

QUALITY ASSURANCE PLAN

for

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General Manager

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QC Manager

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GENERAL QA/QC PROCEDURES	3
1. SAMPLES	3
1.1 Sampling Procedures	3
1.2 Sample Containers	3
1.3 Sample Custody	3
2. INSTRUCTIONS AND PROCEDURES	3
2.1 Instrument Operation Procedures	3
2.2 Analytical Procedures	3
3. CALIBRATION AND STANDARDIZATION	4
3.1 Calibration Procedure and Frequency	4
3.2 Method Validation	4
3.3 Check/Reference Samples	4
3.4 Standards	4
3.5 Duplicate Samples	4
3.6 Specific Routine Procedures to Assess Performance	4
3.7 External Quality Control Checks	5
4. ANALYSES AND ANALYTICAL RESULTS	5
4.1 Data Reduction and Reporting	5
4.2 Hard Copy and Electronic Data Deliverables	5
4.3 Documentation	5
4.4 Hard Copy Data Files and Storage	6
5. MAINTENANCE AND REPAIR	6
5.1 Instruments	6
5.2 Other Equipment	6
6. REVIEW	6
6.1 Analytical Review	6
6.2 Standard Operating Procedures (SOP's):	7
7. QA/QC PROBLEM REPORTING	7
7.1 Responsibilities	7
8. SUBCONTRACT POLICY	7
APPENDICES: ANALYTICAL PROCEDURES	8
I. Sample Preparation Procedures for Stable Isotope Analyses	8
A. Procedures for Stable Isotope Analysis of Water Samples	8
1. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of Dissolved Inorganic Carbon (DIC)	8
2. δD (Hydrogen Isotope Analysis) and $\delta^{18}\text{O}$ (Oxygen Isotope Analysis) of H_2O	9
3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Nitrogen and Oxygen Isotope Analysis) of Dissolved Nitrate	9
4. $\delta^{34}\text{S}$ & $\delta^{18}\text{O}$ (Sulfur and Oxygen Isotope Analysis) of Dissolved Sulfate	12
B. Procedures for Stable Isotope Analysis of Gas Samples	12
1. $\delta^{13}\text{C}$ and δD (Carbon and Hydrogen Isotope Analysis) for Hydrocarbon Gases, Offline Prep Systems	12
2. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of CO_2 Offline Prep Method	14
3. GC-C-IRMS systems, $\delta^{13}\text{C}$, δD , and $\delta^{15}\text{N}$	14
C. Procedures for Stable Isotope Analysis of Organic Solids and Liquids	14
1. ^{13}C & $\delta^{18}\text{O}$ (Carbon and Oxygen Isotope Analysis) of Carbonate	15
2. Organic Solids and Liquids $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$ and $\delta^{34}\text{S}$	16

II. Sample Preparation Procedures for Radiogenic Isotope Analyses	16
A. Procedures for Radiogenic Isotope Analysis of Gases	16
1. ^{14}C (Radiocarbon) and ^3H (Tritium) in CH_4 (Methane)	17
3. ^{14}C (Radiocarbon) in CH_4 and CO_2 by Accelerator Mass Spectrometry (AMS)	18
B. Procedures for Radiogenic Isotope Analysis of Water	19
1. ^{14}C (Radiocarbon) in dissolved inorganic carbon (DIC) by Accelerator Mass Spectrometry (AMS)	19
2. ^3H (Tritium) in H_2O	19
III. Dual Inlet Mass Spectrometric Analysis	21
A. Measurement of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ in CO_2	21
B. Measurement of $^2\text{H}/^1\text{H}$ (Deuterium/Hydrogen) in H_2	22
IV. Gas Chromatographic Analysis of Gases	24
A. Analysis of hydrocarbons	24
B. Analysis of fixed gases	25
V. Radiocarbon Analysis of Prepared Samples	27

GENERAL QA/QC PROCEDURES

1. SAMPLES

1.1 Sampling Procedures It is the responsibility of the person collecting a sample to follow a sound sampling procedure. This will ensure that the sample collected is representative of the whole. We at Isotech will provide advice on sampling methods, sample storage procedures, and sample size requirements.

1.2 Sample Containers Sample containers should be matched in size, type and condition to the anticipated analysis that will give best representation of the source, while preserving the sample integrity prior to analysis. Unless sample containers are provided by Isotech, the responsibility for adequate containers resides with the client. Again, in addition to being able to provide appropriate sample containers, shipping cartons and shipping instructions, Isotech will provide advice on sample containers/cartons and shipping procedures.

1.3 Sample Custody A completed "Chain of Custody" record is the responsibility of the client and, if required, should be submitted with the samples. Isotech will provide a "Chain of Custody/Request for Analysis" form if needed. Isotech assumes full responsibility for all samples received and stored for analysis at our laboratory. If any samples are removed from Isotech for additional analysis at other laboratories, a "Chain of Custody" form will be completed. All samples received for analysis are assigned a unique, non-duplicated laboratory number which is used as an identifier for each analysis performed.

2. INSTRUCTIONS AND PROCEDURES

2.1 Instrument Operation Procedures Analyses performed with manufactured analysis instruments are carried out by the methods either specified or recommended by the manufacturer of the instrument as identified in the instrument manual or provided by on-site training through the manufacturer's service technicians. Much of the operation of these instruments is controlled by personal computers utilizing software written and licensed by the manufacturers.

2.2 Analytical Procedures The analytical procedures used routinely at Isotech are described in written standard operating procedures (SOP's) for each analysis. Additional procedures may be used, as needed, in the process of satisfying a client's specific analysis requirements. These procedures will either follow published analytical methods, or methods developed at Isotech for a specific analysis. If the Isotech developed procedure becomes routine, then a standard operating procedure is written. All procedures are reviewed and approved by the laboratory supervisors. Various procedural tests and verifications performed are recorded in bound maintenance log books.

