic acid titration methods the object should be to bring about the maximum oxidation of organic matter before any appreciable amount of chromic acid has undergone thermal decomposition. Snethlage (27) has shown that the kinetics of the decomposition are complex and best represented by assuming that two reactions, one monomolecular and the other bimolecular, occur simultaneously. The reaction is positively catalyzed by $Cr_2(SO_4)_3$, which is the main product of reduction, and probably by other substances. Ignited soil is one such substance and probably unignited soil also, but because of the difficulty of preparing an unignited soil devoid of organic matter it is difficult to establish the magnitude of the effect. The decomposition proceeds more rapidly as the H_2SO_4 concentration increases, and for this reason mixtures in the ratio of 2

H_2SO_4 to 1 aqueous solution cannot be boiled for long in the presence of catalysts without undergoing considerable decomposition. This fact was thoroughly appreciated by Tiurin (who uses a 1:1 ratio) in framing his method, and by Schollenberger in suggesting the 1:1 modification just referred to.

Several workers have reported the results obtained by supplementing the heat of dilution of the 2:1 mixture with an external source of heat. Smolik (25) boiled the mixture for 1 minute and claimed good agreement with the Dennstedt method on 30 different soils. On the other hand, Novák and Pelisek (18), using the same procedure, obtained excessively high results (as would be expected if there was much decomposition of CrO_3) and so reverted to the original procedure for the remainder of their study of the method. Similarly some of the results of Kelley and Thomas (11), who heated the mixture in a water bath (presumably at 100°C.) for 15 minutes, were unusually high. Whether there is any appreciable thermal decomposition of CrO_3 in the course of a normal determination when the temperature is raised suddenly by the heat of dilution alone to about 110–120°C. and then allowed to cool cannot be stated. There is certainly none in the absence of soil and none in the presence of a large variety of ignited soils.

Silver salts either in the form of $Ag_2Cr_2O_7$ or Ag_2SO_4 have been used (5) as catalysts in CrO_3 digestions, the object being to catalyze the oxidation of CO to CO_2. Whether or not this is the mode of action, higher results are usually obtained when a silver salt is present, the effect being greatest with Tiurin's method of digestion, less with Schollenberger's, and least with the Walkley-Black method (5, 29). Some recent experiments on a variety of soils have shown that the increase in the last method is rarely more than 3 per cent. Since in all three methods the results obtained with added Ag_2SO_4, though higher, are no more consistent, there seems little justification for the use of this salt.

In the method as originally described the soil was first ground to 100 mesh. Subsequent experiments showed that grinding to ½ mm. was sufficient, and this standard of size has been adopted throughout the present work. More recently results have indicated that the extent of oxidation is much the same even in soils of 1 or 2 mm. size. It appears probable then that considerations of sampling alone should decide whether grinding is necessary. If it can be dispensed with, a considerable saving of time will result in routine determinations.

Another change which makes for greater convenience is to omit the 1-minute shaking. The $K_2Cr_2O_7$ solution is added to each flask (24 is a suitable number for a batch), then acid to the first flask, and this after one or two shakes, is set aside while acid is added to the next. When the acid has been added to the last flask, the first is ready for dilution and titration. No appreciable differences have been observed with times of standing varying between 5 and 40 minutes.

Other indicators have been suggested for the titration including *o*-phenanthroline (1, 4) barium diphenylamine sulfonate (1), and phenylanthranilic acid (12). After these were tried, the conclusion was reached that preference for any one is largely a matter of personal taste. In a survey of some 300 Australian soils no sample was found in which the end point could not be recognized

to within 1 or 2 drops of diphenylamine. Smith and Weldon (24) prefer to add excess ferrous ammonium sulfate and back titrate with $KMnO_4$; Novák and Pelisek (18) do likewise but back titrate with $K_2Cr_2O_7$.

It will be seen that by the combined effect of using 100 per cent H_2SO_4, 3 *N* $Na_2Cr_2O_7$, and Ag_2SO_4, it might be possible to raise the recovery of carbon in many soils by some 5 per cent or more. There can be no doubt, however, that the inconvenience would outweigh the advantages. Substantial increase in recovery can probably be achieved only by increasing the time and temperature of digestion. Suitable procedures already exist embodying these refinements (23, 29). This fact having been realized early, the aim of subsequent investigations was to examine the magnitude of the causes of variation rather than to attempt to eliminate them. Variations due to several inorganic oxidizing and reducing agents, however, can be eliminated by appropriate modifications of the method.

