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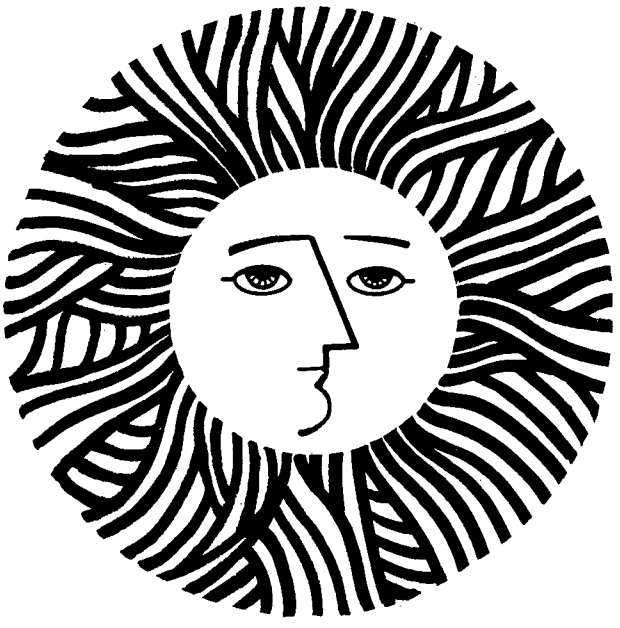

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COULOMETRIC QUANTITATION OF CARBON IN OIL SHALE PROCESS WASTEWATERS VIA UV-PEROXYDISULFATE OR HIGH-TEMPERATURE OXIDATION

G.W. Langlois; B.M. Jones; R.H. Sakaji
Lawrence Berkeley Laboratory
University of California, Berkeley
Berkeley, California 94720

and

C.G. Daughton
Sanitary Engineering and Environmental Health Research Laboratory
University of California, Berkeley
Richmond, California 94804

This work was prepared for the U.S. Department of Energy
under Contract No. DE-AC03-76SF00098

ABSTRACT

The routine quantitation of organic or total carbon (OC and TC, respectively) in aqueous samples is generally achieved after stoichiometric conversion of each carbon atom into identical unit-carbon molecules by chemical/photochemical oxidation or high-temperature combustion followed by detection with nondispersive infrared spectroscopy (IR), flame ionization (FID), or coulometric titrimetry. The quantitation of OC and TC in synfuel process wastewaters presents several major problems to various conformations of instruments designed for the conversion and detection steps.

A carbon analyzer was fabricated from commercially available units and parts. This new design obviates the problems of (i) instrument downtime caused by fouling of high-temperature combustion catalysts and corrosion of furnace combustion tubes, (ii) limited linear dynamic range and upper detection limit (viz., IR), and (iii) frequent detector calibration (viz., IR and FID). This new approach to carbon analysis couples an ultraviolet photochemical reactor with an automatic coulometric titrator. Aqueous acidic peroxydisulfate serves as a source of free-radical oxidant and carries the sample from a sample injector loop to the photoreactor, where oxygen gas assists mixing and serves as a carrier gas for the evolved CO_2. This carbon analyzer was compared statistically with an ASTM-approved high-temperature combustion system. The CO_2 that was generated from each oxidation unit was quantitated by coulometric titrimetry. Low-temperature UV-enhanced persulfate oxidation of pure compound standards compared favorably with the recoveries from the ASTM-approved combustion unit. Results of a two-way analysis of variance indicated there was no significant difference between analyzers for recovery of pure compounds ($\alpha = 0.05$). Neither was there a significant difference in total or dissolved organic carbon values for nine oil shale process waters from each of the two types of analyzers ($\alpha = 0.05$).

INTRODUCTION

Wastes that contain a complex mixture of organic and inorganic compounds present numerous problems when attempts are made to quantify the "total" amount of solutes or to quantitate the degree of contaminant removal by a waste treatment process. Methods that are specific for given compounds or even entire chemical classes may contribute information relevant only to a small portion of the solutes present in complex wastes; these methods can also be inaccurate because of positive and negative interferences by other compounds in the sample matrix. Complex solutions and heterogeneous wastes often necessitate the measurement of "bulk" or colligative properties that are shared by as many solutes in the matrix as possible.

Bulk properties that are conducive to analytical measurements include total dissolved solids, electrical conductivity, and the oxidative states of the solutes. A method that is commonly but incorrectly employed to estimate the total concentration of organic solutes is biochemical oxygen demand (BOD). Although BOD is partially a function of the quantity of carbon and its average oxidative state, it is merely an estimator of the material that can be oxidized by acclimated, aerobic bacteria. The overall oxidative state of solutes in a solution is more closely reflected by chemical oxygen demand (COD), which is often misused as an estimator of organic carbon. Neither of these methods can distinguish organic from certain inorganic compounds (ammonia and thiosulfate will yield BOD and COD values, respectively), and both are unable to detect compounds that are refractory to the particular means of oxidation.

Methods that determine specific elemental concentrations (e.g., C, N, S, or P) can give more direct information. One of the most widely employed element-specific methods is carbon analysis. Inorganic and organic carbon species can be quantitated separately or together. Further qualitative information can be obtained by determining other parameters, such as COD, and relating them to carbon concentration, or by fractionating solutes into chemical classes prior to carbon analysis. For example, by relating the COD of an organic waste to the organic carbon concentration (i.e., "specific COD", see Daughton, Jones, and Sakaji, 1981), the overall oxidative state of organic solutes can be estimated; a rapid method for separating organic compounds into polarity classes uses reverse-phase fractionation (Daughton, Jones, and Sakaji, 1982).

Problems associated with the quantitation of treatment performance for synfuel wastewaters such as oil shale process waters have been discussed (Daughton, Jones, Sakaji, and Thomas, 1982). Retort waters often contain large concentrations of organic and inorganic carbon. A large portion of the organic carbon is refractory to extensive mineralization by biooxidation. The inorganic carbon is partially responsible for the extreme buffering capacity and high alkalinity of these waters, which makes pH adjustment economically infeasible as a step in waste treatment. Of the numerous classes of organic solutes present in oil shale wastewaters, nitrogen heterocycles and nitriles are among the most difficult to oxidize biologically or chemically (e.g., by BOD and COD determinations) (Naik et al., 1972; Standard Methods ..., 1981) and have proved resistant to certain methods of oxidation used for organic carbon measurements (Armstrong, Williams, and Strickland, 1966; Gershey et al., 1979). These compounds also appear to be the major factor that limits the success of biotreatment of these waters (Jones, Sakaji, and Daughton, 1982).

This report discusses the advantages and disadvantages of various instrumental techniques for determining organic and inorganic carbon in highly contaminated waters. A new approach to organic carbon analysis is presented, and the performance of this instrument in quantitating dissolved carbon in oil shale process wastewaters and in standard solutions of pure compounds is compared with that of an ASTM-approved carbon analyzer (ASTM, in press).

Classes of Carbon

There are seven major groups of carbon that can be determined by "carbon analysis". These classes are defined by organic and inorganic carbonaceous content and by whether suspended matter (e.g., particulates and colloids) is included (Fig. 1). Total carbon (TC) includes all forms of carbon in an aqueous sample; this in turn is composed of total organic carbon (TOC) and total inorganic carbon (TIC). "Inorganic carbon" in this report is synonymous with "oxides of carbon", "mineral carbon", and "carbonate carbon"; the predominant species in retort waters are carbonate and bicarbonate salts. If the particulate and colloidal materials are removed from liquid samples (e.g., via numerous centrifugation and filtration techniques), the carbon that remains is called total dissolved carbon (TDC). Total dissolved carbon includes both dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC); usually "dissolved" is arbitrarily defined as material that passes through a membrane filter of specified pore diameter (e.g., 0.10 to 0.45 μm).

An operational definition of "dissolved" or "soluble" is exceedingly complex. Filtration is generally assumed to separate the particulates from the dissolved species, but problems attendant with this approach are numerous. Filtration methods other than molecular weight ultrafilters can allow the passage of colloidal material into the filtrate, while at the other extreme, filtration can actually remove dissolved compounds by any of several mechanisms. For oil shale process wastewaters, several variables influence the eventual separation of filtrate from retentate. The type of filter is the most important feature. "Depth" (e.g., glass fiber) versus "screen" (e.g., membrane) characteristics distinguish the two major groups of filters. The membrane filters include mixed cellulose esters and nylon, which themselves have depth filter characteristics, and polycarbonate. The screen type filters are affected by the loading of particles on their surfaces. During filtration, as the pores become partially blocked by particulates, the nominal pore size is reduced, thereby promoting the retention of particles that would normally not be retained (Laxen and Chandler, 1982); this problem can be partially solved by the use of tangential flow filtration apparatus. The chemical sorption or precipitation of solutes by electrostatic (Zierdt, 1979) or chemical interactions of the solution with the membrane surface can also effect removal of dissolved solutes. In addition, the partitioning of solutes into the immobilized, retained particulate phase has also been hypothesized (Daughton, et al., 1981). The composition of the filtrate can also be influenced by the type of filtration device. Vacuum filtration will remove portions of dissolved gases such as CO_2 and volatile organic species; pressure filtration is recommended in these instances.

Contamination of the filtrate by the filter is a final consideration for samples with low solute concentrations. Water extractable materials (e.g., wetting agents), humectants, and particulate debris, all of which remain after the manufacture of membranes, can significantly contaminate the filtrate (Cooney, 1980). From our experience, polycarbonate membranes offer the best compromise of features for the filtration of oil shale wastewaters.

The rationales for distinguishing between dissolved and total carbon include (i) the importance of dissolved carbon as the major form of nutritionally-available carbon to microorganisms, and (ii) the minimization of sampling error (e.g., size-exclusion dictated by the bore of the syringe needle) for liquids that contain large quantities of both particulate and colloidal forms of carbon. For these reasons, our laboratory has restricted itself to the determination of dissolved organic and inorganic carbon. This report will only address the determination of dissolved species. The investigation of particulate materials should entail another major study.

Carbon Analysis

Approaches to the quantitation of the carbon content in organic compounds generally require two steps: (i) the liberation of each carbon atom as an identical C-1 molecule which is not influenced by the bonding in the parent compounds, and (ii) the detection and quantitation of these units.

The first step usually involves conversion of bound carbon to gaseous species (i.e., CO_2 or CH_4) by chemically- or thermally-mediated oxidation or reduction. The quantitation of organic carbon can be accomplished by either the direct or indirect method (Fox et al., 1980). The indirect method involves the determination of both TDC and DIC; DOC is then calculated by difference. The direct method requires the removal of inorganic carbon prior to the determination of dissolved carbon for the remaining solutes (TDC then becomes equivalent to DOC). The removal of DIC can be accomplished by precipitation with barium hydroxide or by boiling or purging with an inert gas after acidification (Van Hall, Barth, and Stenger, 1965). Acidification allows for the conversion of inorganic carbon to carbonic acid which subsequently hydrolyzes into H_2O and CO_2. The latter approach is the most widely accepted (ASTM, 1977; Standard Methods ..., 1981).

The indirect method requires the least sample manipulation, but lengthens the sample-throughput time because two analyses are required for each sample. The direct method can result in the precipitation of organic compounds such as higher-molecular-weight aliphatic carboxylic acids during acidification and occlusion or partitioning of other organic solutes by these precipitates; subsequent purging of CO_2 can volatilize lower-molecular-weight organic solutes, especially fatty acids (Fox, Farrier, and Poulson, 1978).

Inorganic carbon is determined directly by the conversion of each carbon atom to a uniform, detectable species (i.e., CO_2). This can be accomplished at low temperature (60 ^{o}C) by conversion of mineral carbon species to CO_2 via acidification. The unambiguous determination of inorganic carbon is dependent on the specific conversion of only mineral carbon species to CO_2 and the resistance of all organic compounds to both oxidation and detection by this type of determination.

Commercial Instrumentation

The conversion of carbonaceous species to CO_2 is generally accomplished by one of four methods: high-temperature combustion, chemical oxidation, UV oxidation, or UV-enhanced chemical oxidation. The evolved CO_2 can be detected in batch or continuous mode. Detection methods can be physical, chemical, or electrical and span the range of low-sensitivity gravimetric methods to high-specificity infrared spectroscopy (IR). The advantages and disadvantages of each conversion and detection method are described below.

Methods of Oxidation.

(1) High-temperature combustion (950 ^{o}C).

Both organic and inorganic carbon compounds can be oxidized at high temperatures to yield CO_2. Oxidation generally occurs within a ceramic, stainless steel, or quartz combustion tube which is heated in a temperature-controlled furnace. Combustion tubes are packed with an oxidation catalyst which also serves to lengthen the sample residence time. A wide variety of sample introduction methods exist. These include syringe injection of aqueous samples and "boat" (ladle) introduction for solid or heterogeneous mixtures. Combustion products are swept from the tube to the detector by a carrier gas, usually oxygen or nitrogen; oxygen for carbon oxidation originates from combustion catalysts and water.

One problem associated with the combustion method is the production of large quantities of water vapor and other gases, which can result in excessive pressures in the combustion tube. This procedure is therefore restricted to sample volumes less than several hundred microliters. In addition, samples with

high salt concentrations, especially alkaline metals, may cause the rapid degradation of the catalyst and attack the tube material itself; this is a major problem with quartz. High-temperature combustion characteristically contributes high background values as a result of trace carbon contamination of the catalyst and carrier gas. These systems therefore lack precision and accuracy below 2 mg-C/L (Takahashi, 1979), and Baker et al. (1974) found them unsuitable for the analysis of natural waters containing less than 15 mg-C/L. High-temperature combustion, however, does provide the most complete oxidation (Collins and Williams, 1977; Gershey et al., 1979) within a relatively short analysis time (3-5 minutes; Takahashi, 1979); this is an advantage not shared by alternative oxidation procedures.