3. CALIBRATION AND STANDARDIZATION

3.1 Calibration Procedure and Frequency Depending on the analytical technique, instruments used for quantitative analyses are either calibrated at the beginning of every operating period or the calibration is checked by using a reference sample or a calibration standard. The instrument calibration is also checked at appropriate intervals during analyses. Specific instruments that form components of a sample preparation system are calibrated using duplicate sample analysis as well as analysis of a reference sample at appropriate intervals. Records of calibration results are kept in laboratory notebooks or other secure medium (see Documentation).

3.2 Method Validation Analytical methods are validated by one or more of the following techniques:

3.2.1 check or reference samples are analyzed and the results are compared with the internal documented or external certified (primary and secondary standards) values,

3.2.2 results from the candidate method are compared with those from another method known to be applicable and reliable, or

3.2.2 spiked samples and surrogate samples are analyzed and the method results are compared with the known concentrations.

3.3 Check/Reference Samples A check/reference sample is analyzed approximately every tenth analysis. This, in essence, results in a test of the method. Check/reference samples are chosen which have been analyzed multiple times over an extended period of time with consistent results.

3.4 Standards Primary standards are obtained from the International Atomic Energy Agency, Vienna, Austria, and certified by NIST (National Institute of Standards and Technology, formerly U.S. National Bureau of Standards) or directly from NIST. Secondary standards are obtained from commercially available sources recognized in the industry. Internal Reference standards are prepared by direct calibration against primary and secondary standards.

3.5 Duplicate Samples Duplicate analyses are performed approximately every tenth analysis. This duplicate sample analysis is performed approximately five analyses after the check/reference sample analysis is performed. Therefore, for a particular analysis procedure, a test of the method is performed every five analyses. This assures that at least 20% of all analyses are for maintaining QA/QC.

3.6 Specific Routine Procedures to Assess Performance Standard reference samples, chosen to match the submitted samples as closely as possible, in conjunction with duplicate samples and check samples, provide a matrix for performance evaluation. If a problem is detected with

the reference sample, then the problem is first addressed by checking the integrity of the sample itself. Other reference samples are analyzed to determine if the problem persists. If reference sample integrity is verified, further diagnostic testing is carried out until the cause of the discrepancy is identified.

Isotech willingly participates in round-robin testing whenever the opportunity arises and has participated in studies by IAEA and industry. Instrument calibration is carried out whenever analysis of internal standards and check samples suggests a potential problem.

3.7 External Quality Control Checks Blind duplicates, check samples, blanks, and spiked samples may be submitted by the client, and this practice is encouraged.

4. ANALYSES AND ANALYTICAL RESULTS

4.1 Data Reduction and Reporting Calculations made in reducing raw data to reportable form are verified (preferably by a second person) before reporting the results to the client. If a computer program is used to perform calculations, the accuracy of the input data is verified by comparison with the raw data. In all cases where computer programs are used to make the calculations, the person making the calculations verifies that the proper program is used. Data reduction and calculation is performed automatically by the computers which control the instruments. Reported results are verified relative to the computer printouts.

4.2 Hard Copy and Electronic Data Deliverables Normally, final data is emailed to clients as an Excel workbook file, and also a PDF version of the data. Depending on the sample type, hard copy reports can be either a single page per sample, or can be in tabular format with multiple samples per page. Hard copy reports are not mailed to clients, unless clients specifically request them. Upon request, CD's will be submitted to clients in addition to the hard copy reports. Also, appropriate graphs will be provided upon request. Compositional analyses for natural gas samples are normalized when the Analysis Report is generated. Upon request a QA/QC report containing results for all check samples and duplicates as well as copies of raw data can be provided at additional cost.

4.3 Documentation All laboratory notes, observations, calibrations, manual calculations, and any other pertinent information are kept in bound laboratory notebooks or other secure recording medium. Computer programs used for data storage, retrieval, and calculations, which are developed within Isotech Laboratories, Inc., are documented well enough that someone not intimately familiar with the program development, but who is familiar with the programming language, can understand the operation of the program. Printed and dated copies of the current version and each previous version (insofar as possible) of the program are kept in the developer's files. These copies remain at and are the property of Isotech, should the developer leave employment of Isotech Laboratories, Inc. Electronic backup copies of currently-used computer programs are securely kept by the program's developer or principal user. Backup copies of analyses databases are made periodically. The frequency of making backup copies

depends on the frequency of updating the database, but the minimum frequency for making backup copies is weekly. All laboratory notebooks, data, computer programs, computerized databases, and any other means of recording data, observations, calculations, and other pertinent information developed at or on behalf of Isotech, remain the property of Isotech Laboratories, Inc., unless otherwise designated.

4.4 Hard Copy Data Files and Storage All pertinent paperwork associated with each batch of samples is stored in the client files. Typical paperwork can include chain of custody records, client analysis requests, email communication to/from clients regarding samples, final data, and cover letter mailed to client with final data. Data files are kept indefinitely unless clients request that we dispose of them.

5. MAINTENANCE AND REPAIR

5.1 Instruments Each instrument or machine used to produce quantitative analysis results, or leading up to their production, undergoes periodic preventive maintenance according to manufacturer's instructions, or some established preventive maintenance schedule. Preventive maintenance may be done by laboratory personnel, manufacturer's representative, or a qualified third-party contractor, depending on the abilities of the laboratory operator and the complexity of the equipment. Records of repairs and preventive maintenance are kept by the appropriate laboratory personnel in files or notebooks. Records of equipment problems and solutions are kept in files or notebooks. The analyst is the person best qualified to recognize when the instrument or machine they operate is in need of repair, or the method they practice is in need of corrective action. Corrective action is needed when predetermined limits for data acceptability are exceeded. Analysts are also to use their experience and scientific judgment in deciding when corrective action is needed.