EFFECT OF SOME INORGANIC CONSTITUENTS

Calcium carbonate

The fact that $CaCO_3$ is without influence in titrimetric methods has always been one of the strongest arguments in favor of such methods, particularly for the examination of highly calcareous soils deficient in organic matter, where the complete removal of the carbonate prior to dry combustion is tedious and difficult in many instances. Even when a 10-gm. sample of soil containing 50 per cent $CaCO_3$ is taken for analysis, only about 5 gm., or one seventh, of the total amount of H_2SO_4 is utilized in neutralization. This diminution in strength, as was shown earlier, is not sufficient to affect appreciably the intensity of attack on organic matter. Any slight effect is probably more than compensated by the slightly increased temperature due to the neutralization reaction. The unimportance of $CaCO_3$ has been proved by adding 5 gm. $CaCO_3$ to a number of soils prior to determining the carbon content. The increases in recovery over those for the untreated soils did not exceed 2 per cent. Successful trials of the method on large numbers of calcareous soils have also been conducted.

Chlorides

The disturbing effect of soluble chlorides has been examined in detail and reported elsewhere (31). It was shown that the reaction between the dichromate and the chloride proceeded in such a way that the former was reduced quantitatively, thus permitting the accurate application of a correction factor. The correction consists in subtracting one twelfth of the chlorine content from the apparent carbon content. (1 atom C $\equiv$ 4 atoms Cl, and $12.0/4 \times 35.5 = 1/12$). It was found to be valid up to a Cl:C ratio of 5:1.

Alternatively the oxidation of the chloride can be prevented by using H_2SO_4 containing 25 gm. Ag_2SO_4 per liter for the digestion. Mercuric oxide and mercuric sulfate were found equally effective. The latter has also been found satisfactory for immobilizing chlorine in nitrogen digestions (17). Ratios of

Cl:C up to 5:1 have been encountered in a series of marine swamp soils near Adelaide, South Australia. Their analysis showed that when the correction factors were applied, the correlation with dry combustion figures was as high as for other groups of nonsaline soils.

Higher oxides of manganese

The forms in which the higher oxides of manganese exist in the soil are not known. Recent x-ray diffraction studies (8, 15)[3] have shown that there are four or five different modifications of the oxide approximating to the formula MnO_2, apart from several modifications of that approximating to the formula Mn_2O_3, as well as Mn_3O_4. Many of the oxides show a deficiency of oxygen; for example, the higher oxides show a departure from the stoichiometric formula MnO_n where $n = 2$. Thus though it appears that pyrolusites, whether natural or artificial, have values of n very close to 2, yet for certain other oxides prepared in the wet way, n may be as low as 1.7 or 1.8 and still retain the same structure as an oxide for which $n = 1.97$. Such low values may be due to absorbed manganous ion, or to an actual defect of oxygen in the lattice, or to both. In any event the oxygen readily available ("active oxygen") is probably $n-1$ atoms of oxygen per atom of manganese.

Besides differences in crystal form and content of active oxygen, large differences in reactivity are found. D'Agostino (6) showed that there were big differences between the rates at which different oxides reacted with acidified oxalic acid, his method being to measure gasometrically the rate of production of CO_2, $\left(\frac{dv}{dt}\right)$. Still bigger differences in $\left(\frac{dv}{dt}\right)$ have been found by Wadsley and Walkley[4] in an examination of a number of ores and chemically prepared manganese oxides, the highest value for an ore being about 30 times that for the most slowly reacting ore, and the highest value for a chemically prepared oxide being about five times greater again. There is no obvious correlation between reactivity and structural type. It seems probable at present that surface area is the chief factor responsible, though lattice imperfections and defects also doubtless play a part.