(2) Chemical oxidation (persulfate; chromic acid in H_2SO_4).

Wet chemical methods can be adapted for the oxidation of organic compounds for TDC, DOC, or DIC analyses. These methods typically have lower system background values than high-temperature combustion units, and therefore are capable of lower limits of detection. They are not, however, applicable to all waters; certain organic compounds are resistant to chemical oxidation (Menzel and Vaccaro, 1964). Other classes of organic compounds may require significantly longer contact times with the oxidant, thereby increasing the analysis time beyond practical limits (Van Hall, Safranko, and Stenger, 1963). The persulfate oxidation procedure described by Menzel and Vaccaro (1964) requires less time than other chemical oxidation methods, but yields incomplete recoveries of polycyclic aromatic and long-chain hydrocarbons. Persulfate oxidation, in general, gives significantly lower recoveries (by 10%) than either combustion or photooxidation methods (Gershey et al., 1979; Williams, 1969). In addition, the presence of a high concentration of chloride ion in a sample can consume oxidant, contributing either a positive or negative interference, depending on the detection method.

(3) Ultraviolet oxidation.

Ultraviolet (UV) energy alone is incapable of mineralizing inorganic carbon oxides for the determination of total or inorganic carbon, or of oxidizing particulates for determination of TOC. Therefore, this technique is applicable only to dissolved organic carbon analyses. For this method to be effective, samples must be irradiated at wavelengths less than 210 nm for long periods (0.5 to 3.0 hours), a significant disadvantage when large numbers of samples must be analyzed. Although UV oxidation compares favorably with combustion for the recovery of organic carbon from natural waters (Gershey et al., 1979; Goulden and Brooksbank, 1975), it is incapable of complete mineralization of many of the nitrogen- and sulfur-containing organic compounds (Armstrong et al., 1966; Gershey et al., 1979) that typify oil shale process waters. The effects of extensive UV irradiation of these waters have been reviewed by Jones et al. (May, 1982).

The energy output of the UV lamp is critical for this method of oxidation. The output will decrease during the life of the lamp, and variability in output also exists between individual UV lamps (Collins and Williams, 1977). Ultraviolet oxidation methods are compatible with detectors designed for quantitating low concentrations of carbon (e.g., 0 to 25 mg/L). Baker et al. (1974) report UV oxidation to be as efficient as chemical oxidation for the determination of organic carbon in freshwater. Gershey et al. (1979) found, in fact, that the recovery of DOC from seawaters is higher with UV photooxidation than with chemical oxidation.

(4) UV-enhanced chemical oxidation.

This method is applicable to TDC and DOC analyses, but not to direct DIC analyses. Most methods coupling UV and wet chemical oxidation incorporate the Technicon Auto-Analyzer system; the sample is introduced into the oxidant stream, usually potassium persulfate (Collins and Williams, 1977; Goulden and Brooksbank, 1975), and is pumped through a silica coil surrounding a UV lamp.

Residence time in the coil varies from 8 to 45 minutes. This method results in higher precision than obtained by high-temperature combustion (Goulden and Brooksbank, 1975). Leachable organic material from the pump tubing, however, can contribute a significant background signal; preconditioning of the pump tubing is often required for at least 24 hours to minimize this problem.

Another design for UV-enhanced chemical oxidation uses a UV lamp submerged in a reactor vessel containing the chemical oxidant (Wölfel and Sontheimer, 1974). The sample is introduced directly to the solution and the evolved CO_2 is swept by the carrier gas to the detector. A commercial system that incorporates a UV lamp submerged in an acidic potassium peroxydisulfate solution and nondispersive IR detection of CO_2 was recently introduced (model #DC-80, Dohrmann Division, Xertex, Inc., Santa Clara, CA). The manufacturer reports an analysis time of 3 to 4 minutes, and complete recoveries of several nitrogen heterocycles (e.g., pyridine, proline, and nicotinic acid, each at approximately 100 mg/L concentration) (Takahashi, Martin, and Harper, 1981).

Methods of Detection.

Evolved CO_2 can be quantitated by several physical methods, including manometric, gravimetric, and volumetric determinations. These are limited to batch analysis, are extremely time consuming, suffer from low sensitivity and high lower-detection limits, cannot be automated, and are subject to interferences from co-produced gases. Gravimetric determinations, for example, depend on the absorption of CO_2 on soda-asbestos, soda lime, or into an alkaline solution (Blom and Edelhausen, 1955). The increase in weight as a result of gas absorption is measured and the carbon content is interpolated from the recovery of standard solutions analyzed in parallel.

Thermal conductivity, electrical conductivity, and flame ionization detection (FID), are three methods for directly or indirectly detecting CO_2 in a gas stream on a continuous basis. These methods vary from moderate sensitivity with a narrow linear range (thermal conductivity) to high sensitivity with a wide linear dynamic range (FID). Thermal conductivity detectors determine the change in conductivity within a heated cavity as a result of changes in the gas composition. This method of detection is nonspecific and subject to interferences from co-produced gases. In addition, the sample throughput is limited (25 min/sample). Thermal conductivity is only moderately sensitive compared with other methods of detection (Willard, Merritt, and Dean, 1974). In comparison, flame ionization detection is extremely sensitive. The introduced gases burn in a hydrogen flame (Jeffery and Kipping, 1972) and a proportion of the molecules acquire sufficient energy to ionize. This ionization gives the flame an electrical conductivity which can be detected and amplified (Littlewood, 1962). Since an FID responds only to oxidizable carbon atoms, CO_2 from oxidized or combusted organic material must be reduced to CH_4 over a nickel catalyst prior to detection (Willard et al., 1974). Any hydrocarbon gas that survives the combustion/oxidation step would also be quantitated. The precision of an FID for organic carbon determinations will depend on the efficiency of conversion of CO_2 to CH_4. Flame ionization detectors are reported to have wide linear dynamic ranges (Willard et al., 1974), but require frequent daily calibration.

Non-dispersive IR detection has the advantage of being highly specific for CO_2 with excellent sensitivity. The CO_2 content of the carrier gas is compared with a nonabsorbing reference gas (Delahay, 1962) and the difference in absorbance at 2380 cm^{-1} (4.2 μm) is quantitated (Beckman, 1980). The range of the detector depends on the cell pathlength and detector configuration. Manufacturers claim a range for aqueous samples of 0 to 2000 mg-C/L; the standard curve from an IR detector over this range, however, is notoriously nonlinear. The precision of the instrument relies on a constant gas flow rate. Carbon dioxide is quantitated by peak height interpolated from a standard curve. This type of detector requires frequent calibration and, for high

precision, the samples should fall within the linear portion of the standard curve.

Detection of CO_2 by coulometry, as in any titrimetric technique, requires the addition of reagent until a predetermined endpoint has been attained. For coulometry, the reagent (i.e., electrons) is generated electrolytically, and the quantity of titrant required for the stoichiometric indirect titration of the CO_2 is equivalent to the number of coulombs generated (Ewing, 1981). Stoichiometric titration obviates the need for frequent calibration because the electron itself becomes a primary standard (Willard et al., 1974). We have found this detection method to possess an excellent linear dynamic range (at least three orders of magnitude) and, with appropriate gas scrubbers, to be accurate and precise for the quantitation of CO_2. For oil shale wastewaters, we have decided that coulometric detection is the method of choice.

COMPARISON STUDY

Of the four oxidation/combustion methods discussed previously, only high-temperature combustion and UV-enhanced persulfate oxidation appeared to be suitable for the routine determination of organic carbon in oil shale process waters. The alternative methods, chemical and UV oxidation, were not applicable to oil shale process waters due to reported incomplete oxidation of certain organic compounds and lengthy analysis times. We have fabricated a hybrid carbon analyzer that combines the strengths of two commercial carbon analyzers while avoiding their weaknesses. A study was initiated to statistically compare this newly configured instrument with an ASTM-approved carbon analyzer which this laboratory has used routinely for analysis of oil shale wastewaters.

Nearly all commercial instruments for carbon analysis employ one of two designs: (1) high-temperature combustion coupled with coulometric titrimetry (e.g., Coulometrics, Inc.) or IR detection (e.g., Ionics; O.I. Corp.; Beckman), or (2) low-temperature oxidation coupled with IR detection (e.g., Dohrmann; Astro; O.I. Corp.; Ionics). While both high-temperature combustion and IR detection are applicable to the analysis of oil shale process waters, we have experienced significant problems with each. High-temperature combustion units have been subject to frequent and unpredictable downtimes because of damaged combustion tubes and fouled catalysts. Infrared detectors have exhibited substantial drift, requiring frequent standard curve determinations.

The ASTM-approved analyzer used in this study was obtained from Coulometrics, Inc. (Wheat Ridge, CO). This system couples high-temperature combustion (quartz combustion tube) with an automatic coulometric titrator. The newly-configured analyzer, subject of this comparison study, combines a commercially available photochemical reactor with the same automatic coulometric titrator. The major anticipated advantages of this new approach were reduced maintenance and downtime, lower capital and maintenance costs, and ease of automation.

High-Temperature Combustion

The Coulometrics high-temperature combustion system (model #5020, Coulometrics, Inc., Wheat Ridge, CO) (Fig. 2) oxidizes both organic and inorganic carbonaceous compounds. Samples are introduced to a quartz combustion tube by direct injection with a Hamilton (Reno, NV) CR-700 "constant rate" carbon analyzer syringe. This syringe can be set for any volume up to 200 µL, and the contents are forcibly expelled by a spring-driven piston through a 90° bevel needle to ensure reproducible emplacement of the sample within the heated portion of the combustion tube. The syringe and injection port form a gas-tight Luer union. The combustion tube, packed with a WO_3-coated quartz wool plug, barium chromate catalyst, and followed by a

sintered plug of reduced silver for removal of HI and HBr, is heated to 950 °C in a digitally-controlled furnace. Oxygen (99.6 percent purity) is used as a carrier gas and as an additional oxidant source. The oxygen is pretreated by passage though a heated (950 °C) "precombustion" tube packed with barium chromate; contaminative combustion products (e.g., acidic gases) and CO_2 are removed by a gas scrubber containing 45% KOH before the oxygen passes into the injection port. The scrubbed oxygen stream sweeps the volatilized injected sample through the combustion tube. Combustion of the liquid sample results in conversion of organic and inorganic carbon to CO_2, production of acidic gases (e.g., SO_2, SO_3, and NO_x), and steam. Much of the water vapor condenses and is collected in an ambient temperature burette trap. The gaseous phase then passes through a drying tube (magnesium perchlorate) followed by a scrubber packed with acid dichromate-manganese dioxide for removal of contaminative acidic gases. The gas stream, theoretically containing only CO_2 and O_2, then enters the coulometric titration cell where the CO_2 is absorbed and quantitated. The dry gas could possibly evaporate a noticeable amount of coulometer solution during extended operation, thereby changing the absorbance; we have not experienced this problem, however.

High-temperature combustion of organic compounds provides complete oxidation within a short period of time and is thus well suited to the analysis of DOC in retort waters. These wastewaters characteristically contain large numbers of nitrogen and oxygen heterocycles that may be resistant to wet chemical or UV oxidation. Problems have been encountered, however, with combustion tube deterioration and sample introduction methods. The high salt concentration in retort water causes rapid deterioration of the combustion catalyst and the alkaline metals attack the quartz combustion tube. This results in frequent downtime for replacement and conditioning of new combustion tubes; these tubes can rarely be reused because of stress fractures that almost always develop during cooling. The life of the combustion tube and packing material can be prolonged with the use of tungsten trioxide at the influent end of the combustion tube packing; WO_3 aids in the rapid oxidation of carbonates and prevents the formation of sodium carbonates, which are more thermally stable (ASTM, in press). In addition, the sample introduction method is somewhat unsatisfactory. The constant-rate syringe lacks precision and accuracy for reproducibly measuring repetitive sample volumes; this necessitates volume corrections for each data point. The volume set-point for this syringe is also easily disrupted during operation. Sample analysis time is increased because the syringe must remain in the injection port throughout the analysis period; this prevents rapid preparation of the subsequent sample for injection. The restricted internal diameter of the needle severely limits the utility of this approach for particulate sampling.

Low-Temperature UV-Persulfate Oxidation

To circumvent the disadvantages associated with high-temperature combustion, the alternative approach of low-temperature oxidation was evaluated. The high-temperature system with syringe injection was replaced with a modified Dohrmann UV-persulfate reactor for sample oxidation and a low-pressure injection loop for sample introduction (Fig. 3).

The design of the Dohrmann photochemical reactor obviates many of the disadvantages of conventional UV-persulfate reactors. Direct immersion of a low-pressure mercury vapor lamp in the persulfate solution (85 mL) eliminates the need for a silica coil around a UV lamp; this significantly reduces the sample residence time for complete oxidation. In addition, attenuation of the UV output by the lamp quartz envelope, dead air space, and coil wall is minimized. Therefore, more UV energy is available and the time required for complete sample oxidation is minimized. A carrier gas/sparging system (O_2, N_2, He, Ar, or purified air) provides complete mixing of the reactor

contents. The system described in this report uses O_2 (99.6%).