5.2 Other Equipment Other laboratory equipment such as vacuum pumps, ovens, test meters and non-instruments such as glassware are maintained by Isotech personnel. In most cases this is performed by the same person who utilizes the equipment for analysis. Visual checks backed by mechanical and electronic gauges provide constant maintenance checks directly to the operators.

6. REVIEW

6.1 Analytical Review At the time of each analysis or sample preparation, the staff chemist performing the analysis reports anomalies to the QC Manager. Staff chemists are all trained on a variety of techniques and work closely together. Constant communication between staff members results in most problems being addressed when they occur. Unusual problems are brought to the attention of the management team. Whenever possible, a sample that is questionable for any reason is re-analyzed to verify results, regardless of when the sample

was analyzed initially. This means that more than 10% of samples will be duplicates if the data appears to be unusual in any way.

Before final reports are printed, data is checked to verify that the final data agrees with the raw printouts, and raw percentages for compositional analyses are checked to ensure that all components are identified. Reproducibility of duplicate isotopic samples is compared to stated precision limits. Analytical data is reviewed for anomalies by project coordinators and/or managers.

6.2 Standard Operating Procedures (SOP's): These procedures are developed from specific analytical methods for operating specified equipment to obtain high quality data reflective of each sample analyzed. In addition to revisions due to procedural or equipment changes these SOP's are reviewed by the QC Manager annually.

7. QA/QC PROBLEM REPORTING

7.1 Responsibilities QA/QC is the responsibility of every person who collects or analyzes samples. If any Isotech Laboratories employee observes any QA/QC problem, that employee will discuss the problem with the analyst, QC Manager, Lab Manager or General Manager. No negative action will ever be brought against nor will accrue to any staff member who reports QA/QC problems.

8. SUBCONTRACT POLICY

Samples for analysis of ^{14}C (radiocarbon) are converted to purified carbon dioxide and then submitted to an established radiocarbon dating laboratory for the final analysis. When analyses are requested for which Isotech does not have either the necessary equipment or expertise to provide high quality results, these analyses too may, with the knowledge of the client, be submitted to a subcontract laboratory. Only established, reputable laboratories which maintain strict QA/QC control are utilized. All samples are prepared and packaged using techniques that have been recommended or approved by the subcontract laboratory. Analysis of reference samples and standards is the responsibility of the subcontract laboratory. Duplicate analyses of samples submitted to a subcontract laboratory should be requested by the client and will be charged as regular samples.

APPENDICES: ANALYTICAL PROCEDURES

I. Sample Preparation Procedures for Stable Isotope Analyses

A. Procedures for Stable Isotope Analysis of Water Samples

1. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of Dissolved Inorganic Carbon (DIC)

Equipment and Supplies

Thermo GasBench II
Thermo Delta V Plus
12mL Exetainer[®] with septum cap
Micro spin bar
1mL syringe
23G needle
85% Phosphoric acid
0.1N HCl

Method/Procedure The $\delta^{13}\text{C}$ of DIC is determined by injecting up to 1 ml of sample water into a helium flushed 12mL Exetainer[®] containing 0.1mL of 85% phosphoric acid and a magnetic spin bar. Sample size is determined based on alkalinity, which is measured by titration with 0.1N HCl.

The sample is stirred for a minimum of one hour and then allowed to equilibrate for 24 hours. At time of analysis the sample vials are placed in the GasBench tray. The CO_2 generated is flushed out of the vial via a two port needle. Water is removed by two nafion traps, and pure CO_2 is separated using a GC column. The CO_2 /helium mixture then enters the mass spectrometer and is compared against a reference standard a total of six times.

Maintenance Vials are recycled and the spin bars are thoroughly cleaned and reused. Gas flow rates through the GasBench system are periodically checked.

QA/QC At a minimum, every tenth analysis is a replicate. A check standard is analyzed every tenth analysis.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against internal lab standards is performed using Microsoft Excel.

Documentation All procedural tests and verifications performed are recorded in bound maintenance log books. All sample data including the date prepared with analyst identification are recorded on laboratory log sheets and in bound log books.

2. δD (Hydrogen Isotope Analysis) and $\delta^{18}\text{O}$ (Oxygen Isotope Analysis) of H_2O

Equipment

3mL syringes
0.2 micron syringe filters
2mL glass vials with septum caps
Picarro CRDS (cavity ringdown spectrometer) model L1102-i fitted with a Leap autosampler

Method/Procedure Water samples are individually filtered into 2mL vials with 0.2 micron syringe filters. If samples are high salinity brines, they should be vacuum distilled prior to loading. The vials are then loaded onto trays which are installed on the autosampler. Samples are analyzed by the CRDS in replicate in accordance with the manufacturer's recommendation.

QA/QC Two reference water samples are used to verify accuracy and reproducibility. These reference waters are analyzed approximately every tenth analysis. The system is calibrated by analysis of primary reference standards obtained from IAEA or NIST. At a minimum, every tenth sample analysis is a replicate.

Calculation Calculations are performed by the software on the CRDS at the time of analysis. Data normalization against internal lab standards is performed using Microsoft Excel.

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification in bound log books.

3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Nitrogen and Oxygen Isotope Analysis) of Dissolved Nitrate

Equipment and Supplies

0.45 nylon filter paper
Glass filtration apparatus
1N HCl
 BaCl_2
Cation exchange resin
Anion exchange resin
1N HBr
 Ag_2O
Flasks

Stirbars
Freezer
Oven
Freeze-dryer
Teflon beakers
Thermo Delta V Plus
Mettler Toledo MX5 Ultra-Microbalance
Thermo TC/EA
Thermo ConFlo II

Method/Procedure Nitrate is extracted from groundwater samples and converted into AgNO_3 using ion-exchange techniques. The nitrate concentration is determined using an Orion AquaFAST™ colorimeter. The appropriate sample size is filtered and placed on a hot plate to boil. The pH is adjusted to 1-3 using 1N HCl. BaCl_2 is added to remove dissolved sulfates, and the sample volume is decreased to 250mL. Precipitated BaSO_4 is filtered from the sample and placed into separatory funnels. The sample is allowed to flow through a cation column and then through the anion column, where nitrate is held within the column. 1N HBr is added to the column to strip the nitrate. The eluent is collected and silver oxide is added to create AgNO_3 . The sample is filtered, frozen in a Teflon beaker, and placed in a freeze drying vacuum oven until only the AgNO_3 crystals remain. The crystals are then analyzed using for $\delta^{15}\text{N}$ using an EA-IRMS and analyzed for $\delta^{18}\text{O}$ using a TC/EA-IRMS system.

