COLLECTION OF CO_2 FOR $^{13}C/^{12}C$ MEASUREMENTS AND SIMULTANEOUS C, H, N, AND S ANALYSIS USING AN ELEMENTAL ANALYZER[1]

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INTRODUCTION

Organic matter $^{13}C/^{12}C$ ratios as well as elemental analyses of organic C, H, N, and S are widely used in hydrocarbon exploration and in studies of sediment provenance and diagenesis. Simultaneous isotopic and elemental analysis is achieved by linking a combustion device with a gas chromatograph and mass spectrometer. Available commercial systems are generally expensive (> $250,000) or lack the sensitivity to resolve small isotopic variations. Here we describe a simple method for extracting CO_2 for subsequent stable isotope analysis while simultaneously collecting concentration data using a conventional GC-based elemental analyzer. This procedure is a viable alternative to the commonly used "sealed-tube" method of CO_2 extraction from organic matter. Advantages include: high-precision isotopic and elemental analyses on the same sample aliquot, improved sample throughput for $\delta^{13}C_{org}$ determinations, and an inexpensive means of linking existing elemental analysis and stable isotope laboratories.

Early $\delta^{13}C_{org}$ techniques used on-line combustion of organic material with oxygen derived from thermal decomposition of CuO (Craig 1953). Off-line combustion in sealed glass tubes (Buchanan and Corcoran 1959; Boutton et al. 1983; Engel and Maynard 1989) has streamlined the procedure, but the routine analysis of large numbers of samples has remained cumbersome and time consuming. By attaching a simple extraction line to a CHNS or CHN elemental analyzer, the process of combusting organic matter and purifying the resulting CO_2 is quicker and easier. One sample for $\delta^{13}C_{org}$ analysis can be obtained in as little as 4 to 10 minutes. The following procedure is designed to provide CO_2 for $\delta^{13}C_{org}$ while simultaneously obtaining elemental C, H, N, and S analyses of a given sample using an elemental analyzer. It should be noted that virtually any elemental analyzer (e.g., Carlo-Erba, Perkin Elmer, Hewlett Packard, Heraeus) can be used with this extraction line. Several labs are using this method; the procedure was first suggested to us by Gerold Wefer and Gerhard Fischer (Universität Bremen), who have briefly described a similar system (Fischer 1989, in German).

MATERIALS AND METHODS

Figure 1 illustrates a system for collecting and purifying CO_2 gas as it exits the exhaust port of an elemental analyzer. We describe an "off-line" arrangement where each CO_2 sample is sealed in glass tubing prior to isotopic analysis. This simple line may also be hooked up directly to the inlet system of a mass spectrometer. Elemental analyzers operate based on combustion of a sample contained within an aluminum or tin capsule in a high temperature combustion/reduction column. Flash combustion of the capsule (to > 1500°C) occurs when the combustion chamber is temporarily enriched in oxygen, either from decomposition of an oxygen-bearing catalyst or injection of a small quantity of UHP (ultra-high purity) O_2. The combusting sample generates one or more of these gases: N_xO_x, CO_2, H_2O, and SO_2. In the Carlo-Erba NA-1500 elemental analyzer we use at Rice, the combustion/reduction column also contains tungsten trioxide on alumina (required for samples containing sulfur and halogens) and reduced copper wire for the reduction of nitrogen oxides to N_2. Combustion gases move through the system in a stream of UHP He carrier gas. A water trap containing magnesium perchlorate (anhydrone) is installed to remove H_2O if elemental analysis of H is not desired.

Separation of CO_2, N_2, H_2O, and SO_2 occurs within a GC column; gas concentrations are measured with a thermal conductivity detector. After detection, the gases exit an exhaust port (in the following order: N_2, CO_2, H_2O, and SO_2) and enter the CO_2 extraction line (Fig. 1). Collection of CO_2 is achieved by directing the initial flow of gases through a coil immersed in liquid nitrogen (LN_2), allowing non-condensable He and N_2 to pass through the coil and exit the vent line downstream of valve 3. Once the CO_2 is frozen in the coil, the gas flow is redirected from the coil and out through valve 1 to prevent the collection of H_2O and SO_2. While keeping the CO_2 frozen in LN_2, the extraction line is evacuated to remove any remaining non-condensable gases. The extraction line is then isolated from the vacuum pump. LN_2 is removed from the coil and replaced with an isopropyl alcohol (IPA) and dry ice slush (−78°C) to retain any remaining water. Gaseous CO_2 is then transferred to a collection tube with LN_2 and subsequently sealed.