The photoreactor unit (Fig. 3) was assembled from parts that were purchased from Dohrmann (Xertex Inc., Santa Clara, CA). The following major parts were required: reactor body assembly (#512-090), reactor cap assembly (#512-091), silicone connectors (#517-798) for joining 1/16" Teflon tubing to the reactor, silicone plugs for unused reactor ports (#577-803), UV lamp (#512-092), Teflon sleeve for tapered joint of reactor cap (#050-409), and transformer for UV lamp (#010-454). A power supply for the UV lamp was fabricated from the Dohrmann transformer, using readily available electrical supplies which included an aluminum instrument housing (9"l x 11"w x 6"d), instrument fan, ready light and on-off toggle switch, and an electrical outlet for auxiliary power supply to other equipment. In-line fuses were installed for the transformer and auxiliary electrical outlet. A Teflon gas delivery line was connected to the fritted glass impinger in the reactor bottom with a 1/4" to 1/8" silicone reducing connector; the effluent gas line was similarly connected to the reactor cap.

The low-pressure injection valve (model #50-20, Rheodyne, Berkeley, CA) incorporates a calibrated 200-µL sample loop, which minimizes error in sample volume measurement and reproducibility. The system is designed so that the samples and reagents only contact Teflon, glass, and stainless steel. The sample is loaded into the 200-µL loop with a Glenco (#19925, Houston, TX) 1.0-mL gas-tight syringe (rotary valve in "load" position) via a Valco zero-volume fill port assembly (#VISF-1, Houston, TX); excess sample is expelled through the waste line. Five to ten loop volumes are loaded to ensure complete flushing of the previous sample from the loop (Rheodyne, 1979). When the valve is switched to the "inject" position, peroxydisulfate solution sweeps through the loop and carries the sample to the reactor.

The sample enters the bottom of the reactor through a sidearm (Fig. 3). The sample fluid and persulfate solution immediately enter a region of high turbulence created by impinged oxygen that is introduced through the bottom of the reactor. A portion of the reactor fluid is withdrawn for recycle from a sidearm at the mid-portion of the reactor; this fluid is combined with the flow of fresh persulfate reagent from a reservoir and recycled through the injection valve and back into the reactor via the lower sidearm. A glass loop connects the top and bottom of the reactor contents. Reactor fluid is drawn off to waste from the top horizontal section of the loop. The upward flow of the impinged oxygen creates a downward flow of reactor fluid through the loop; this ensures that nonoxidized sample is not isolated from the main reactor and promotes further mixing. By ensuring that the pumping rate for the waste is equal to or greater than the influent rate for fresh persulfate, the volume within the reactor is maintained at a constant level; identical pumping rates can be ensured by setting the wastage rate higher than the influent and removing the waste from a set surface level. The wastage rate is limited, however, by careful consideration of the amount of reactor headspace that is removed; since the carrier gas flow rate is 200 cm^3/min, a wastage rate of up to 2 mL/min would result in loss of nearly 1% of the evolved CO_2, depending upon the volume of gas that enters the waste line. The gaseous oxidation products are swept through the effluent line connected to the reactor cap by the oxygen carrier gas.

The influent, waste, and recycle lines were plumbed through a four-channel peristaltic pump (model 375-A, Sage Instruments Division, Orion Research Inc., Cambridge, MA). Organic contaminants were found to leach from both silicone and Tygon pump tubes, which resulted in high background carbon counts (10 mg/L-min); this was most likely a result of plasticizers and unreacted oligomers. Overnight preconditioning of tubing in a hypochlorite solution could only temporarily reduce the background (3.3 mg/L-min). Collins and Williams (1977) reported the need for tubing preconditioning and observed decreased background contributions during operation because of a reduction in leachable materials.

To avoid these problems, the influent and recirculation tubes were replaced with Viton tubing (a copolymer of vinylidene fluoride and hexafluoropropylene; Cole-Parmer Instrument Co., Chicago, IL) which gave an acceptable background carbon concentration (2.0 to 3.2 mg/L-min) without preconditioning. The disadvantage of Viton tubing is its reduced elasticity which necessitates more frequent replacement (lifetime = 50 to 80 hours of operation) and its higher cost. The recirculation pump tube (0.063" i.d.) was manifolded to yield the desired flow rate of 3.0 mL/min, then recombined after the pump and joined, via a stainless steel tee with the influent persulfate line (0.031" i.d.) (0.6 mL/min) to yield a 3.6-mL/min flow rate through the injection valve into the reactor. The flow rate of the waste (silicone pump tube, 1.0 mm i.d.) was 0.6 mL/min, balancing the flow of fresh reagent into the reactor.

Sample material entering the reactor is exposed to the individual and combined effects of persulfate- and UV-oxidation. Ultraviolet radiation enhances the disproportionation of persulfate into sulfate free radicals and hydroxyl free radicals, two powerful oxidants (House, 1962; Takahashi, et al., 1981).

$$S_2O_8^{-2} + h\nu = 2SO_4^{\bar{\bullet}}$$
$$H_2O + h\nu = H\bullet + \bullet OH$$
$$SO_4^{\bar{\bullet}} + H_2O = SO_4^{-2} + \bullet OH + H^+$$

Ultraviolet energy can also cause excitation of organic compounds, facilitating their oxidation to CO_2 by sulfate and hydroxyl radicals:

$$R + h\nu = R^*$$
$$R^* + SO_4^{\bar{\bullet}} + H_2O = nCO_2 + \ldots$$
$$R^* + \bullet OH + H_2O = nCO_2 + \ldots$$

The oxidation of retort water organic solutes by hydroxyl radical has been discussed by Jones et al. (May, 1982).

High chloride ion concentration in a sample can interfere with the mineralizaton of organic analytes by competing for oxidant (House, 1962).

$$SO_4^{\bar{\bullet}} + Cl^- = SO_4^{-2} + Cl\bullet$$

This interference could possibly be minimized by complexing the excess chloride ions with mercuric ion (Takahashi et al., 1981).

The oxygen carrier gas is passed through a KOH scrubber for removal of contaminative acidic gases prior to entering the UV-persulfate reactor. The CO_2 produced in the reactor is swept through two magnesium perchlorate drying tubes, an acid dichromate/manganese dioxide scrubber, and into the coulometer for quantitation.

Coulometric Titrimetry

The automatic CO_2 coulometric titrator was obtained from Coulometrics, Inc. (model #5010). The titration cell consists of a 200-mL Berzelius tall-form Pyrex beaker and a rubber stopper which holds the cathode, influent gas line, and anode cell. For absorption/titration of evolved CO_2, the coulometer cell is filled with approximately 75 mL of a proprietary ethanolamine solution which contains thymolphthalein blue as an indicator (pK_a 9.4-10.0); the solution changes from blue to colorless upon acidification. The anode cell is a fritted glass tube that contains KI pellets, a proprietary anode solution, and a silver electrode which is connected to the coulometer circuitry. The anode solution is

most likely a saturated KI solution that acts as a salt bridge; use of KCl in place of KI would result in the precipitation of AgCl within the anode cell. The platinum wire cathode surrounds the outside of the fritted-end of the anode cell. The major components of the coulometer are a colorimeter, for detection of the titration endpoint (displayed as percent transmittance), and anticipator circuitry, which switches the titration current from high (100 milliamps) to low (5 milliamps) and from low to off as the colorimetric endpoint (i.e., transmittance of 30% at 612 nm) is approached. The rate of current generation for titration is determined by comparing the colorimeter output with preset voltages to determine the distance from the endpoint. A logic block receives the comparator signal and sets the current source at the determined rate (Huffman, 1977). The current passing through the cell is converted to a digital readout which can be manipulated to display carbon concentration as milligrams per liter.

Carbon dioxide in the gas stream is quantitatively absorbed by monoethanolamine (MEA), forming hydroxyethylcarbamic acid. Dissociation of the acid yields one hydrogen ion per molecule of CO_2 absorbed. The transient carbamate is hydrolyzed by water, producing bicarbonate and regenerating MEA. The equilibrium reactions occurring in the bulk solution are (Danckwerts and McNeil, 1967; Danckwerts and Sharma, 1966):

$$RNH_2 + CO_2 = RNHCOO^- + H^+$$
$$RNHCOO^- + H_2O = HCO_3^- + RNH_2,$$

where R is the 2-hydroxyethyl moiety of MEA and the carbamic acid.

Absorption of CO_2 with the concomitant production of hydrogen ion decreases the pH of the coulometer solution; the hydrogen ion protonates the thymolphthalein blue indicator, yielding the colorless form. The increased transmittance of the solution is detected by the photometer which initiates the generation of electrons at the silver anode. Two possible fates for the electrons have been postulated. Hydrogen ions, produced stoichiometrically with CO_2 absorption, could be reduced by electrons leaving the platinum cathode, yielding hydrogen gas. Alternatively, the electrons leaving the platinum cathode could cause the hydrolysis of water, producing hydroxide ion and hydrogen gas. The hydroxide ion would then reduce the hydrogen ion (produced from CO_2 absorption), regenerating water. As the CO_2 concentration decreases during titration, the increase in pH causes dissociation of the indicator to the colored form. When all the CO_2 has been titrated, the photodetector determines that the endpoint has been reached. The generation of current is then suspended, and the integrated measurement of the number of coulombs used is converted to display mg-C/L.

The major advantage of coulometric titration is that titrant is generated stoichiometrically with 100 percent efficiency. The linear dynamic range and upper limit of the coulometer exceed those of detection by nondispersive infrared spectroscopy, flame ionization, and thermal conductivity. This often eliminates the need for dilution of samples. The coulometer calibration, performed electronically, is extremely stable and obviates the need for frequent empirical calibration with standards, as is required for other detectors. Coulometric titrimetry for detection of CO_2 seems particularly well-suited for analysis of carbon in retort waters because of the wide range of concentrations of inorganic and organic carbon present. An occasional problem of sample over-titration, however, has been observed; this problem appears to be related to the rate at which CO_2 enters the coulometer cell and the response lag-time for the high-to-low titration trip-point.

Inorganic Carbon Determination.

The Coulometrics carbonate-carbon apparatus (model #5030) uses the acidification/purge technique (Fig. 4). The sample is injected into the reaction tube with a 200-µL gas-tight syringe fitted with a septum-piercing needle (e.g., Unimetrics TP 4250S with repetitive volume adjustment). A repipette (e.g., 5-mL Dispensette, Brinkman Instruments Co., Westbury, NY), connected to the top of the reactor tube with Teflon tubing and unions, is used to dispense 2.0 mL of 2N perchloric acid. Ambient air, scrubbed through KOH, sweeps the acid and sample into the bottom of the reactor tube where the mixture is heated to 60 °C. The CO_2 that evolves from the carbon oxides is swept through a silver sulfate scrubber for removal of interfering acidic gases (e.g., SO_2, SO_3, and NO_x) and into the coulometer. This method of inorganic carbon determination is only accurate if organic compounds are not oxidized by the acid treatment.

METHODS AND MATERIALS

The two carbon analyzers were evaluated and compared for the quantitation of TDC and direct and indirect DOC in nine oil shale process wastewaters. The recovery of 17 pure compounds in standard solutions was also investigated. Of the organic solutes present in oil shale process wastewaters, nitrogen heterocycles were of primary interest because they are proposed to be responsible for much of the difficulty in treatment processes (Jones et al., 1982) and also because they resist many oxidation schemes. A series of water-soluble methyl-substituted pyridines was selected for recovery studies based on their reported occurrence in synfuel wastewaters (Raphaelian and Harrison, 1981; Torpy, Raphaelian, and Luthy, 1981) and because of their adequate solubilities in water. Acetonitrile and cyanuric acid were selected because they are resistant to complete and rapid oxidation by photochemical methods (Dohrmann-Envirotech, 1981; Takahashi et al., 1981). Several other water-soluble aromatic and nitrogen-heterocyclic organic compounds were also included in this study. A compound known to be quantitatively mineralized by less rigorous oxidative methods, potassium acid phthalate, was quantitated at several concentrations to determine the linear response of each unit.

The nitrogen heterocycle standards were of the highest grade commercially available (Noah Chemical, Farmingdale, NY; Jewel Nero Consulting, Sun Valley, CA). The acetonitrile was of HPLC grade; all other standards were of analytical reagent grade. A solution of each compound was prepared with acidified, CO_2-free ASTM type I water. The mass of compound added to a Class A 50-mL volumetric flask was determined with a semi-micro Mettler analytical balance (model HL52). From the resulting concentration, the theoretical carbon concentration of each standard was calculated. The CO_2-free water was prepared by boiling ASTM Type I water for one hour; upon cooling, the boiling vessel was connected to a series of three drying tubes containing calcium chloride, Ascarite, and soda lime. The cooled water was acidified to pH 3 to minimize the uptake of atmospheric CO_2. This procedure precluded the need to purge samples prior to analysis for DOC and therefore minimized the possibility of loss of carbon from volatilization; the TOC and DOC of these standards were therefore equivalent. Standard solutions and diluted samples were stored at 4 °C in 25-mL glass scintillation vials with Teflon-lined screw caps. Ten single-operator replicate injections of CO_2-free water (blanks) were analyzed on each instrument to determine the background contribution during a 5-minute analysis time. Ten single-operator replicates of each standard were then analyzed for TDC (in this instance DOC) concentration on each carbon analyzer.