Analysis of $\delta^{15}\text{N}$ is performed using a Carlo Erba Elemental Analyzer. 1.2 milligrams of AgNO_3 is weighed into tin boats and placed in an Autosampler with helium purge. The sample is flash combusted inside the combustion reactor, as shown in this reaction $\text{N} + \text{O}_2 \rightarrow \text{N}_x\text{O}_y + \text{N}_2$. The products of combustion reaction are then carried to the reduction reactor where excess oxygen is removed, and nitrogen oxides (N_xO_y) are reduced to elemental nitrogen (N_2). The N_2 gas is introduced to the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Analysis of $\delta^{18}\text{O}$ is performed using a Thermo TC/EA. 300 micrograms of AgNO_3 is weighed into silver boats and placed in a zero blank autosampler. The sample is thermally converted to CO gas in the EA furnace. The CO gas is introduced into the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Maintenance Glassware is washed and rinsed with deionized water to remove residual sample and residual AgNO_3 .

QA/QC At a minimum, every tenth sample preparation is a duplicate. Approximately every tenth EA/TCEA analysis a set of standards is analyzed after every ten samples, along with at least one check standard per analysis run.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against primary international standards is performed using Microsoft Excel.

Documentation All records of sample preparation and notes are hand written in bound log books. All sample data including the date prepared are stored electronically and in print.

Sample Handling Samples should be collected and frozen until analyzed. Samples should be shipped overnight in a cooler on ice. Filtering prior to shipment is preferred but is not required.

4. $\delta^{34}\text{S}$ & $\delta^{18}\text{O}$ (Sulfur and Oxygen Isotope Analysis) of Dissolved Sulfate

Equipment and Supplies

Thermo Delta V Plus
Mettler Toledo MX5 Ultra-Microbalance
Elementar Vario EL
Thermo TC/EA
Thermo ConFlo II
Thermo AQUAFast II TM Colorimeter
0.45 micron nylon filter
1N HCl
BaCl₂ solution
Filtering apparatus
Various sized beakers
Drying oven
Petri dishes
Tin boats
Silver boats

Method/Procedure The $\delta^{34}\text{S}$ & $\delta^{18}\text{O}$ of dissolved sulfate is determined by the barium sulfate precipitation technique. Prior to preparation the sulfate concentration must be obtained from the client or determined using a Thermo AQUAFast II TM colorimeter; a minimum sulfate concentration of 5ppm is required for this analysis. Once the sulfate concentration is known, the amount of sample needed to obtain 25mg of barium sulfate is weighed into a clean beaker. Samples are then filtered to remove particulate matter before being brought to a boiling temperature. Calcium carbonate in the sample is removed by adding 1N hydrochloric acid until the sample reaches a pH of 1-3. An appropriate amount of barium chloride solution is added based on the concentration of sulfate in the sample. The reaction is given sufficient time to complete under heat; a testing solution is used to ensure that all dissolved sulfate has precipitated. The precipitant is then filtered and dried, the final amount is weighed.

The $\delta^{34}\text{S}$ of the dried barium sulfate is then determined by combustion to SO_2 gas using an Elementar Vario EL EA. Approximately 1.2mg BaSO_4 is weighed into a tin capsule and loaded into an autosampler. The sample is then combusted and passed over a reduction furnace. The resulting SO_2 gas is passed through a ConFlo II interfaced to the IRMS, where it is compared against a reference gas.

Analysis of $\delta^{18}\text{O}$ is performed using a Thermo TC/EA. Approximately 300 micrograms of BaSO_4 is weighed into silver boats and placed in a zero blank autosampler. The sample is thermally converted to CO gas in the EA furnace. The CO gas is introduced into the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Maintenance Glassware is washed and rinsed with deionized water to remove residual BaSO_4 .

QA/QC At a minimum, every tenth sample preparation is a duplicate. Approximately every tenth EA/TCEA analysis a set of standards is analyzed after every ten samples, along with at least one check standard per analysis run.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against primary international standards is performed using Microsoft Excel.

Documentation All records of sample preparation and notes are hand written in bound log books. All sample data including the date prepared are stored electronically and in print.

Sample Handling Samples should be collected and stored at 4°C until analyzed. Samples should be shipped overnight in a cooler on ice. Filtering prior to shipment is preferred but is not required.

B. Procedures for Stable Isotope Analysis of Gas Samples

1. $\delta^{13}\text{C}$ and δD (Carbon and Hydrogen Isotope Analysis) for Hydrocarbon Gases, Offline Prep Systems

Equipment and Supplies

3 SRI 8610C Gas chromatographs
Evacuated transfer system
Copper oxide combustion furnace
Dry ice
Isopropyl alcohol
Liquid nitrogen
Electronic manometer
Electronic vacuum gauge

Helium
Oxygen
Gas-oxygen torch

Method/Procedure The determination of carbon and hydrogen isotopic ratios for hydrocarbons in gas mixtures (e.g. natural gas) requires a sample preparation system capable of first separating the individual hydrocarbons and then quantitatively converting them into carbon dioxide (CO₂) and water for mass-spectrometric analysis. There are 2 systems utilized for processing natural gases. The systems employed are helium purged flow systems consisting of two major units.