Standard Swagelok fittings and Cajon Ultra-torr unions are used to fabricate and attach this extraction line to the elemental analyzer. The extraction line consists of ¼″ stainless steel tubing (with the exception of the coil and vent tube which are ⅛″ ss) and the sample collection tube, which is 6 mm borosilicate glass. Total length of the coil and vent line are 1 meter each. Two types of valves are used: Whitey SS-1RS4 regulating valves (n = 3), and Nupro SS4BK bellows valves (n = 2) for the vacuum portion of the line. The regulating valves hold vacuum to 10^{-3} torr and also assist in regulating gas flow through the extraction

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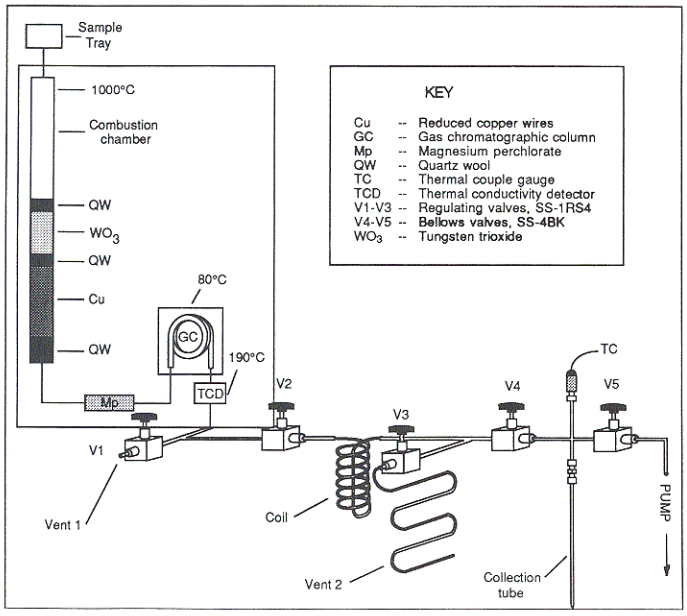

FIG. 1.—Schematic representation of the Carlo-Erba NA1500 elemental analyzer and $\delta^{13}C_{org}$ extraction line. The combustion/reaction column consists of quartz wool, tungsten trioxide on alumina and reduced copper wires, all heated to 1000°C. An optional magnesium perchlorate water trap can be installed if hydrogen analyses are not desired. Gas separation occurs in a gas chromatograph column heated to 80°C; gas concentration is measured by a thermal conductivity detector with a filament temperature of 190°C. The extraction line separates CO_2 gas from He, N_2 and H_2O using the proper sequence of valve operation in conjunction with LN_2 and/or IPA dry ice slush on the spiral coil. Extraction line gas pressure is measured by a thermocouple vacuum gauge.

line. A thermocouple gauge (1 to 1000 μm) is used to measure the vacuum of the line. A rotary vacuum pump capable of at least 10^{-3} torr vacuum is suitable for this application.

The gas collection apparatus on the extraction line can be modified to suit laboratory needs. We use a 6 mm borosilicate glass tube, 70 cm long, to collect the CO_2, because it yields 5 to 6 ampules 10 to 12 cm long after sealing with a glassblowers torch. This collection tube design prevents frequent exposure of the line to atmosphere and expedites off-line sample handling. Ampules are later inserted into a glass sample tube breaker (DesMarais and Hayes 1976; Coleman 1981; Caldwell et al. 1983) attached to the inlet manifold of a mass spectrometer.

EXTRACTION PROCEDURE

Although the following procedure was developed using a Carlo-Erba NA-1500 elemental analyzer, the protocol for other GC-based elemental analyzers is very similar. Configuration of the combustion/reduction column and parameters such as oven temperature, carrier gas flow rates, and retention times for the Carlo-Erba instrument are given in Table 1. We use a total run time of 520 to 540 seconds when analyzing for CHNS and as little as 240 to 280 seconds for CHN (e.g., samples which do not contain S).