Samples of nine oil shale process wastewaters (Table I) were filtered (0.4-µm pore-diameter polycarbonate membranes, Bio-Rad Laboratories, Richmond, CA) under pressure and diluted to yield concentrations of

approximately 500 mg-C/L for TDC and DOC analyses. These samples were stored in a manner identical to the standards. Samples for direct DOC analysis were acidified with concentrated sulfuric acid (100 µL acid per 10.00 mL of sample) and purged for 10 minutes with high purity helium (60 cm^3/min). This represents less than a one-percent dilution error, and the final DOC values were not corrected. It may be important to note that the procedural order (i.e., filtration, dilution, and acidification) and the rate of acidification may affect the carbon concentration of a sample. The appropriate blank value for each system was determined by the method previously described. Ten single-operator replicates of each retort water sample were analyzed on each system for both TDC and direct DOC.

Each analyzer was interfaced with a programmable printing calculator (Hewlett-Packard, model HP 97S) which monitored the coulometer output at 15-second intervals. Values for the system blank and sample dilution were stored in the calculator memory. The DOC value recorded after the 5-min analysis time was subjected to a stability test prior to print-out. This test compared the final value with the value that was recorded 15 seconds earlier. If the difference in values was greater than 1%, the data-acquisition loop was reentered and a subsequent value obtained and tested for stability. When the stability test was satisfied, the final value (minus the system blank and multiplied by the sample dilution factor) was automatically printed.

Samples of each retort water were also analyzed for DIC concentration (10 replicates). The analysis time for DIC determinations was 3 minutes and the data were manipulated as described above. The mean DIC values were subtracted from the respective mean TDC values for each retort water; this yielded an indirect DOC value for comparison with the direct DOC determination. All statistical analyses were based on the appropriate sections in Sokal and Rohlf (1969) and Rohlf and Sokal (1969).

Detailed operating protocols for all instruments used in the comparison study are appended.

RESULTS AND DISCUSSION

Pure Compounds: Recovery and Reproducibility Comparison Study

The theoretical concentrations and the observed recoveries for the high-temperature combustion of pure compound solutions are presented in Table II. Complete recoveries were obtained for all compounds except pyridine (95%). The degree and position of alkyl substitution for the N-heterocycles did not affect the recoveries. The relative standard deviations (rsd) were less than 1% for most compounds, and did not exceed 3% for any compound. Recovery of the potassium acid phthalate standards deviated slightly from linearity at the lowest concentration (100 mg-C/L). With increasing concentrations of acid phthalate standards, the precision of recovery increased.

Ultraviolet-enhanced peroxydisulfate oxidation resulted in complete recoveries for the majority of pure compounds tested; acetonitrile and cyanuric acid, however, were resistant to oxidation (Table III) as reported by others (Takahashi et al., 1981; Dohrmann-Envirotech, 1981). The recovery of pyridine (95%) was identical to that for the high-temperature system; this may indicate that the pyridine contained impurities that reduced its actual concentration. The quantitation of acetonitrile was incomplete after the five-minute analysis period; higher recoveries could have been obtained by increasing the analysis time. Cyanuric acid, an s-triazine, was completely resistant to UV-persulfate oxidation, regardless of the analysis time. Similar findings were reported by the manufacturer of the UV reactor for cyanuric acid and melamine (Dohrmann-Envirotech, 1981). It is not known whether other triazines present a similar problem, but these compounds have not been reported in oil shale process waters. The accuracy and precision of sample recoveries for the UV-persulfate

oxidation system were in general slightly lower than those achieved by high-temperature combustion. With the exception of cyanuric acid, the relative standard deviations for sample recoveries were less than 2% for most samples, and did not exceed 4%. The UV-persulfate system was slightly more accurate, however, than the high-temperature system for the recovery of acid phthalate standards; the UV-persulfate system also exhibited a small deviation from linearity at the lowest concentration.

The close agreement between analyzers for the recovery of all the pure compounds, except cyanuric acid, is illustrated in Figure 5. The pattern of small deviations above and below 100 percent recovery is similar for both analyzers; this is probably the result of impurities in the stock reference compounds. The ranges of percent recoveries suggest that the high-temperature analyzer was slightly more precise.

To determine if the observed differences in sample recoveries were significant, a two-way analysis of variance (anova) was conducted. The calculated F-value (F_s) for the variability between analyzers was less than 1, which was less than the critical F-value (F_α) of 4.49 at $\alpha = 0.05$. Therefore, there was no significant difference between carbon analyzers for the recovery of carbon from solutions of pure compounds.

Process Wastewaters: TDC and DOC Reproducibility Comparison Study

The values obtained from each carbon analyzer for TDC, DIC, and direct and indirect DOC concentrations in nine oil shale process wastewaters are presented in Table IV. There was close agreement between the two systems for TDC and DOC determinations for each water; for a given process water, the difference between analyzers (each labeled "a" or "b" in Table IV) for TDC or direct DOC was less than the maximum of 5% (Oxy-6 gas condensate TDC). For most of the paired values, the value was higher for the UV-persulfate unit. Since high-temperature combustion techniques are generally assumed to give complete recovery of carbon, even though there is no definitive means of proving the completeness of mineralization (Gershey et al., 1979), it can therefore be concluded from these results that UV-enhanced persulfate oxidation of oil shale process waters yields complete oxidation of dissolved organic material. If compounds resistant to UV-persulfate oxidation were present in retort wastewaters, their concentrations were too low to significantly affect the overall recovery of carbon.

In contrast to the standard solutions, ultraviolet-enhanced persulfate oxidation was possibly more precise than the high-temperature system for the recovery of TDC and DOC in the wastewaters. This difference was slight, however, as rsd values for the recovery of TDC and DOC by either analyzer were less than 3% and generally less than 2%. To determine if a significant difference existed between carbon analyzers for the recovery of TDC, a two-way anova was conducted on the square root-transformed data. For the variability between analyzers, $F_s < F_\alpha$ ($4.88 < 5.32$), at $\alpha = 0.05$. Therefore, there was no significant difference between analyzers for TDC recovery. There was a significant interaction effect between analyzers and wastewaters, $F_s > F_{.05}$ ($3.99 > 1.94$), but the results of Tukey's test indicated that an insignificant portion was due to nonadditive effects, $F_s < F_{.05}$ ($0.21 < 5.59$), and therefore did not violate the assumptions of the anova model. The interaction between treatments (i.e., between wastewaters and analyzers) obviously resulted from the wide range in TDC values between wastewaters and was therefore disregarded.

A two-way anova was also conducted on the square root-transformed DOC data with similar results. There was no significant difference between carbon analyzers for the quantitation of DOC: $F_s < F_{.05}$ ($0.98 < 5.32$). The interaction term was significant but additive, and therefore did not violate the assumptions of the statistical model.

For each carbon analyzer, the direct and indirect DOC data for the nine process waters (Table IV) were also compared by a two-way anova on the

log-transformed values. There was no significant difference between direct DOC and indirect DOC measurements for either high-temperature combustion or UV-persulfate oxidation: $F_s<1<F_{.05}$ (5.59) for both anova's. The purging of samples for direct DOC analysis therefore did not appear to remove measurable quantities of volatile organic carbon compounds nor did the acidification step result in noticeable loss of organic species by precipitation. This is in agreement with the results from indirect versus direct carbon determinations on oil shale wastewaters reported by Fox et al. (1980).

It should be noted, however, that the percentage differences between direct and indirect DOC (Table IV) do exhibit certain trends. Although the only instance in which a direct DOC was more than three percent lower than an indirect DOC was that of Omega-9 retort water (minus 5% and 10% for high-temperature and UV-persulfate, respectively), three waters (150-Ton, T.V., and Rio Blanco Sour) gave direct DOC values that were 2 to 11 percent higher than their respective indirect DOC values. Oxy-6 gas condensate gave an anomalous direct DOC value that was 20 percent greater than the indirect DOC when determined by high-temperature combustion.

The discrepancies between some of the paired direct and indirect DOC values possibly resulted from problems with determining DIC values required for calculation of indirect DOC. TDC values for S-55, Omega-9, 150-Ton, and Oxy-6 gas condensate (Table IV) were 14, 26, 31, and 40 percent lower, respectively, than values from earlier analyses. There was agreement, however, for DOC values between data sets from different days, indicating that the TDC discrepancies resulted from variability in DIC concentrations. Although the rsd's for DIC were less than 2% (Table IV), several of the process waters exhibited TDC values which were lower than values obtained in previous analyses. The following are offered as possible origins to this problem: (i) Samples containing more DIC than 1000 mg-C/L must be diluted prior to determination of DIC. Sodium carbonate standards of 1000 mg-C/L routinely gave 95 percent recovery, whereas standards diluted from the same stock gave 100 percent recovery. It is unknown whether this was a problem with inadequate acidification/purging or with inefficient absorption of the CO_2 by the coulometer solution. The latter was not a problem, however, when the same amount of CO_2 was generated by the high-temperature or UV-persulfate units. (ii) Certain samples (e.g., Oxy-6 gas condensate, S-55, Omega-9, and 150-Ton) yielded significantly lower TDC values when diluted and stored (4 ^{o}C) for more than one week. It is not known whether storage of these diluted samples under headspace would result in uptake or loss of CO_2, but the former would seem more likely for these alkaline waters. (iii) Certain samples (e.g., Paraho) would not yield stable DIC values on particular days. This problem seemed to be related to gross interference by other gases that evolved during acidification/purging.

The number of problems that have been encountered with the DIC determinations on oil shale wastewaters is surprising, and this method requires further validation. For this reason, we recommend that DOC be determined directly. An alternative route to DIC quantitation that deserves investigation is by the use of the photochemical reactor with the UV-lamp turned off. This would preclude the need for the Coulometrics DIC unit, although it may be necessary to replace the acidic persulfate reagent with a nonoxidizing acid (e.g., dilute perchloric or sulfuric acid).

The statistical analyses of data from the comparison study indicated that no significant difference existed between the two carbon analyzers for the precision and accuracy of DOC recoveries from pure compounds, or for the quantitation of TDC and DOC in retort wastewaters. Since the UV-persulfate system gave incomplete recoveries for two of the 17 pure compounds analyzed, use of this oxidation procedure for the analysis of waters other than those reported should be preceded by a similar validation study. The routine determination of direct DOC should always be validated by indirect DOC measurements. Incomplete

recovery of cyanuric acid may indicate an inability to completely oxidize other symmetrical triazines containing electron-donating substituents (e.g., melamine).

Some important qualitative differences did exist in the performance and operation of the analyzers. The syringe injection method and the downtime from exhausted packing material and deteriorated combustion tubes severely hampered the routine use of the high-temperature unit. Following the DOC analyses of the pure compounds and retort wastewaters in the study reported here (approximately 320 sample injections), replacement of the combustion tube was necessary. Symptoms of the malfunctioning tube were an increased system blank and incomplete recoveries of acid phthalate standards. The calibration of the constant rate syringe was easily disturbed during use and required frequent checking. When calibrated according to the manufacturer's instructions, the actual volume delivered was never within several microliters of 200 µL; this necessitated different volume-correction terms for all the reported data.

The design of the UV-persulfate oxidation/coulometric titration carbon analyzer circumvented these problems. There was a minimum of downtime associated with the UV-persulfate reactor, and maintenance was limited to replacement of worn pump tubing and replenishment of persulfate reagent. The 200-µL sample loop required flushing with at least 10 loop-volumes of sample to eliminate the dilution effect of the persulfate reagent which had flushed the previous sample from the loop. If large sample volumes (e.g., 5 mL) are not available, a septum injection system (Dohrmann P/N 880-034), used in conjunction with a gas-tight syringe, could easily be installed for sample introduction. The loop injector has the main advantages of ease of use, increased precision, and reduction of intersample preparation time; it can also be easily automated.

A cost comparison of the UV-persulfate system and the Coulometric high-temperature total carbon analyzer shows that the UV-persulfate system ($8,526) is slightly less expensive that the Coulometrics analyzer ($9,200). The parts for the photochemical system include: UV-lamp ($212), reactor body and cap ($366), transformer ($147), injection value ($90), 4-channel peristaltic pump ($975), syringe ($28), miscellaneous electrical parts and plumbing ($408), and coulometric titrator ($6300). The photochemical system is significantly less expensive with regard to downtime, supplies, and maintenance costs. Routine annual supplies and maintenance costs include potassium persulfate ($70), Viton pump tubes ($200), and UV lamp ($212; assuming at most one per year) compared with combustion tubes ($2,000; assuming about one per month) and precombustion tubes ($250) for the high-temperature system.

Based on recoveries of the potassium acid phthalate standards (Tables II and III), it appeared that the operation of both analyzers was best at higher carbon concentrations (>500 mg/L); this affords an advantage to either system for the analysis of oil shale process waters. We have concluded, however, that the UV-persulfate oxidation/coulometric titration carbon analyzer provided improved performance over the high-temperature combustion/coulometric detection system for analysis of oil shale wastewaters on the basis of accuracy and precision of sample recovery, ease of operation, downtime, and maintenance costs.

REFERENCES

Armstrong, F.A.J.; Williams, P.M.; Strickland, J.D.H.
"Photo-oxidation of Organic Matter in Sea Water by Ultra-Violet Radiation, Analytical and other Applications", Nature (London) **1966**, 211, 481-3.