The first unit consists of sample injection syringes, SRI 8610C gas chromatographs, a personal computer, and several flow-control valves. This configuration separates the hydrocarbon of interest from the sample and channels it into the combustion-collection unit. The second unit is the combined combustion-collection unit which includes quartz combustion tubes filled with cupric oxide (CuO), and vacuum lines. This system converts the hydrocarbon of interest into CO₂ and water, which are then collected and purified for isotopic analysis.

The water of combustion is transferred into a length of Pyrex tubing that has been sealed at one end and contains a weighed quantity of zinc turnings. The sample tube is sealed off for later mass spectrometric analysis. Similarly, the CO₂ is then transferred into Pyrex tubing and sealed off for later mass spectrometric analysis.

Maintenance The packed columns are baked at manufacturer's recommended temperature when peak separation decreases. At the end of every work day, O₂ is flowed through the copper oxide combustion furnaces to regenerate the CuO. Valve o-ring seals within the evacuated transfer system are replaced as necessary.

Reference Samples The system is tested by analyzing a reference sample every tenth analysis performed.

Replication A duplicate analysis of one of the samples is performed approximately every tenth analysis. This duplicate analysis is performed approximately five analyses after the reference sample analysis is performed. Therefore, a test of the system operation is performed every five analyses.

Calculation The expected yield is calculated from the injection volume and the hydrocarbon concentration

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification are recorded on laboratory log sheets and/or in bound log books. Digital copies of all chromatograms are stored and backed up regularly.

2. $\delta^{13}\text{C}$ (Carbon Isotope Analysis) of CO_2 , Offline Prep Method

Method/Procedure Preparation of samples for measurement of the $\delta^{13}\text{C}$ of CO_2 is performed on the same system as the hydrocarbons. The procedure is identical to that for the hydrocarbons, with two exceptions. First, CO_2 does not pass through a combustion furnace; gas is channeled directly from the GC outlet to the collection trap. Second, there is no water of combustion.

3. GC-C-IRMS systems, $\delta^{13}\text{C}$, δD , and $\delta^{15}\text{N}$

Equipment and Supplies

HP6890 GC interfaced to ThermoFinnigan Delta Plus Advantage

HP 6890/7890 interfaced to Thermo Scientific Delta V Plus

Customized autosampler

Method/Procedure The GC-C-IRMS systems, also referred to as “online” or “continuous flow”, consist of an Agilent GC combustion unit interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage), and are used to analyze the carbon isotopic value of hydrocarbon components in gas samples. Samples are injected into the GC split/splitless injector either manually, or using customized autosamplers. The hydrocarbon components are separated by the GC column, and each individual component slated for isotopic analysis is combusted in a combustion furnace supplied by the instrument manufacturer. The resultant CO_2 is introduced directly into the mass spectrometer, and Finnegan’s Isodat software is utilized for peak detection and quantification. Cryogenic focusing of hydrocarbons is achieved using liquid nitrogen, allowing the air to be removed, resulting in enriched concentrations of hydrocarbons.

Hydrogen isotopic values for methane are completed using the same system, but the gas is channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converts methane into H_2 and carbon, and the H_2 gas is introduced directly into the mass spectrometer.

Nitrogen isotopic data for elemental nitrogen (N_2) is generated using the same system.

Maintenance Septa on the GC inlet system are replaced daily when the system is operational. Pyrolysis and combustion tubes are replaced as needed. Combustion tubes are oxidized daily during analysis sequences.

Reference Samples Reference gases are analyzed at the start of each analysis sequence, and then at least 10% of all analyses during a sequence are check samples.

Replication At least 10% of client samples are analyzed in duplicate.

C. Procedures for Stable Isotope Analysis of Solids and Liquids

1. $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ (Carbon and Oxygen Isotope Analysis) of Carbonate

Equipment and Supplies

Thermo GasBench II
Thermo Delta V Plus
Mettler Toledo MX5 Ultra-Microbalance
12mL Exetainer[®] with septum cap
100% Phosphoric acid

Method/Procedure The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonate is determined by weighing approximately 200 micrograms of sample into an Exetainer[®] fitted with a septum cap. The vials are placed in a temperature controlled sample block at 70°C and flushed with helium to purge any air from the vial.

The sample is reacted with 100% phosphoric acid for a minimum of one hour and then analyzed. The CO_2 generated is flushed out of the vial via a two port needle. Water is removed by two nafion traps, and pure CO_2 is separated using a GC column. The CO_2 /helium mixture then enters the mass spectrometer and is compared against a reference standard a total of six times.

Maintenance Vials are rinsed to remove acid and the glass is recycled.

QA/QC At a minimum, every tenth analysis is a replicate. A set of standards is analyzed after every ten samples, along with at least one check standard per analysis run.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against internal lab standards is performed using Microsoft Excel.

Documentation All procedural tests and verifications performed are recorded in bound maintenance log books. All sample data including the date prepared are stored electronically and in print.

2. Organic Solids and Liquids $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$ and $\delta^{34}\text{S}$

Equipment and Supplies

Carlo Erba Elemental Analyzer connected to a Finnigan Delta S Mass Spectrometer
ThermoElectron TCEA interfaced to a Thermo Electron Delta V Plus Mass Spectrometer
Elementar EL Vario III interfaced to a Thermo Scientific Delta V Plus Mass Spectrometer

Method/Procedure The determination of carbon, nitrogen, oxygen, hydrogen, and sulfur isotopic ratios for organic solids and liquids is accomplished by combustion or pyrolysis of the materials for mass-spectrometric analysis. The systems employed are standard elemental analyzers with carousel auto samplers, connected to isotope ratio mass spectrometers through an interface supplied by the manufacturer. The combustion products of interest from the elemental analyzers are: carbon dioxide (CO₂) for carbon isotope analysis, N₂ for nitrogen isotope analysis, and sulfur dioxide (SO₂) for sulfur isotope analysis. Oxygen and hydrogen isotopic ratios are analyzed on the TCEA, which converts hydrogen from the organic materials to H₂ gas for hydrogen isotopic measurements, and oxygen within the organic materials is converted to carbon monoxide (CO) for oxygen isotope analysis.