There seems no reason why all the structural forms found in ore bodies should not occur in soils. But what is probably more important, the range of reactivities (D'Agostino values) encountered in natural and chemically prepared samples could almost certainly occur in soils. Such a range of reactivities would be quite sufficient to account for the differences in the percentage of total manganese reduced and leached from various soils by buffered quinol solutions (14).

When MnO_2 and $K_2Cr_2O_7$ are heated with an oxidizable substance in the presence of an acid, the two oxidizing agents compete with each another, and the proportion of the total oxidation effected by the MnO_2 depends on its re-

[3] Cole, W. F., Wadsley, A. D. and Walkley, A. Unpublished work, 1946.
[4] Wadsley, A. D. and Walkley, A. Unpublished work, 1946.

activity. Thus even if the active oxygen content of the soil were known accurately, it would not be possible to correct for it. This difference in behavior of different oxides is well shown in the results (table 1) of several experiments where samples of oxides in amounts equivalent to 0.200 gm. MnO_2, were added to 0.040 gm. sucrose and digested as usual. After dilution with water the digests were filtered through sintered glass to remove unattacked oxide, and the filtrate was titrated with $FeSO_4$. Determinations were also conducted in the absence of MnO_2 to serve as standard. The amounts of $K_2Cr_2O_7$ and MnO_2 were sufficient for each to oxidize all the sucrose completely even if the other were absent.

Clearly the rate of attack by the first three ores is so slow that the sucrose is oxidized almost entirely by the $K_2Cr_2O_7$ and only the artificial oxide plays any important part. The correspondence between the figures in the last two columns

TABLE 1

Fraction of sucrose oxidized by samples of MnO_2 of different origins

0.200 gm. MnO_2 added to 0.40 gm. sucrose

ORIGIN OF OXIDE	MINERAL COMPOSITION*	D'AGOSTINO VALUE $\left(\frac{dv}{dt}\right)$†	PERCENTAGE OF SUCROSE OXIDIZED BY MnO_2
Gold Coast ore	γ MnO_2 mostly; some pyrolusite	0.14	<1
Western Australian ore	Cryptomelane	0.19	<1
South Australian ore	Pyrolusite	0.48	<1
New Zealand ore	γ MnO_2 and cryptomelane	2.0	6
Chemically prepared oxide	Unknown oxide with layer lattice structure	8.0	49
Chemically prepared oxide‡			21

* See text footnote 3.

† See text footnote 4.

‡ Same sample as preceding, but only 0.100 gm. MnO_2 added.

suggests that the D'Agostino value gives a good indication of the amount of disturbance in the method likely to be caused by any one type of MnO_2. The most reactive type represented here may perhaps correspond to the freshly precipitated soil manganese which is in circulation, which readily takes part in oxidation reduction reactions, and which is therefore of significance in the nutrition of the plant; whereas the least reactive types may correspond more to the inert reserve material. In normal soils the amounts of such readily reducible oxide will certainly be small, and even in highly manganiferous soils it does not seem likely that there would be more than a small fraction of the whole present in this state. It is considered that the average reactivities of the oxides in any one manganiferous soil is more likely to be nearer those of the first four samples, and therefore with the ratio MnO_2 to carbon existing there (8.5:1) the error in the carbon determinations would be only 0 to 6 per cent. The highest ratio reported in the Waite Institute collection of Australian soils was 0.8, the soil in question (a basaltic red loam from Queensland) having the

most serious quinhydrone error of a number examined by Best (3). The recovery of carbon was 72 per cent, which is not abnormal, and subsequent examination of a series of 30 similar soils confirmed that the magnitude of the error was very small in all instances. The method has been reported (32) successful on a variety of Hawaiian soils, though no mention was made of whether these were the highly manganiferous soils.