Annual Book of ASTM Standards, Part 31, Water; American Society for Testing and Materials: Philadelphia, PA, **1977**, (1110 pp.).

ASTM
"Standard Method of Test for Total and Organic Carbon in Water: Oxidation-Coulometric Detection", D-4129 (in press).

Baker, C.D.; Bartlett, P.D.; Farr, I.S.; Williams, G.I.
"Improved Methods for the Measurement of Dissolved and Particulate Organic Carbon in Fresh Water and Their Application to Chalk Streams", Freshwater Biol. **1974**, 4, 467-81.

Beckman Instruments, Inc.
"Models 864/865 Non-Dispersive Infrared Analyzers", Beckman Instruments, Inc., Process Instuments, Bulletin 4201A: Fullerton, CA, **1980** (11 pp.).

Blom, L.; Edelhausen, L.
"Direct Titration of Carbon Dioxide", Anal. Chim. Acta **1955**, 13, 120-8.

Collins, K.J.; Williams, P.J. le B.
"An Automated Photochemical Method for the Determination of Dissolved Organic Carbon in Sea and Estuarine Waters", Mar. Chem. **1977**, 5, 123-41.

Cooney, D.O.
"Interference of Contaminants from Membrane Filters in Ultraviolet Spectrophotometry", Anal. Chem. **1980**, 52, 1068-71.

Danckwerts, P.V.; McNeil, K.M.
"The Absorption of Carbon Dioxide into Aqueous Amine Solutions and the Effects of Catalysis. Part I: Theoretical Treatment of Equilibria and Absorption Kinetics", Trans. Inst. Chem. Eng. **1967**, 45, 32-49.

Danckwerts, P.V.; Sharma, M.M.
"The Absorption of Carbon Dioxide into Solutions of Alkalis and Amines (with some Notes on Hydrogen Sulphide and Carbonyl Sulphide)", Chem. Eng. (London) **1966**, Rev. Ser. 2, 244-80.

Daughton, C.G.; Jones, B.M.; Sakaji, R.H.
"Analytical Problems in Monitoring Retort Water Treatment", in Energy and Environment Division 1980 Annual Report, Lawrence Berkeley Laboratory, **1981**, LBL-11989.

Daughton, C.G.; Jones, B.M.; Sakaji, R.H.
"Rapid Fractionation of Oil Shale Wastewaters by Reverse-Phase Separation", LBL-SEEHRL Oil Shale Waste Treatment Program, February **1982**, Lawrence Berkeley Laboratory, LBID-485 (17 pp.).

Daughton, C.G.; Jones, B.M.; Sakaji, R.H.; Thomas, J.F.
"Analytical Methods for Quantitating Performance of Oil Shale Wastewater Treatment", in Energy and Environment Division 1981 Annual Report, Lawrence Berkeley Laboratory, **1982**, LBL-13500.

Delahay, P.
Instrumental Analysis; The Macmillan Company: New York, NY, **1962**; p 225.

Dohrmann-Envirotech
Equipment Manual, DC-80 Total Organic Carbon Analyzer System, 3rd ed. Dohrmann Divison, Envirotech Corp.: Santa Clara, CA, July **1981**, P/N 915-121.

Ewing, G.W.
"Titrate with Electrons", Am. Lab. **1981**, 13(6), 16-22.

Fox, J.P.; Farrier, D.S.; Poulson, R.E.
"Chemical Characterization and Analytical Considerations for an In Situ Oil Shale Process Water", Laramie Energy Technology Center, **1978**, LETC/RI-78/7.

Fox, J.P.; Jackson, D.E.; Sakaji, R.H.; Daughton, C.G.; Selleck, R.E.
"Spent Shale as a Control Technology for Oil Shale Retort Water", in Energy and Environment Division 1979 Annual Report, Lawrence Berkeley Laboratory, 1980, LBL-10746.

Gershey, R.M.; Mackinnon, M.D.; Williams, P.J. le B.; Moore, R.M.
"Comparison of Three Oxidation Methods Used for the Analysis of the Dissolved Organic Carbon in Seawater", Mar. Chem. 1979, 7, 289-306.

Goulden, P.D.; Brooksbank, P.
"Automated Determinations of Dissolved Organic Carbon in Lake Water", Anal. Chem. 1975, 47, 1943-6.

House, D.A.
"Kinetics and Mechanism of Oxidations by Peroxydisulfate", Chem. Rev. 1962, 62, 185-203.

Huffman, E.W.D., Jr.
"Performance of a New Automatic Carbon Dioxide Coulometer", Microchem. J. 1977, 22, 567-3.

Jeffery, P.G.; Kipping, P.J.
Gas Analysis by Gas Chromatography; Pergamon Press: New York, NY, 1972; pp 65-6.

Jones, B.M.; Langlois, G.W.; Sakaji, R.H.; Daughton, C.G.
"Ozonation and UV Irradiation: Effect on Oil Shale Wastewater Biorefractory Organic Solutes", LBL-SEEHRL Oil Shale Waste Treatment Program, May 1982, Lawrence Berkeley Laboratory, LBID-549 (27 pp.).

Jones, B.M.; Sakaji, R.H.; Daughton, C.G.
"Physicochemical Treatment Methods for Oil Shale Wastewater: Evaluation as Aids to Biooxidation", Fifteenth Oil Shale Symposium Proceedings; Gary, J.H., Ed.; Colorado School of Mines: Golden, CO, 1982; LBL-14666 (in press).

Laxen, D.P.H.; Chandler, I.M.
"Comparison of Filtration Techniques for Size Distribution in Freshwaters", Anal. Chem. 1982, 54, 1350-5.

Littlewood, A.B.
Gas Chromatography; Academic Press: New York, NY, 1962; pp 288-94.

Menzel, D.W.; Vaccaro, R.F.
"The Measurement of Dissolved Organic and Particulate Carbon in Seawater", Limnol. Oceanog. 1964, 9, 138-42.

Naik, M.N.; Jackson, R.B.; Stokes, J.; Swaby, R.J.
"Microbial Degradation and Phytotoxicity of Picloram and other Substituted Pyridines", Soil Biol. Biochem. 1972, 4, 313-23.

Raphaelian, L.A.; Harrison, W.
"Organic Constituents in Process Water from the In-Situ Retorting of Oil from Oil-Shale Kerogen", Argonne National Laboratory Report, February 1981, ANL/PAG-5, (33 pp.).

Rheodyne Inc.
"HPLC Sample Injectors: Design Characteristics and Accuracy/Precision Capabilities", Rheodyne, Inc.: Berkeley, CA, Technical Notes, Sept. 1979, 1 (8 pp.).

Rohlf, J.F.; Sokal, R.R.
Statistical Tables; W.H. Freeman and Co.: San Francisco, CA, 1969; 253 pp.

Sokal, R.R.; Rohlf, J.F.
Biometry; W.H. Freeman and Co.: San Francisco, CA, 1969; 776 pp.

"Standard Methods for the Examination of Water and Wastewater", 15th ed.; American Public Health Association; American Water Works Association; Water Pollution Control Federation: Washington, D.C., 1981, pp 471-5.

Takahashi, Y.
"A Review of Analysis Techniques for Organic Carbon and Organic Halide in Drinking Water", Proceedings of the Conference on Practical Application of Adsorption Techniques in Drinking Water, 1979 (preprint).

Takahashi, Y.; Martin, J.T.; Harper, F.C.
Advances in Total Organic Carbon Analysis for High Chloride Water Samples, Dohrmann Division, Xertex Corp.: Santa Clara, CA, Oct. 1981.

Torpy, M.F.; Raphaelian, L.A.; Luthy, R.G.
"Wastewater and Sludge Control-Technology Options for Synfuels Industries, Vol. 2: Tar-Sand-Combustion Process Water -- Removal of Organic Constituents by Activated-Sludge Treatment", Argonne National Laboratory Report, November 1981, ANL/ES-115, Vol. 2 (53 pp.).

Van Hall, C.E.; Barth, D.; Stenger, V.A.
"Elimination of Carbonates from Aqueous Solutions prior to Organic Carbon Determination", Anal. Chem. 1965, 37, 769-71.

Van Hall, C.E.; Safranko, J.; Stenger, V.A.
"Rapid Combustion Method for the Determination of Organic Substances in Aqueous Solutions", Anal. Chem. 1963, 35, 315-9.

Willard, H.H.; Merritt, L.L., Jr.; Dean, J.A.
Instrumental Methods of Analysis, 5th ed.; D. Van Nostrand Company: New York, NY, 1974; pp 528-9, 702.

Williams, P.M.
"The Determination of Dissolved Organic Carbon in Seawater: A Comparison of Two Methods", Limnol. Oceanog. 1969, 14, 297-8.

Wölfel, P.; Sontheimer, H.
"Ein neues Verfahren zur Bestimmung von organisch gebundenem Kohlenstoff im Wasser durch photochemische Oxidation" Vom Wasser 1974, 43, 315-25 (Ger.).

Zierdt, C.H.
"Adherence of Bacteria, Yeast, Blood Cells, and Latex Spheres to Large-Porosity Membrane Filters" Appl. Environ. Microbiol. 1979, 38, 1166-72.

Table I. Origins of Oil Shale Process Wastewaters Used in the Comparison Study

process water	water type	retort/process	shale source	retorting atmosphere	max. retorting temp. (°C)	operator/ collection date
		Field in-situ Retorts				
Oxy-6 RW	RW[1]	retort #6/MIS[2]	Logan Wash, CO	air/steam	unknown[3]	Occidental Oil Shale Inc., 1979
Oxy-6 GC	GC[4]	retort #6/MIS	Logan Wash, CO	air/steam	unknown	Occidental Oil Shale Inc., 1979
Geokinetics	RW	retort #9/hor. TIS[5]	Book Cliff, UT	air	unknown	Geokinetics, Inc., 1978
Omega-9	RW	site #9/hor. TIS	Rock Springs, WY	air	unknown	LETC, 1976
Rio Blanco Sour	RW	retort #0/MIS	Tract C-a, CO	air/steam	unknown	Rio Blanco Oil Shale Co., 1980
		Field Surface Retorts				
Paraho	RW	Paraho direct mode	Anvil Points, CO	air/ recycle gas	750	Development Engineering, Inc., 1977-1978
TV	GC & RW	near-term commercial	confidential	unknown	unknown	confidential
		Simulated in-situ Retorts				
150-Ton	GC & RW	LETC 150-ton, run 13	Anvil Points, CO	air	800	LETC, 1976
S-55	GC & RW	LETC 10-ton, run 55	Anvil Points, CO	air/steam	650	LETC, 1978

[1] retort water. [2] modified in situ. [3] retorting temperatures for MIS field retorts are not accurately known; localized temperatures may reach 1000 °C. [4] gas condensate. [5] horizontal true in situ.

Table II. Recovery Study: High-Temperature Combustion Carbon Analyzer

Compound	DOC Concentration (mg-C/L) theoretical (a)	observed[1] (b)	(b/a) X 100	rsd[1]
potassium acid phthalate	100.0	104.3	104.3	1.39
potassium acid phthalate	500.0	506.5	101.3	0.54
potassium acid phthalate	1000.0	1002.6	100.3	0.50
phenol	606.8	606.0	99.9	0.61
acetonitrile	479.0	465.6	97.2	2.79
3,5-dimethylpyrazole	501.5	502.3	100.2	0.45
pyridine	476.3	454.1	95.3	0.64
2-methylpyridine	435.2	434.1	99.7	0.81
4-methylpyridine	455.3	453.5	99.6	0.69
2,4-dimethylpyridine	437.5	435.7	99.6	0.66
2,6-dimethylpyridine	431.6	430.4	99.7	1.09
2,4,6-trimethylpyridine	420.7	424.3	100.8	0.73
2,3,6-trimethylpyridine	416.7	430.4	103.3	0.58
2-ethylpyridine	443.4	441.7	99.6	0.92
3-ethylpyridine	447.8	449.3	100.3	0.69
3-ethyl-4-methylpyridine	472.1	503.8	106.7	0.21
2-*n*-propylpyridine	435.4	441.1	101.3	0.55
2-methylpyrazine	502.5	503.6	100.2	1.77
cyanuric acid	252.2	253.5	100.5	1.05

[1] n=10 for each standard solution

Table III. Recovery Study: UV-Persulfate Carbon Analyzer

Compound	DOC Concentration (mg-C/L) theoretical (a)	observed[1] (b)	(b/a) X 100	rsd[1]
potassium acid phthalate	100.0	102.8	102.8	3.72
potassium acid phthalate	500.0	503.3	100.7	0.70
potassium acid phthalate	1000.0	999.4	99.9	0.44
phenol	606.8	602.9	99.4	0.90
acetonitrile	479.0	426.3	89.1	3.44
3,5-dimethylpyrazole	501.5	502.5	100.2	0.70
pyridine	476.3	454.5	95.4	0.65
2-methylpyridine	435.2	438.9	100.8	1.01
4-methylpyridine	455.3	447.5	98.3	1.29
2,4-dimethylpyridine	437.5	434.2	99.3	1.16
2,6-dimethylpyridine	431.6	429.9	99.6	0.88
2,4,6-trimethylpyridine	420.7	421.7	100.2	0.66
2,3,6-trimethylpyridine	416.7	430.6	103.3	0.80
2-ethylpyridine	443.4	436.3	98.4	1.66
3-ethylpyridine	447.8	453.1	101.2	1.38
3-ethyl-4-methylpyridine	472.1	495.7	104.9	0.71
2-*n*-propylpyridine	435.3	435.2	100.0	0.87
2-methylpyrazine	502.5	500.0	99.5	0.68
cyanuric acid	252.2	5.4	2.2	123