Samples are weighed on a Mettler balance and loaded into a standard EA tin capsule for carbon, nitrogen, or sulfur isotopic analysis, or into a silver capsule for oxygen or hydrogen isotopic analysis. Once the samples are loaded into the EA, a run is started and all instrument control is done by software provided by the MS manufacturer. Samples are combusted as per normal EA operating procedures, and the CO₂, N₂, and SO₂ are separated by the EA. Similarly, the pyrolysis products H₂ and CO from the TCEA are separated within the instrument. The vents of the EA and the TCEA are connected to the mass spectrometers via the interface, where a small portion of the EA or TCEA output flows directly into the MS. The MS measures the isotopic value of the component of interest (CO₂, N₂, SO₂, CO, or H₂) and the final isotopic value is generated by software provided by the manufacturer.

Maintenance Ash is removed from the top of the combustion column in the EA or the top of the pyrolysis reactor in the TCEA as directed by the manufacturer, or when peak tailing becomes apparent. Combustion and reduction furnaces in the EA are replaced at appropriate intervals as outlined by the dealer, or when peak shape deteriorates. The TCEA contains glassy carbon, which is periodically replaced.

Reference Samples The systems are tested by analyzing at least one reference at least once per batch of 25 samples loaded into the auto sampler. A blank is also run at the start of each batch.

Replication Approximately 10% of all samples analyzed are replicates.

Documentation All final data including the date analyzed are recorded on laboratory log sheets and/or in bound log books. Digital copies of chromatograms are stored and backed up regularly.

II. Sample Preparation Procedures for Radiogenic Isotope Analyses

A. Procedures for Radiogenic Isotope Analysis of Gases

1. ^{14}C (Radiocarbon) and ^3H (Tritium) in CH_4 (Methane) by Radiometric Analysis

Equipment

Peristaltic pump
Flow meters
Gas regulators
Vacuum gauge
Molecular sieve trap
High temperature tube furnaces
Quartz combustion chamber
Vacuum traps and gauges
Vacuum pumps
Mercury manometer

Method/Procedure

1.1 Methane Combustion

The system used for tritium (^3H) analysis of methane and for radiocarbon (^{14}C) analysis of methane consists of a peristaltic pump, a CO_2 removal unit, and a sample combustion/collection flow unit. The combustion/collection unit is composed of a tube furnace, a flow control valve, and a series of gas purification and collection traps. The system is attached to a vacuum manifold.

The gas sample enters the system through a flow control valve or is pumped in slowly by a peristaltic pump. The CO_2 associated with the sample is absorbed by the molecular sieve and removed from the sample quantitatively. Methane in the sample is then carried through the combustion tube where it is reacted to CO_2 and H_2O .

The water of combustion is collected in a trap immediately after the combustion furnace by immersing the trap in a dry ice/isopropanol bath. Once the entire sample has been combusted, the frozen water of combustion is melted and transferred to a glass vial to await tritium analysis.

The CO_2 formed by combustion is collected in two liquid nitrogen cooled traps, measured volumetrically, and transferred into a storage cylinder. Storage cylinders are effectively leak-tested during each use by evacuation prior to transferring the sample CO_2 . Each cylinder is tagged with sample identification and is forwarded to a subcontractor for ^{14}C analysis along with a chain-of-custody form.

1.2 Tritium Analysis

The water of combustion from methane samples is ready to be analyzed in the liquid scintillation counter (LSC). There is no pre-treatment necessary for the sample, as it is essentially distilled water when it is collected.

The scintillation counting vials are prepared by pipetting 10 ml of commercial scintillation cocktail into a 20 ml plastic vial and then weighing to ± 1 mg. The sample is then pipetted or poured into the counting vial and the vial is re-weighed. If the amount of sample is less than 10ml, then tritium-free water is added to bring the total volume of water to about 10ml. Details of the tritium analysis procedure are given later in this document.

Maintenance After each sample, the molecular sieve is baked and evacuated at 350°C. The vacuum system is thoroughly evacuated to remove all residual gas and water vapor after each sample. The water trapping system is disassembled and thoroughly dried and evacuated after each sample.

Calibration/Standardization Gas storage volumes have been calibrated using known quantities of carbon dioxide gas. No further standardization of this system is necessary. Calibration and standardization of the final ^{14}C analysis is performed by the subcontracted laboratory.

Replication and Reference Samples Replicate or reference sample analysis for these analyses are performed only when requested and supported by the client.

Calculation Yields are calculated by comparing the volume of CO_2 generated and the weight of the water collected to the amount expected based on the amount of CO_2 collected. ^{14}C concentrations are determined by the subcontracted laboratory and corrected for isotope fractionation by Isotech's database program.

2. ^{14}C (Radiocarbon) in CH_4 and CO_2 by Accelerator Mass Spectrometry (AMS)

Equipment:

Same as for $\delta^{13}\text{C}$ of CO_2 and $\delta^{13}\text{C}$ of Hydrocarbons.

Method/Procedure:

The same method is employed for sample preparation as for $\delta^{13}\text{C}$ of either CH_4 or CO_2 . Once the purified CO_2 has been sealed into Pyrex tubing, the tube is tagged with a piece of label tape and sent to the subcontractor along with a chain of custody form for ^{14}C analysis. When there is only enough material available for one sample preparation, the $\delta^{13}\text{C}$ is first determined by MS analysis.