If large quantities of very reactive oxides should be encountered, their effect can readily be annulled by a preliminary treatment with $FeSO_4$. Such active oxides react rapidly with cold acidified N $FeSO_4$, and their amount can thus be determined by a preliminary titration. Two milliliters H_3PO_4, 5 ml. of water, and 1 ml. indicator are added to the soil, followed by sufficient N $FeSO_4$ to give an excess as judged by the color of the indicator (5 ml. will usually suffice). The mixture is allowed to stand with an occasional shake for 10 minutes and the excess $FeSO_4$ is titrated with $K_2Cr_2O_7$. The amount of $FeSO_4$ oxidized by the MnO_2, as determined by this titration, is then added to a fresh sample of soil

TABLE 2

Effect of $FeSO_4$ in removing disturbance due to reactive MnO_2 in carbon determinations

	$\frac{MnO_2}{C}$	CARBON CONTENT FOUND
		per cent
Soil alone	..	1.06
Soil plus chemically prepared oxide	10	0.45
Soil plus chemically prepared oxide, with $FeSO_4$ pretreatment	10	1.02
Soil plus Gold Coast ore	10	1.02
Soil plus Gold Coast ore, with $FeSO_4$ pretreatment	10	1.09

together with 2 ml. H_3PO_4. After standing about 5 minutes, most of the MnO_2 will have dissolved, and what remains may be neglected. Ten milliliters N $K_2Cr_2O_7$ is then added and the digestion conducted as usual.

The effectiveness of this simple method of pretreatment is clearly shown in table 2. Soil samples to which 10 per cent of reactive and 10 per cent of unreactive oxides had been added were digested with an without $FeSO_4$ pretreatment. The results also show that the pretreatment, though effective, is unnecessary for such unreactive material as Gold Coast ore.

Reduced iron

There can be no doubt that soluble ferrous compounds, if present, will lead to high results. The only question at issue is the prevalence of such compounds (9). Lee (13), in a study on the utility of rapid titration methods in paddy soils, quoted results which show that in gleied subsoils the results may be very high. He used Tiurin's CrO_3 method and Istscherekov's (10) $KMnO_4$ method. In these horizons he found that the ferrous iron, as shown by Morgan's rapid approximate method (16), was also high. He rightly pointed out that lack of an

adequate method makes it impossible to distinguish reduction due to organic matter from that due to ferrous salts or to any other reducing agents. The same reasons prevent the application of any accurate correction.

A considerable number of swamp soils from different parts of Australia have been examined by this method and found to give normal recovery figures. In all instances the samples were air-dry. Had they been examined straight from the field the results might well have been different. Some of these soils were from marine swamps (already referred to) which were covered by the tides daily; others were from fresh-water swamps. In some instances the fresh samples smelled strongly of H_2S. In spite of this, air-drying for a day or two apparently allowed oxidation to occur to such an extent that the recovery figures all fell within the range of normal agricultural soils. The results of determinations by the method on a wide variety of soils and subsoils have made it quite obvious that the amounts of soluble ferrous compounds in air-dried samples are usually trifling compared with the content of organic carbon.

Elementary carbon

It is convenient to treat elementary carbon among the various inorganic components, for like them, and unlike soil organic matter, it is not universally present. Moreover, it has long been recognized as a source of disturbance in methods for determining the organic matter. As with the manganese oxides, the magnitude of the disturbance due to carbon depends on its reactivity. Riley (20) has examined the rate of oxidation of different forms of elementary carbon by means of $CrO_3-H_3PO_4$ and $CrO_3-H_2SO_4$ mixtures and has shown that the rate of attack depends not only on the surface area, but also on the nature of the carbon, the most highly graphitized forms reacting most quickly. He has produced evidence which suggests that the accessibility to the chromic acid of the hexagon layer surfaces of the graphite crystallites is reduced by the presence of hydrogen or residual hydrocarbons which are bonded to these surfaces. The higher the carbonization temperatures, the less of these bonded materials will be present.

The results of some determinations by the soil digestion method on a few samples of elementary carbon are shown in table 3. The samples are merely finer than 70 mesh and so are not necessarily comparable in surface area.

The last sample, although the most highly graphitized, had a lower recovery than most of the others. This may be accounted for by the fact that it was the coarsest of all, flake graphite being always difficult to grind. Oxidation of this sample stopped at the graphite oxide stage, as could be readily detected by filtering the residue and then washing and warming it, when the swelling reaction typical of such lamellar compounds occurred.