[1] n=10 for each standard solution

Table IV. Comparison of Analyzers: Quantitation of Direct/Indirect Organic Carbon in Oil Shale Process Waters

	Carbon Concentration[1] (mg/L)							
Wastewater	DOC (direct)	rsd	DOC (indirect) (TDC-DIC)	% dif[2]	TDC	rsd	DIC	rsd
Paraho							209.8	1.3
a (high temperature)	41809	1.4	43205	-3.3	43415	0.55		
b (UV-persulfate)	42066	1.1	42470	-1.0	42680	0.66		
150-Ton							1932	1.8
a	3147	0.58	2925	7.1	4857	0.44		
b	3259	0.46	3128	4.0	5060	0.53		
Oxy-6 retort water							984.9	1.0
a	2829	0.80	2832	-0.1	3817	1.2		
b	2942	0.40	2967	-0.9	3952	0.54		
Geokinetics							1994	0.67
a	1627	1.1	1680	-3.3	3674	1.3		
b	1656	0.55	1688	-1.9	3682	0.45		
T.V.							824.8	0.54
a	2651	0.23	2545	4.0	3370	0.59		
b	2726	0.61	2661	2.4	3486	0.97		
Oxy-6 gas condensate							2213	0.38
a	651.7	2.6	522.0	19.9	2735	0.63		
b	641.0	0.51	653.0	-1.9	2866	0.47		
S-55							339.5	1.6
a	2213	0.40	2256	-1.9	2595	1.8		
b	2285	0.34	2294	-0.4	2633	0.51		
Omega-9							1387	1.3
a	694.7	0.34	732.0	-5.4	2119	2.1		
b	718.4	0.44	787.0	-9.6	2174	0.29		
Rio Blanco sour							364.3	1.4
a	206.3	1.4	191.3	7.3	555.6	0.25		
b	207.0	1.3	183.8	11.2	548.1	0.47		

[1] mean of 10 single-operator replicates. [2] (direct DOC - indirect DOC)/direct DOC x 100.

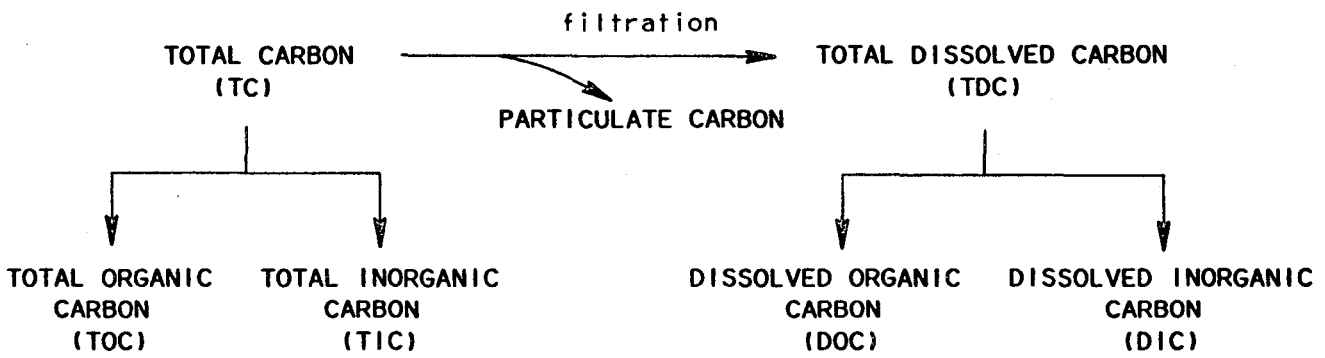

Figure 1. Terminology for carbon classifications used in carbon analysis.

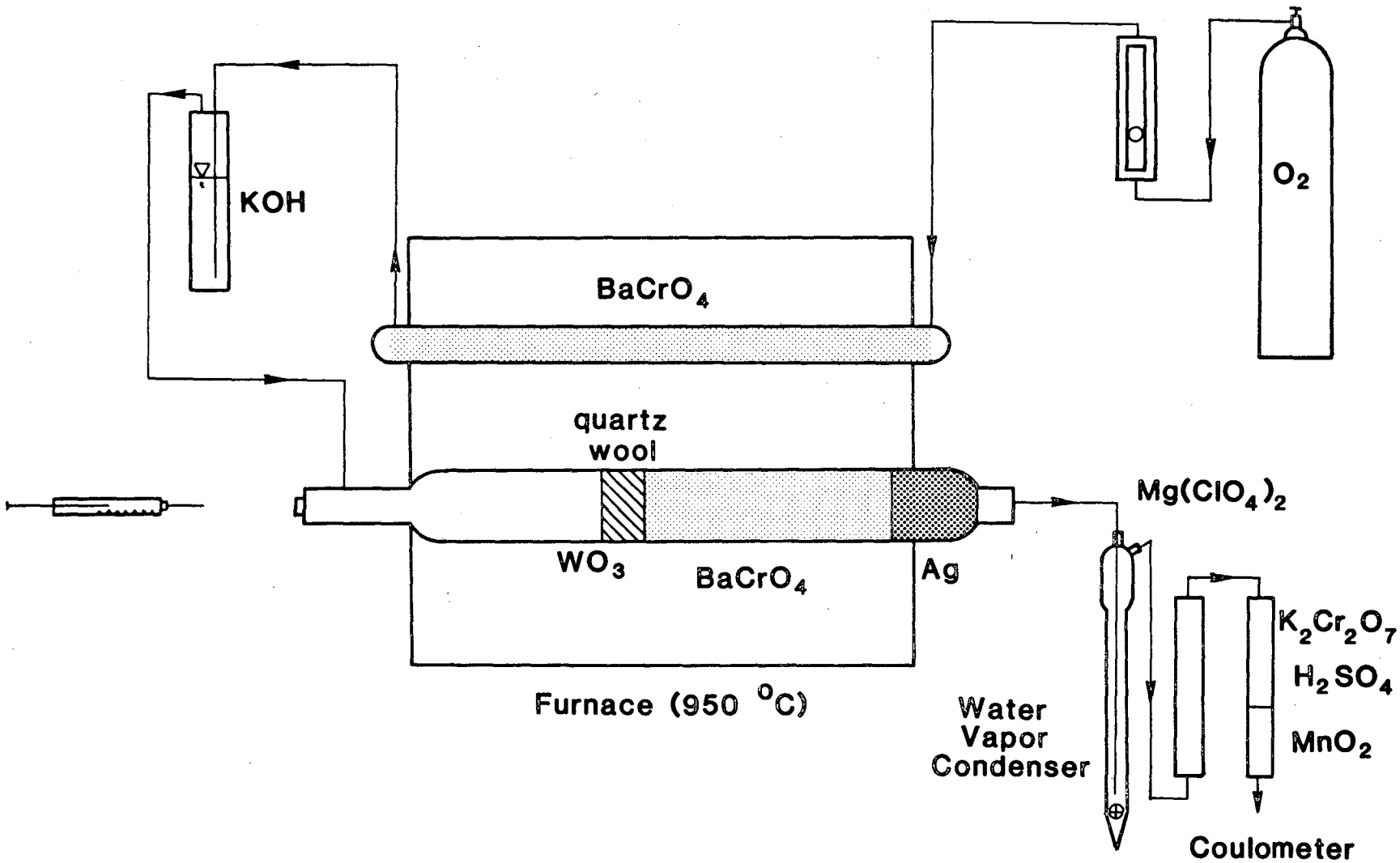

Figure 2. Schematic of Coulometrics high-temperature combustion apparatus.

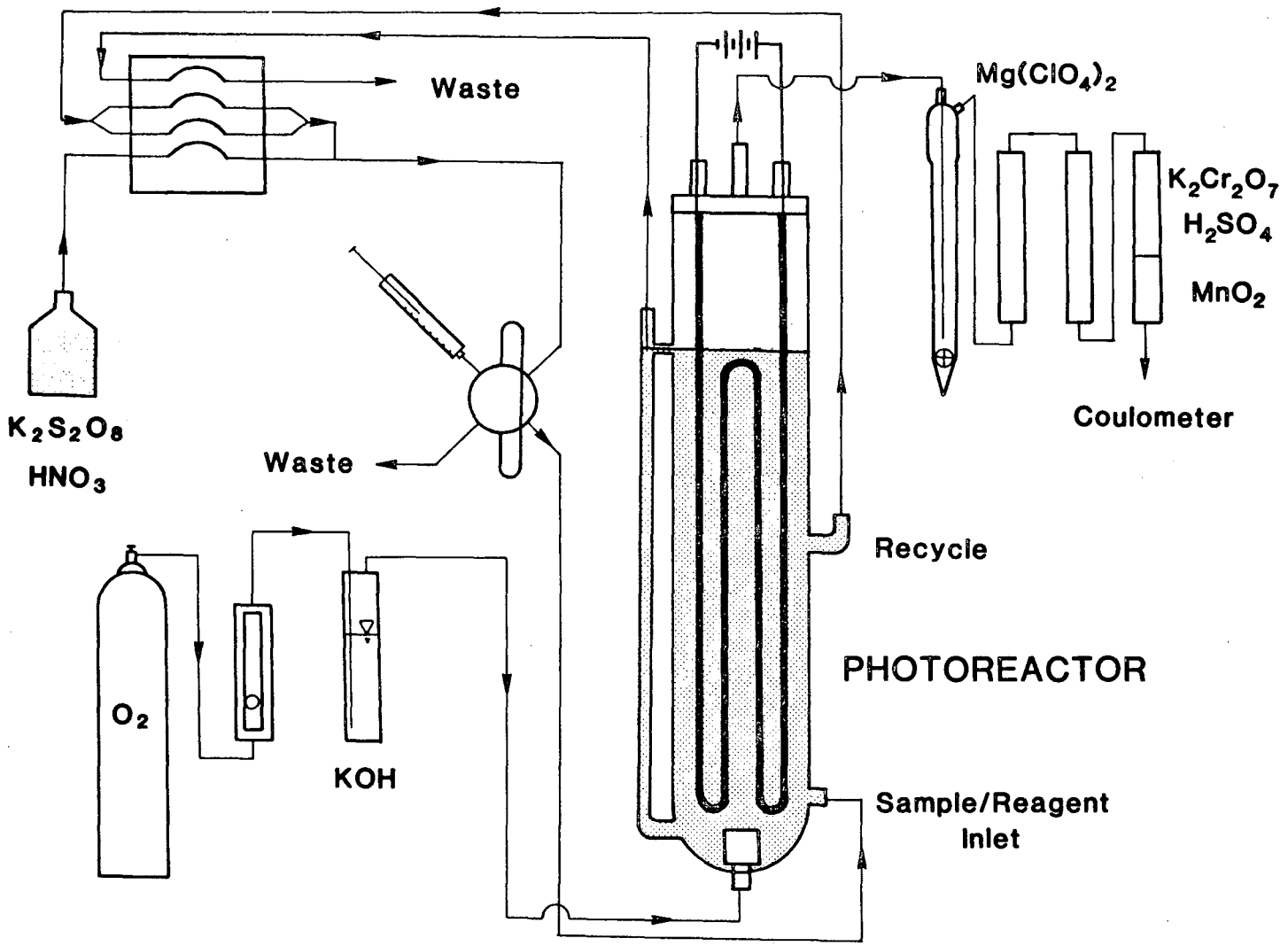

Figure 3. Schematic of UV-peroxydisulfate low-temperature oxidation apparatus.