Before starting a sample run, close valves 1 and 4, open valves 2 and 3 one-quarter to one-half turn and open valve 5 completely (refer to Fig. 1 for valve locations). Place a full 0.5 liter dewar of LN_2 on the coil and allow approximately 10–20 seconds for the He flow to stabilize and the coil to reach LN_2 temperature. Begin a sample run in the manual mode (e.g., each start triggered by the operator). N_2 will elute first, then CO_2. After 170–180 seconds, open valve 1 one-quarter to one-half turn and close valves 2 and 3. This will redirect the He flow and vent both H_2O and SO_2 out valve 1. With valves 2 and 3 closed, open valve 4 and pump away the He through valve 5 until the thermocouple vacuum gauge reaches baseline. Close valve 5 and remove LN_2 from coil and replace with an IPA dry ice slush mixture to separate the H_2O from CO_2 gas. Place a small dewar (or foam cup) mounted in an adjustable ring support on the bottom to the collection tube. Fill the cup one-half full with LN_2 and allow 3 minutes for the CO_2 to transfer into the collection tube. When the transfer is complete, top off the dewar with LN_2 and flame seal the glass tube with a glassblower's torch about 1.5 to 2.5 cm above the level of the cup. When the tube is sealed, it may be removed from the LN_2. Open valve 5, remove the IPA dry ice slush, warm the coil and evacuate any water vapor before starting the next sample.

TABLE 1.—*Set-up parameters for the Carlo-Erba NA1500 elemental analyzer*

Instrument Temperatures (°C)	
Combustion/reduction oven	1000
Chromatographic column	80
Filament	190
Flow Rates (ml min^{-1})	
Helium (Grade 5 UHP)	105–110
Oxygen	20–25
Element Retention Times (seconds)	
Nitrogen as N_2	56–60
Carbon as CO_2	80–86
Hydrogen as H_2O	200–220
Sulfur as SO_2	380–400
Additional Parameters (seconds)	
Sample combustion	65
Oxygen injection	85
Sample period	80
Run time for N and C	150–180
Run time for N, C, H, S	480–520
Column Configuration (cm)	
Quartz comb./red. column (l × w)	45.0 × 1.8
From top to bottom	
—Quartz wool	3.0
—Reduced copper wires (40 g)	12.0
—Quartz wool	1.5
—Tungsten trioxide (WO_3)	6.25
—Quartz wool	1.5

RESULTS

The mass spectrometer used in this study is a semi-automated VG 602E (upgraded with SIRA series electronics) equipped with a manifold designed to use sample tube breakers modified after Caldwell et al. (1983). All data are expressed in the conventional delta (δ) notation in which the $^{13}C/^{12}C$ isotopic ratio is reported relative to the international PDB standard (Craig 1957). Reproducibility was tested using NBS-21($\delta^{13}C = -28.14‰$; C = 100%) and Sulfanilamide CHNS Standard ($\delta^{13}C = -24.76‰$; N = 16.27%, C = 41.84%, H = 4.68%, S = 18.62%). Precision (2σ) for isotopic analysis of 21 NBS-21 and 18 Sulfanilamide standards was 0.08‰ and 0.09‰, respectively. Precision for elemental analyses is unaffected by the operation of the CO_2 extraction line. For NBS-21 over a weight range of 0.15–1.00 mg and Sulfanilamide over a range of 0.8–3.0 mg, sample weight has no effect on $\delta^{13}C$ using this technique. In addition, there was no He flow restriction through the coil by frozen CO_2 using these weight ranges. Precision using the sealed tube method is similar: 0.08‰ for 97 *Spartina* grass replicates and 0.11‰ for 10 NBS-21 analyses.

The benefits of this technique are numerous and the cost to set up the extraction line is small (< $2000). With a combustion/purification time of 10 minutes or less, many samples can be analyzed in a day without sacrificing precision. New elemental analyzers range in price from $20,000 to $40,000, considerably less than the price of automated ^{13}C preparation systems available from mass spectrometer vendors. Many universities already have separate elemental analysis and mass spectrometry facilities; with off-line CO_2 collection these labs can easily be linked.

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