It is clear that the recoveries are in all instances much less than those found for soil organic matter. When a sample of the wood charcoal listed in table 3 was added to soil of known carbon content and both were digested together, the recovery of charcoal carbon was even less, being only 6 per cent. As the composite soil contained 1.4 per cent organic carbon and 3.9 per cent charcoal

carbon, the dry combustion method would have indicated 5.3 per cent total carbon. On the other hand, the carbon content as revealed by the rapid titrimetric method was 1.6 per cent (using a multiplying factor of 1.3). The method has thus discriminated well between the two varieties of carbon. Soils rich in elementary carbon may sometimes be detected by their wide C:N ratio (in the foregoing instance 50:1) and sometimes by inspection of the coarse fraction. From Riley's work it does not seem likely that forms of carbon more reactive than natural graphite need be considered. This is sometimes seen as shining flakes in soils derived from graphitic schists.

If the oxidations are prolonged, the recoveries increase. The same sample of charcoal when digested by Tiurin's method gave an 84 per cent recovery of carbon. Schollenberger's digestion was not tried, but it is possible that the result would have been lower, for as Balfour *et al.* (2) showed, the optimum digestion rate occurs with acids between 70 and 90 per cent, whereas Schollenberger uses concentrated H_2SO_4. Allison (1) has quoted an example to show

TABLE 3

Recoveries of several varieties of elementary carbon by soil digestion method

	CARBON CONTENT	CARBON RECOVERY
	per cent	*per cent*
Bituminous coal	78	11
Gas coke	93	2
Wood charcoal	79	11
Natural microcrystalline graphite (Queensland)	88	10
Natural flake graphite (South Australia)	94	4

that his modification of Schollenberger's method discriminates between organic carbon and that in the form of cinders and coal, though the actual amounts of such materials present are not stated.

CONCLUSIONS

It has been shown that differences in conditions of digestion and in strength of reagents are chiefly of importance insofar as they determine the final temperature attained. The concentration of H_2SO_4 is of importance, but the concentration of $K_2Cr_2O_7$ is not. Boiling the 2:1 H_2SO_4:$K_2Cr_2O_7$ mixture with the object of attaining a constant and reproducible temperature is not permissible, but the reproducibility required to tie up results obtained over a period of time can be achieved by the inclusion of a standard soil in each batch of analyses.

The effect of $CaCO_3$ can be neglected, and that due to soluble chlorides can be readily allowed for. The effects due to reduced iron, higher oxides of manganese, and elemental carbon cannot be allowed for, but evidence has been presented in each instance which shows either the unimportance of the error or its probable limiting magnitude. A modification of the method can be used to eliminate the effect of the manganese oxides in the few instances where this may be neces-

sary. The main causes of variation in the recovery factor are thus not any of the foregoing, but are undoubtedly to be found in the variable nature of the soil organic matter itself.

SUMMARY

The causes of variation in the recovery factor of the Walkley-Black method have been separated into three groups, two of which are discussed here.

In the first, the magnitude of the effects due to strength of H_2SO_4 and of $K_2Cr_2O_7$, to time and temperature of digestion, and to addition of catalysts, has been investigated.

In the second, the effects of $CaCO_3$, soluble chlorides, higher oxides of Mn, reduced Fe, and elementary C have been critically examined.

Several of the causes can be eliminated or allowed for. Where this is not possible, the errors can be shown to be unimportant in most instances.

REFERENCES

(1) ALLISON, L. E. 1935 Organic soil carbon by reduction of CrO_3. *Soil. Sci.* 40: 311–320.

(2) BALFOUR, A. E., ET AL. 1938 The wet oxidation of carbon. *Jour. Soc. Chem. Indus.* 57: 1–6.

(3) BEST, R. J. 1931 A comparison of methods for determining hydrogen-ion concentration of soils. *Jour. Agr. Sci.* 21: 337–365.

(4) CONSTABLE, E. W., and MILES, I. E. 1941 Soil testing methods and apparatus designed for economy in time and labor. *Jour. Amer. Soc. Agron.* 33: 623–631.

(5) CROWTHER, E. M. 1935 Reports of the organic carbon committee. *Trans. Third. Internatl. Cong. Soil. Sci.* 1: 114–127; 3: 82–83.

(6) D'AGOSTINO, C. 1938 Determination of the chemical reactivity of manganese dioxide. *Ricerca Sci.* 9: 195–206.