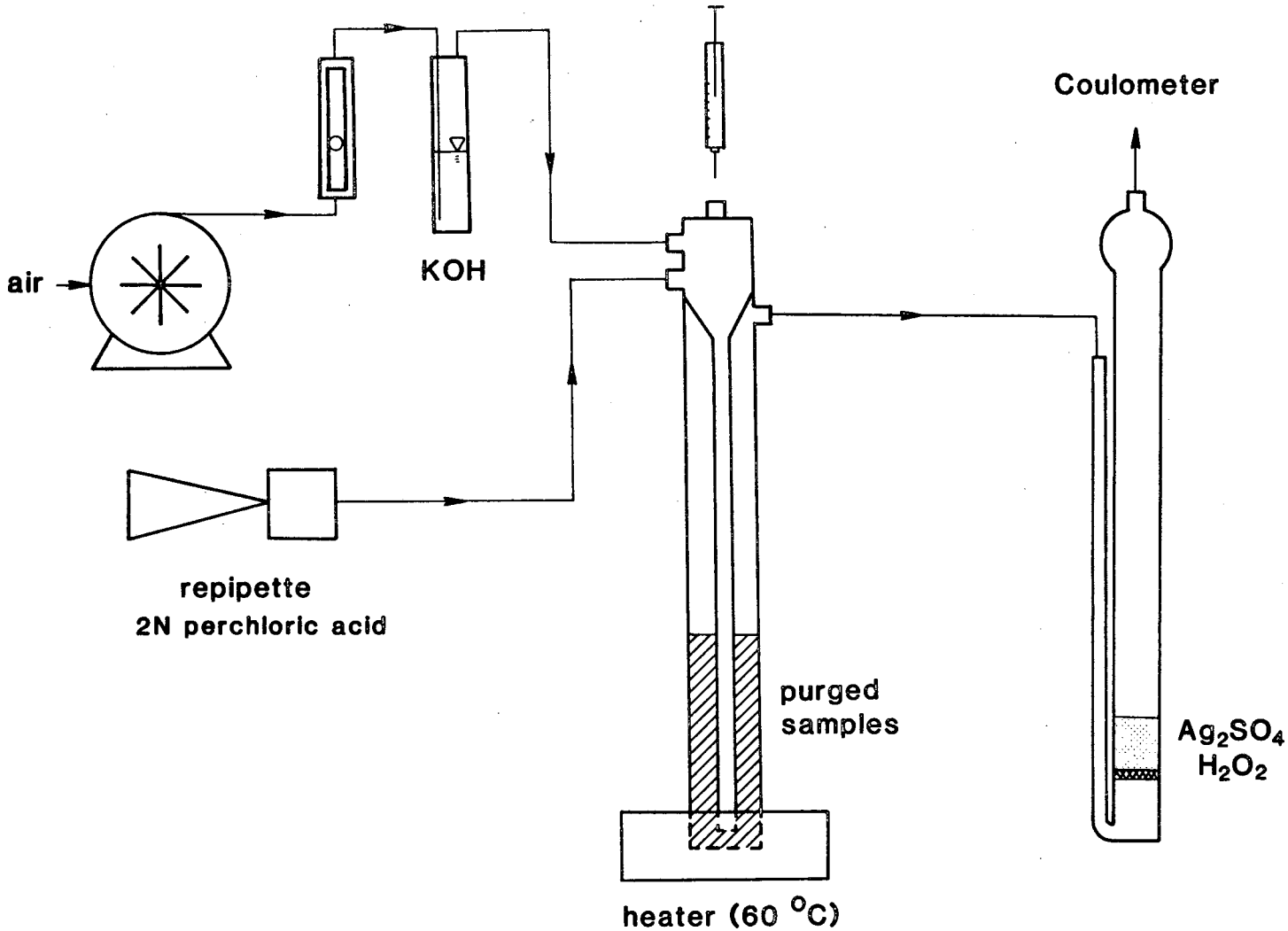

Figure 4. Schematic of Coulometrics acidification/purge apparatus for inorganic carbon.

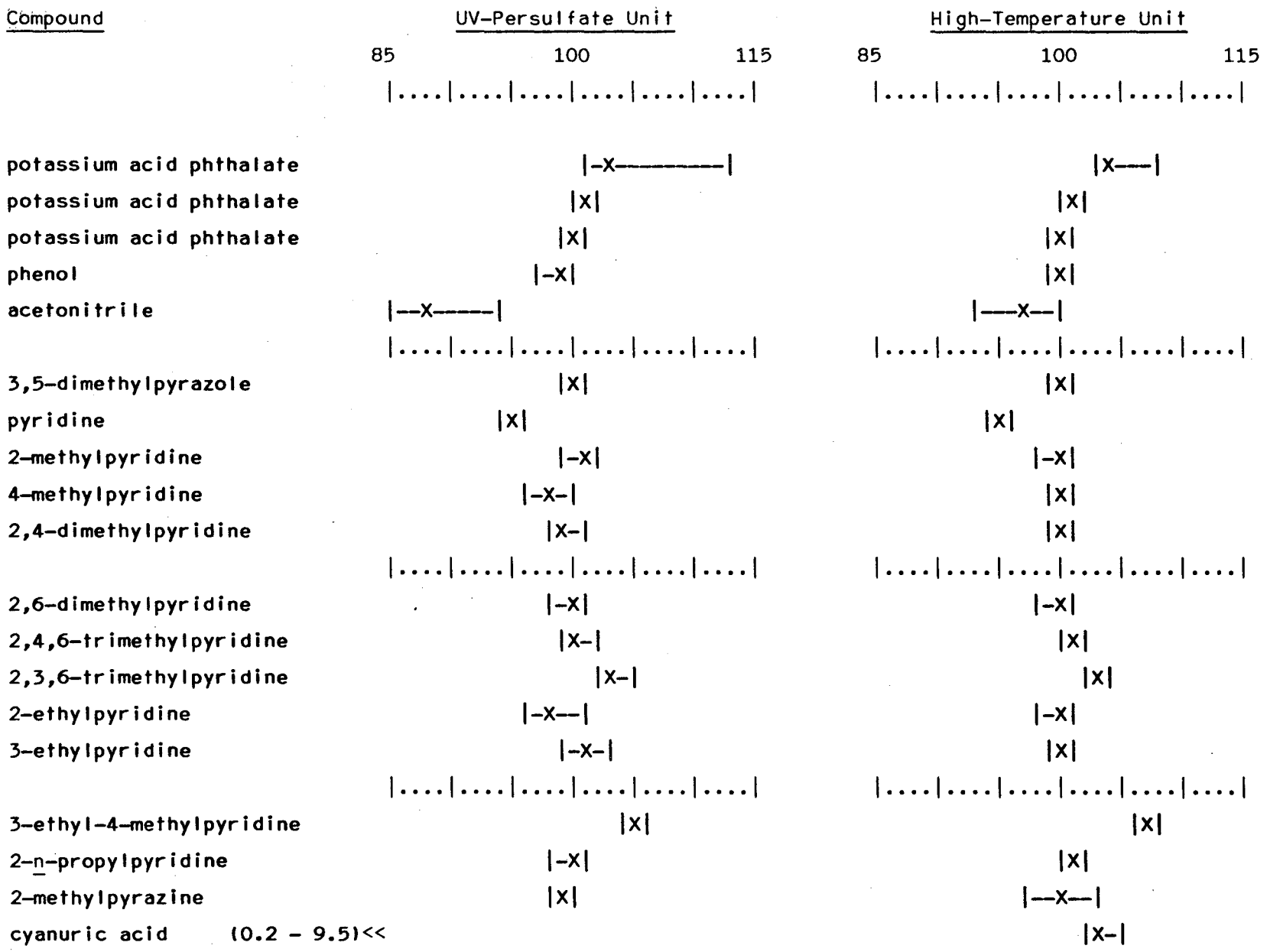

Figure 5. Comparison of percent recovery means (X) and ranges (---) for standard solutions; concentrations of compounds are identical to those presented in Tables II & III.

High-Temperature Combustion/Coulometric Titration

A. START-UP

1. Turn the combustion furnace temperature control knob to 950 °C. Allow 0.5 to 1 hour for the furnace to reach temperature.
2. Increase the oxygen flow rate to 100 cm^3/min.
   a. ensure that the oxygen delivery pressure is 15 psig.
   b. ensure that at least 500 psig of oxygen is in the cylinder.
   c. if foaming occurs in the KOH scrubber, add a small amount of ASTM Type I water to the KOH; if foaming persists, replace the contents with approximately 12 mL of fresh 45% KOH solution.
3. Repack the magnesium perchlorate scrubber. This scrubber is positioned directly after the burette water-trap.
   NOTE: Using the old, wetted packing could result in formation of a plug, increasing the back-pressure.
   a. wash out the old packing, rinse the scrubber tube with ASTM Type I water, then air- or oven-dry the tube.
   b. repack and reconnect the tube.
4. Check the acid dichromate/manganese dioxide scrubber for exhaustion. This scrubber is positioned after the magnesium perchlorate scrubber.
   a. the acid dichromate packing will change from yellow-orange (oxidized) to green-orange (reduced) as it becomes exhausted. This color change will be seen as a front progressing in the direction of gas flow. When almost all of the acid dichromate has changed color, the entire scrubber must be repacked.
   b. when the manganese dioxide packing is exhausted, it will change from black to dark brown; the entire scrubber must then be repacked.
5. Assemble the coulometer cell.
   a. fill the coulometer cell with 75 mL of coulometer solution.
   b. add the stir bar.
   c. position the rubber stopper on the coulometer cell such that the anode, cathode, and gas line face the back wall of the cell (that portion of the beaker containing the volume graduations).
   d. add 3 pellets of potassium iodide to the anode compartment.
   e. add anode solution to the anode compartment. The anode solution level should be slightly higher than that of the coulometer cell solution.
   f. place the silver anode in the anode compartment. Ensure that the tip of the silver anode is wetted by the anode solution.
   g. place the assembled coulometer cell in the cell holder of the instrument; the volume graduations should face the rear of the instrument.
   h. plug the anode (red) and cathode (black) wires into the coulometer.

   DO NOT TURN ON THE ELECTROLYSIS CURRENT.

   i. connect the coulometer cell gas line to the one-way valve in-line from the nitrogen oxide scrubber. Check that the stopcock on the burette water trap is open. (The gas flow must be diverted from the coulometer cell during adjustment of cell transmittance per step A.8).

6. Connect the HP 97S to the coulometer interface cable.
   a. turn on the HP 97S.
   b. with the calculator in the RUN mode, load the "background" program as per the user instructions (Appendix A).
7. Turn on the main power supply. Allow a warm-up period of several minutes.
8. Adjust the coulometer cell transmittance.
   a. rotate the coulometer cell until a maximum transmittance is obtained.
   b. adjust the transmittance to 100% using the "100% adjust" knob.
   c. close the stopcock on the burette water trap.
   d. check that the gas flow into the coulometer cell does not deflect the 100% transmittance setting. If a deflection occurs, reposition the gas line to eliminate this interference; open the burette stopcock and repeat steps a-d.

   NOTE: The gas line must be submerged in the coulometer solution.
9. Turn on the electrolysis current and initiate the background program.
   a. allow several minutes for the titration of endogenous CO_2 in the coulometer solution.
   b. following this initial titration, check the coulometer stability. A stable background count of 1.0 to 1.2 mg/L per minute should be obtained when the range plug is set to display mg/L. Stabilization may take as long as 30 minutes.

B. SAMPLE PREPARATION -- TOTAL DISSOLVED CARBON (TDC)
1. Filter all samples through a 0.4-µm pore diameter polycarbonate membrane filter.
2. Dilute sample filtrates with ASTM Type I water to yield TDC concentrations between 40 and 200 mg/L.
3. Prepare a TDC sample blank; a 10-mL aliquot of ASTM Type I water should be processed with the TDC samples.
4. Refrigerate samples until analysis time.

C. SAMPLE PREPARATION -- DISSOLVED ORGANIC CARBON (DOC)
1. Filter all samples through a 0.4-µm pore diameter polycarbonate membrane filter.
2. Dilute sample filtrates with ASTM Type I water to yield DOC concentrations between 40 and 200 mg/L.
3. Prepare a DOC sample blank; a 10-mL aliquot of ASTM Type I water should be processed with the DOC samples.
4. Acidify the blank and DOC samples with 0.10 mL concentrated sulfuric acid (Analytical Reagent grade) per 10 mL of sample. A positive displacement pipette or a repipette should be used.

   NOTE: Samples should have pH values of 2 after acidification.
5. Refrigerate samples until analysis time.

D. PURGING OF DOC SAMPLES
1. Open the helium cylinder valve and set the delivery pressure to 10 psig. The needle valve on the helium flow meter is preset to deliver 775 cm^3/min at 10 psig.
2. Rinse the glass capillaries by submersion in the vials of concentrated HCl, and wipe dry.

3. Submerge each capillary in a sample and purge for 10 minutes.
4. Remove the capillaries, wipe dry, and repeat steps 2-3 for all samples.
5. After all the samples have been purged, repeat step 2 and place the capillaries in a clean, dry vial.
6. Turn off the helium cylinder valve.
   NOTE: Purging should be conducted in an enclosed compartment to prevent deposition of acidic aerosols on equipment.

E. PREPARATION OF STANDARDS
   (NOTE: Use Analytical Reagent grade chemicals only).
1. Prepare a stock solution of potassium acid phthalate (DOC =1000.00 mg/L as C).
   a. weigh 1063.7 mg of dried potassium acid phthalate and quantitatively transfer to a 500-mL volumetric flask.
   NOTE: Glassware should be acid-washed.
   b. bring to volume with ASTM Type I water.
   c. acidify the standards as instructed in section C.4.
2. Prepare working standards of 50, 100, and 200 mg/L.
   NOTE: additional standard concentrations should be made if the sample DOC concentration is expected to be outside of this range.
   a. 50 mg/L : pipette 0.5 mL of stock solution into a 10-mL volumetric flask and bring to volume with ASTM Type I water.
   b. 100 mg/L : pipette 1.0 mL of stock solution into a 10-mL volumetric flask and bring to volume with ASTM Type I water.
   c. 200 mg/L : pipette 2.0 mL of stock solution into a 10-mL volumetric flask and bring to volume with ASTM Type I water.
   NOTE: Use air- or positive-displacement pipettes.
3. Prepare a stock solution of phenol for recovery determinations (DOC = 2371.7 mg/L as C).
   a. weigh 155.0 mg of phenol and quantitatively transfer to a 50-mL volumetric flask.
   b. bring to volume with ASTM Type I water.
   c. dilute this stock solution 1:10 with ASTM Type I water and acidify as instructed in section C.4 (DOC = 237.17 mg/L as C).
4. Prepare a stock solution of pyridine for recovery determinations (DOC = 1000 mg/L as C).
   a. dispense approximately 65 µL of pyridine into a tared 50-mL volumetric flask and record the exact weight.
   b. bring to volume with ASTM Type I water.
   c. acidify as instructed in section C.4.
   d. calculate the theoretical DOC of this solution:
      DOC (mg/L) = (15.18) x (mg pyridine added/0.050 L).
   e. dilute this stock solution 1:5 with ASTM Type I water (DOC = 200 mg/L as C).