B. Procedures for Radiogenic Isotope Analysis of Water

1. ^{14}C (Radiocarbon) in dissolved inorganic carbon (DIC) by Accelerator Mass Spectrometry (AMS)

Equipment and Supplies

Vacuum pumps and gauges
Glass and metal vacuum system
Dry ice
Isopropyl alcohol
Liquid nitrogen
Phosphoric acid
Gas-Oxygen torch

Method/Procedure The ^{14}C of DIC is determined by injecting sample water into an evacuated serum bottle containing 2mL of 85% phosphoric acid and a magnetic spin bar. Sample size is determined based on alkalinity, which is measured by titration with 0.1N HCl. The sample is stirred for a minimum of 15 minutes and then connected to the vacuum system via a needle port. The CO_2 generated is liberated from the water and transferred through a trap cooled in a dry-ice/isopropyl-alcohol mixture (for H_2O removal) to a U-trap which is cooled in liquid nitrogen. The CO_2 is then purified and cryogenically collected in Pyrex tubing. The tube is sealed off and tagged with a piece of labeled and sent to the subcontractor, along with a chain of custody form, for ^{14}C analysis.

Maintenance The system is thoroughly evacuated between samples. Vials are washed and dried.

2. ^3H (Tritium) in H_2O

Equipment

Vacuum pumps and gauges
Distillation column
Electrolytic enrichment cells
Electrolysis power source and cooling system
Liquid scintillation counting system
Assorted chemicals and glassware
Dry ice/ isopropyl alcohol
Drying oven

Method/Procedure--Direct Counting of Higher Tritium Content Water (greater than 15 TU). Approximately 15ml of the water sample is treated with 0.1 M KMnO_4 at 70°C for about an hour. This sample is then vacuum distilled. Ten ml of the distillate is accurately weighed and mixed with 10ml of an appropriate organic scintillator cocktail in a 20ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

Method/Procedure--Enrichment of Lower Tritium Content Water (less than 15 TU). About 300 ml of the water sample is conventionally distilled to near completion. Exactly 200g is added to an enrichment cell along with 2ml of 9M tritium-free sodium hydroxide and is electrolytically enriched down to about 11-13 ml (final weight is exactly determined), and then neutralized with carbon dioxide for 20 minutes. The enrichment procedure is carried out under conditions of about 2°C and constant voltage of 4V. Ten ml of the enriched sample is accurately weighed and mixed with an appropriate organic scintillator cocktail in a 20 ml plastic vial and counted in a liquid scintillation spectrometer for 1000 minutes. Background and a NIST standard are also similarly counted and the tritium content calculated.

General QA/QC Procedures Critically reviewing TU/cpm/g of NIST standard versus existing data, critically reviewing background cpm versus existing data, and comparing data from splits of NIST and other samples with outside established laboratories. A criteria of exceeding 1 sigma limits from existing data triggers investigation of possible errors. Electrolytic enrichment cells are calibrated using working standards approximately every 6 months, or whenever duplicates prepared in different cells suggest a possible change in enrichment factor.

Maintenance The vacuum system is thoroughly evacuated between samples. All glassware and electrolytic cells are cleaned with deionized water and baked at about 130°C between samples.

Replication At a minimum, every tenth analysis is a replicate. Periodically a blind split is sent to another established tritium analysis laboratory for check purposes.

Reference Sample A NIST water standard (a dilution of NIST 4361B) is used for each sample set to verify accuracy and reproducibility. A glass-sealed high tritium sample is routinely checked to verify that the counter is operating satisfactorily. QA/QC plots are maintained for both standard and background counts using deviation of 1 sigma as a criteria for a more detailed evaluation of the data.

Calculation Calculations are performed utilizing a spreadsheet to calculate tritium concentration in TU on the date counted.

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared, with analyst identification, are recorded on laboratory log sheets or in bound log books.

III. Dual Inlet Mass Spectrometric Analysis

A. Measurement of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ in CO_2

Equipment Finnigan MAT Delta S Isotope Ratio Mass Spectrometer

Method/Procedure Because $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ analyses are performed simultaneously, the procedure described here generates both measurements. A mass spectrometric analysis involves comparisons of a sample to a reference standard; in this case the comparisons are measurements of mass 44, 45, and 46, giving the both the oxygen and carbon isotopic compositions. This is accomplished by a dual inlet system where the sample and the reference standard are measured alternately. At the beginning of each day, a reference standard is introduced into the standard side of the inlet system, and this gas is generally used for the entire session. There are two different reference standards in aluminum cylinders which are permanently mounted on the MS inlet system. The sample to be analyzed against the standard is introduced into the system via an evacuated inlet system and tube-cracker. With the inlet system fully evacuated, the sample (which is sealed into $\frac{1}{4}$ " Pyrex tubing) is introduced by breaking the glass sample tube and allowing the sample to fill a variable volume bellows. Once the sample has been introduced into the MS, the actual analysis is computer controlled using equipment obtained from the manufacturer. Each analysis is given a specific reference name and/or number, utilizing the lab number as the primary reference. Final results are calculated by the manufacturer's software, and are stored on the hard drive of the computer, recorded in a bound lab notebook, and stored as the computer generated printout.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first analysis of each session is a zero enrichment, where the working standard is analyzed against itself to check machine stability. Isotope ratio determination involves multiple direct comparisons of the sample to a reference standard (generally at least 6 comparisons). Stable carbon and oxygen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta X_{(\text{sample})} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$$

Where X represents the isotope of interest, ^{13}C or ^{18}O , and R represents the ratio of $^{13}\text{C}/^{12}\text{C}$, or $^{18}\text{O}/^{16}\text{O}$. The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech, both of which have been calibrated multiple times relative to several standards (graphite, oil, carbonates, waters, etc.) available from the International Atomic Energy Agency and the National Institute of Standards and Technology.

Replication Because of replicate sample preparations, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the software obtained from the manufacturer.