(7) DUKE, F. R. 1945 Indirect stabilization of $FeSO_4$ solution. *Indus. and Engin. Chem., Analyt. Ed.* 17: 530.

(8) FLEISCHER, M., AND RICHMOND, W. E. 1943 The manganese oxide minerals: a preliminary report. *Econ. Geol.* 38: 269–286.

(9) IGNATIEFF, V. 1939 Ferrous iron in soils. *Nature* 143: 562–563.

(10) ISTSCHEREKOV, V., AND TIURINA, E. 1927 Methods for the determination of humus. *Pedology* 22: 61–80.

(11) KELLEY, C. W., AND THOMAS, R. P. 1942 A method of estimating the organic exchange complex of a soil. *Proc. Soil Sci. Soc. Amer.* 7: 201–206.

(12) KIRSANOV, A., AND CHERKASOV, W. 1936 New oxidation reduction indicators. *Bull. Soc. Chim.* 5: 817–821.

(13) LEE, C. K. 1939 The determination of organic matter in paddy soils. The reliability of rapid titration methods. *Indus. and Engin. Chem., Analyt. Ed.* 11: 428.

(14) LEEPER, G. W. 1935 Manganese deficiency of cereals: plot experiments and a new hypothesis. *Proc. Roy. Soc. Victoria* 47: 225–261.

(15) McMURDIE, H. F. 1944 Microscopic and diffraction studies on dry cells and their raw materials. *Trans. Electrochem. Soc.* 86: 313–326.

(16) MORGAN, M. F. 1935 Universal soil testing system. *Conn. Agr. Exp. Sta. Bul.* 372: 457–483.

(17) NARAYANAYYA, Y. V., AND SUBRAHMANYAN, V. 1935 Fumeless digestion of nitrogen. *Current Sci.* 3: 423.

(18) NOVÁK, V., AND PELISEK, J. 1938 The determination of humus by titration in soil surveying. *Sbornik Ceskoslov. Acad. Zemedelske* 13: 57–63.

(19) PIPER, C. S. 1942 Soil and plant analysis. Waite Agricultural Research Institute Monograph, Adelaide.
(20) RILEY, H. L 1938 Carbonising conditions and carbon reactivity. *Trans. Faraday Soc.* 34: 1011–1016.
(21) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65–68.
(22) SCHOLLENBERGER, C. J. 1931 The determination of soil organic matter. *Soil Sci.* 31: 483–486.
(23) SCHOLLENBERGER, C. J. 1945 The determination of soil organic matter. *Soil Sci.* 59: 53–56.
(24) SMITH, H. W., AND WELDON, M. D. 1940 A comparison of some methods for the determination of soil organic matter. *Proc. Soil. Sci. Soc. Amer.* 5: 177–182.
(25) SMOLIK, L. 1937 The oxidimetric determination of humus in soils. *Sbornik Ceskoslov. Acad. Zemedelske* 12: 370–373.
(26) SNETHLAGE, H. C. S. 1935 The acitvity of sulphuric acid in the oxidation of organic substances by means of chromic acid. *Rec. Trav. Chim. Pays-Bas* 54: 651–656.
(27) SNETHLAGE, H. C. S. 1936 On the catalytic influence of $Cr_2(SO_4)_3$ on the speed of decomposition of CrO_3 by heat, when dissolved in H_2SO_4 of varying strengths. *Rec. Trav. Chim. Pays-Bas* 55: 874–880.
(28) TIURIN, I. V. 1931 A new modification of the volumetric method of determining soil organic matter by means of chromic acid. *Pedology* 26: 36–47.
(29) TIURIN, I. V. 1934 Contribution to methods of studying the biochemical aspects of soil organic matter. *Trans. Dokuchaiev Inst. Soil Sci.* [U.S.S.R.] 10: 27–37.
(30) WALKLEY, A., AND BLACK, T. A. 1934 An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29–38.
(31) WALKLEY, A. 1935 An examination of methods for determining organic carbon and nitrogen in soils. *Jour. Agr. Sci.* 25: 598–609.
(32) WATANABE, M., AND DEAN, L. A. 1938 Carbon content of Hawaiian soils. *Hawaii Agr. Exp. Sta. Ann. Rpt.* 1937: 40–47.