B. Measurement of $^2\text{H}/^1\text{H}$ (Deuterium/Hydrogen) in H_2

Equipment

Finnigan Delta Plus XL isotope ratio mass spectrometer

Aluminum heating block

Personal computer

Method/Procedure The H_3 factor, which is the portion of the mass 3 signal attributable to $^1\text{H}\text{-}^1\text{H}\text{-}^1\text{H}$ (instead of $^2\text{H}\text{-}^2\text{H}$), is determined before each run early in the day and periodically throughout the day based on machine performance (if the values start drifting, a new H_3 factor is determined). The reference standard must be replenished at least once during an 8 hour period.

Water samples for deuterium/hydrogen analysis are sealed into 1/4" Pyrex tubing as H_2O , along with a measured quantity of zinc. Each sample tube is labeled and reacted in a heating block at 500°C for 35 minutes to generate hydrogen gas. Once the sample has been reacted, it is introduced into the sample side of the MS inlet system and analyzed against the working standard. Each analysis is given a unique label, using the lab number as the primary reference.

Once the sample has been introduced into the MS, the analysis is computer controlled. The raw result is calculated by the manufacturer's software and recorded into a bound lab notebook, as well as being stored on computer hard disk and computer generated printout of results.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first run each day is a zero-enrichment where the standard is run against itself to check machine stability. Stable hydrogen isotope compositions are always

reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta D_{(\text{sample})} = [({}^2\text{H}/{}^1\text{H}_{\text{sample}} - {}^2\text{H}/{}^1\text{H}_{\text{standard}}) / {}^2\text{H}/{}^1\text{H}_{\text{standard}}] \times 1000$$

The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech which have been calibrated relative to several water standards available from the International Atomic Energy Agency and the National Institute of Standards and Technology.

Replication Because of replicate preparation of samples, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the manufacturer's computer software. The raw data is then converted to final data using a spreadsheet on a personal computer. The spreadsheets are stored on computer hard disk and a copy is attached to the raw printouts for each batch of analyses.

IV. Gas Chromatographic Analysis of Gases

A. Analysis of hydrocarbons

Equipment

Shimadzu 2010 Gas Chromatograph. This (complete) GC system is equipped with two 2010 instruments; one containing a thermal conductivity detector (TCD) and a flame ionization detector (FID), and the other containing dual TCD's. Data processing is done on GC solutions software and a personal computer.

Shimadzu 2014 Gas Chromatograph. This (partial) GC system is equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors. Data processing is done on GC solutions software and a personal computer.

Method/Procedure The sample loop on the GC is evacuated between each sample. Samples are injected into the evacuated sample loop and adjusted to atmospheric pressure. Sample identification is entered into the GC solutions software and the run is initiated.

The Shimadzu 2010 and 2014 utilizes several different packed columns and valve switching to separate the various components. Instrument configuration was designed by Shimadzu specifically to meet the requirements of Isotech. Helium is used as the carrier gas. All valve switching during the analysis is computer-controlled. The resulting component peak areas are then quantified by the software (given raw percent values) by comparing them to previously run standards. The lab technician checks the raw total for each analysis to ensure that all components have been detected. The raw total can vary from day to day depending on atmospheric pressure, with acceptable raw totals of 96% to 104%. The lab technician also checks all baselines for accuracy from the chromatograms shown on the computer screen. This raw computer record is maintained for each sample corresponding to its individual lab number.

The raw percentage values for each sample are downloaded into the main sample database, and are normalized to 100% when the Analysis Report is generated.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. Septa in the sampling valves are replaced as needed.

Calibration/Standardization Multiple reference gases are used for standardization of the Shimadzu gas chromatographs. All standards are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The minimum and maximum concentration used for calibration cover the range of the majority of natural gases submitted for analysis. At least four points are used for each component. For each new standardization, the peak area of each concentration for each compound is inserted into a

table within the GC Solutions software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis.

Reference Samples The reference sample used as the 1st run of each day and every tenth sample thereafter is representative of the majority of natural gas samples received for analysis. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a replicate. This replicate analysis is done approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the GC Solutions software.

B. Analysis of fixed gases

Equipment

Shimadzu 2010 Gas Chromatograph. This GC system is equipped with two 2010 instruments; one containing a thermal conductivity detector (TCD) and a flame ionization detector (FID), and the other containing dual TCD's but quantification of fixed gases is done using only the TCD's. Data processing is done on GC solutions software and a personal computer.

Shimadzu 2014 Gas Chromatograph. This GC system is equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors but quantification of fixed gases is done using only the TCD. Data processing is done on GC solutions software and a personal computer.

Method/Procedure The procedure for analysis of fixed gases is identical to that for analysis of hydrocarbons, with one exception (for 2010 only). For separation of oxygen and argon, an external column on the Shimadzu 2010 is used. This column operates at -78 °C; therefore a dewar of dry ice/isopropyl alcohol is placed on the column before each run. The lab technician checks all baselines to verify peak integration. The Shimadzu 2014 system is not equipped with the external column, thus argon and oxygen values are reported as one value. Also the 2014 system cannot detect helium and can only quantify hydrogen at limited concentrations.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. The septum on the injection valve is periodically replaced.

Calibration/Standardization Multiple reference gases are used for standardization of the Shimadzu gas chromatographs. All standards are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The minimum and maximum concentration used for calibration cover the range of the majority of natural gases submitted for analysis. At least four points are used for each component. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the GC Solutions software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis.

Check Sample Multiple reference sample are used to verify instrument performance and calibration. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a duplicate. This duplicate analysis is performed approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the GC Solutions software.

V. Radiocarbon Analysis of Prepared Samples

Radiocarbon analyses of purified CO₂ samples prepared by Isotech are currently being subcontracted to either Beta Analytic Inc., Coral Gables, Florida or to Illinois State Geological Survey, Champaign, Illinois. Beta Analytic is the largest commercial radiocarbon dating laboratory in the world. The attached QA/QC plans have been provided by

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