F. SAMPLE ANALYSIS
1. Load the "Water Analysis" program into the HP 97S.
   a. turn off the coulometer main power.
   b. with the HP 97S in the RUN mode, run the program card through the HP 97S card reader.
   c. initiate the program as per the user instructions (Appendix B).

d. turn on the coulometer main power.

2. If the Hamilton constant rate carbon analyzer syringe is used, check that it is set and locked at 200 µL. Recheck frequently during sample analysis.
   NOTE: a sample injection volume of 200 µL is recommended; excessive injection volumes can result in damage to the quartz tube and are unsafe due to the combustive expansion of gases.
3. Rinse the syringe 10 times with the sample to be analyzed.
   a. insert the syringe needle into the sample injection port; ensure that the Luer fittings are seated.
   b. inject the sample and simultaneously initiate the sample program as per the user instructions (Appendix B).
   c. the syringe must remain in the injection port throughout the analysis; proper flushing by the oxygen will not occur if the port is not sealed.
   d. the suggested analysis time for each sample is 3 minutes.
   e. for replicates, rinse the syringe twice with the sample to be analyzed and repeat steps a-e.
   f. check the burette water trap. This trap should be emptied between analyses so that the gas line does not become submerged in the condensate. Collect the condensate in an acid-washed vial for later validation (i.e., by DOC) of complete combustion.
4. Repeat step 3 for each sample.
5. Samples should be analyzed in the following order:
   a. the sample blank; the mean DOC value from the blanks must be subtracted from the DOC value of each standard and sample. This calculation is performed automatically by the HP 97S "Water Analysis" program.
   b. the acid phthalate standards.
   NOTE: If standard recoveries deviate more than 5% from the theoretical values, check for the following in decreasing order of priority: accuracy of standard stock solution and standard dilutions; exhaustion of scrubbers; clogging of anode-cell glass frit; silver deposition on platinum wire cathode; condition of combustion tube; coulometer performance.
   c. the recovery standards (phenol and pyridine).
   d. the DOC samples.
   NOTE: if a large number of DOC samples is to be analyzed, the series of standards should be analyzed at intervals throughout the DOC analyses.
   e. upon completion of the DOC analyses, the series of standards and blanks should be reanalyzed.
   f. the collected condensate sample should also be analyzed for DOC concentration. A DOC value greater than the background count indicates carry-over of uncombusted carbon.

G. SHUT-DOWN
1. Turn off the HP 97S.
2. Remove the syringe and replace the end-plug over the sample injection port.
3. Reduce the furnace temperature to approximately 750 ^{o}C.
4. Reduce the oxygen flow rate to 40 cm^3/min.

5. Open the stopcock on the burette water trap.
6. Disassemble the coulometer cell.
   a. turn off the electrolysis current.
   b. turn off the main power.
   c. unplug the anode and cathode wires from the coulometer.
   d. disconnect the gas line at the one-way valve in-line between the coulometer cell and the nitrogen oxide scrubber.
   e. remove the coulometer cell from the coulometer.
   f. remove the silver anode, rinse with ASTM Type I water, and air-dry on a clean surface.
   g. remove the rubber stopper from the coulometer cell and rinse the anode cell with acetone -- ensure that no potassium iodide deposits remain in the anode cell. Using a vacuum source and the perforated serum stopper, draw a small volume of acetone through the fritted-glass end of the anode cell.
   h. rinse the exteriors of the anode, cathode, and gas line with ASTM Type I water and air-dry on a clean surface.
   i. rinse the coulometer cell and stir bar several times with ASTM Type I water and air-dry on a clean surface.

H. DATA REDUCTION
1. Calculate the mean value for each set of DOC replicates:
   a. $\bar{x}(DOC) = \Sigma(x_i - b)/n$
      where x_i = each data point in a set of replicates;
      b = the mean value of all DOC blank analyses
      n = the number of replicates per sample.
2. The HP 97S "Water Analysis" program automatically calculates $(x_i - b)$ X (dilution factor) for each data point. Therefore the mean for a set of replicates equals the sum of data outputs divided by the number of replicates (n).
3. Determine whether suspected outliers should be discarded.
   a. suspected outliers should be subjected to statistical analysis before being discarded (1).
   b. if an outlying value is known to be the result of a mechanical or operator error, it may be rejected without statistical verification.

I. MAINTENANCE
1. Record the appropriate information in the C-Analyzer Log Book, including:
   a. date and duration of usage.
   b. number of injections (retort water and total) and sample dilutions.
   c. symptoms of malfunctioning.
   d. repairs.
   e. initial all entries.

J. REFERENCES
1. ASTM
Annual Book of ASTM Standards, Part 31, Water; American Society for Testing and Materials: Philadelphia, PA, 1977; 1110 pp.

Prepared by: G.W. Langlois, B.M. Jones, R.H. Sakaji, and C.G. Daughton.

UV-Enhanced Persulfate Oxidation/Coulometric Titration

A. START-UP

NOTE: All chemicals are Analytical Reagent grade unless otherwise specified. The dipotassium salt of peroxydisulfuric acid is referred to as "persulfate".

1. Prepare the persulfate solution.
   a. weigh 20 g of persulfate and quantitatively transfer to 300 mL of ASTM Type I water in a 1000-mL volumetric flask.
   b. add 1.0 mL of concentrated nitric acid and bring to volume with ASTM Type I water.
2. Increase the oxygen flow rate to 190 cm^3/min.
   a. ensure that the oxygen delivery pressure is 15 psig.
   b. ensure that at least 500 psig of oxygen is in the cylinder.
   c. if foaming occurs in the KOH scrubber, add a small amount of ASTM Type I water to the KOH; if foaming persists, replace the contents with approximately 12 mL of fresh 45% KOH solution.
3. Repack the magnesium perchlorate scrubbers. These scrubbers are positioned directly after the burette water-trap.
   NOTE: Using the old, wetted packing could result in formation of a plug, increasing the back-pressure.
   a. wash out the old packing, rinse the scrubber tube with ASTM Type I water, then air- or oven-dry the tube.
   b. repack and reconnect the tube.
4. Check the acid dichromate/manganese dioxide scrubber for exhaustion. This scrubber is positioned after the magnesium perchlorate scrubber.
   a. the acid dichromate packing will change from yellow-orange (oxidized) to green-orange (reduced) as it becomes exhausted. This color change will be seen as a front progressing in the direction of gas flow. When almost all of the acid dichromate has changed color, the entire scrubber must be repacked.
   b. when the manganese dioxide packing is exhausted, it will change from black to dark brown; the entire scrubber must then be repacked.
5. Position the recirculation (0.063" id) and reagent delivery (0.031" id) Viton pump tubes and the silicone waste-line pump tube (1.0-mm id) in the peristaltic pump (Sage Instruments, model 375A) and close the platten lid.
   a. the Viton pump tubes require the 11-lb pressure plates (grey); the silicone pump tube requires the 2.12-lb pressure plate (tan).
6. Fill the UV reactor with the persulfate solution, connect the persulfate resevoir in line using the Omnifit Teflon fittings, and connect the waste line to an appropriate receptacle.
7. Turn on the pump.
   a. the pump setting should be preset to deliver approximately 0.6 mL/min of fresh persulfate solution to the reactor. The contents of the reactor should recycle at a rate of 3.0 mL/min through the valve. Combined flow of fresh and recycled reagent will be 3.6 mL/min. The contents of the reactor are pumped to waste at a rate of at least 0.6 mL/min.

NOTE: Check for leaks at all tubing connections during initial pumping; a misaligned sample injection valve rotor will increase

back-pressure and cause leaking.

8. Assemble the coulometer cell.
   a. fill the coulometer cell with 75 mL of coulometer solution.
   b. add the stir bar.
   c. position the rubber stopper on the coulometer cell such that the anode, cathode, and gas line face the back wall of the cell (that portion of the beaker containing the volume graduations).
   d. add 3 pellets of potassium iodide to the anode compartment.
   e. add anode solution to the anode compartment. The anode solution level should be slightly higher than that of the coulometer cell solution.
   f. place the silver anode in the anode compartment. Ensure that the tip of the silver anode is wetted by the anode solution.
   g. place the assembled coulometer cell in the cell holder of the instrument; the volume graduations should face the rear of the instrument.
   h. plug the anode (red) and cathode (black) wires into the coulometer.

   DO NOT TURN ON THE ELECTROLYSIS CURRENT.

   i. connect the coulometer cell gas line to the one-way valve in-line from the nitrogen oxide scrubber. Check that the stopcock on the burette water trap is open (the gas flow must be diverted from the coulometer cell during adjustment of cell transmittance per step A.11).
9. Connect the HP 97S to the coulometer interface cable.
   a. turn on the HP 97S.
   b. with the calculator in the RUN mode, load the "background" program as per the user instructions (Appendix A).
10. Turn on the main power supply. Allow a warm-up period of several minutes.
11. Adjust the coulometer cell transmittance.
   a. rotate the coulometer cell until a maximum transmittance is obtained.
   b. adjust the transmittance to 100% using the "100% adjust" knob.
   c. close the stopcock on the burette water trap.
   d. check that the gas flow into the coulometer cell does not deflect the 100% transmittance setting. If a deflection occurs, reposition the gas line to eliminate this interference. Open the burette stopcock and repeat steps a-d.

   NOTE: The gas line must be submerged in the coulometer solution.
12. Turn on the electrolysis current.
13. Start the UV-lamp and initiate the background program.
   a. when the coulometer has stabilized, the background (counts per minute) should be approximately 2.0 to 3.2 mg/L. Stabilization should be complete within 0.5 to 2.0 hours.
   b. if high background counts persist (greater than 4 mg/L per minute) for more than two hours, replace the Viton pump tubing and repeat step 13.a.

   NOTE: Should the high background persist after installing new Viton tubing, check for the following in decreasing order of priority: exhaustion of scrubbers; clogging of anode-cell glass frit; silver deposition on platinum wire cathode; contamination of persulfate solution; coulometer performance.

B. SAMPLE PREPARATION -- TOTAL DISSOLVED CARBON (TDC)
1. Filter all samples through a 0.4-μm pore diameter polycarbonate membrane filter.
2. Dilute sample filtrates with ASTM Type I water to yield TDC concentrations between 200 and 1000 mg/L.
3. Prepare a TDC sample blank; a 10-mL aliquot of ASTM Type I water should be processed with the TDC samples.
4. Refrigerate samples until analysis time.

C. SAMPLE PREPARATION -- DISSOLVED ORGANIC CARBON (DOC)
1. Filter all samples through a 0.4-μm pore size polycarbonate membrane filter.
2. Dilute sample filtrates with ASTM Type I water to yield DOC concentrations between 200 and 2000 mg/L.
3. Prepare a DOC sample blank; a 10-mL aliquot of ASTM Type I water should be processed with the DOC samples.
4. Acidify the blank and DOC samples with 0.10 mL concentrated sulfuric acid per 10 mL of sample. A positive displacement pipette or a repipette should be used.
   NOTE: Samples should have pH values of 2 after acidification.
5. Refrigerate samples until analysis time.

D. PURGING OF DOC SAMPLES
1. Open the helium cylinder valve and set the delivery pressure to 10 psig. The needle valve on the helium flow meter is preset to deliver 775 cm^3/min at 10 psig.
2. Rinse the glass capillaries by submersion in the vials of concentrated HCl, and wipe dry.
3. Submerge each capillary in a sample and purge for 10 minutes.
4. Remove the capillaries, wipe dry, and repeat steps 2-3 for all samples.
5. After all the samples have been purged, repeat step 2 and place the capillaries in a clean, dry vial.
6. Turn off the helium cylinder valve.
   NOTE: Purging should be conducted in an enclosed compartment to prevent deposition of acidic aerosols on nearby equipment.

E. PREPARATION OF STANDARDS
   (NOTE: Use Analytical Reagent grade reagents only).
1. Prepare a stock solution of potassium acid phthalate (DOC = 1000.0 mg/L as C).
   a. weigh 1063.6 mg of dried potassium acid phthalate and quantitatively transfer to a 500-mL volumetric flask.
   NOTE: All glassware should be acid-washed.
   b. bring to volume with ASTM Type I water.
   c. acidify the standards as instructed in section C.4.
2. Prepare working standards of 100, 500, and 1000 mg/L.
   NOTE: additional standard concentrations should be made if the sample DOC concentration is expected to be outside of this range.
   a. 100 mg/L : pipette 1.0 mL of stock solution and 9.0 mL of ASTM Type I water into a DOC vial.

NOTE: use air- or positive-displacement pipettes suitable for analytical work.

b. 500 mg/L : pipette 5.0 mL of stock solution and 5.0 mL of ASTM Type I water into a DOC vial.

c. 1000 mg/L : pipette 10.0 mL of stock solution into a DOC vial.

3. Prepare a stock solution of phenol for recovery determinations (DOC = 2371.7 mg/L as C).
   a. weigh 155.0 mg of phenol and quantitatively transfer to a 50-mL volumetric flask.
   b. bring to volume with ASTM Type I water.
   c. Dilute this stock solution 1:5 with ASTM Type I water and acidify (DOC = 474.3 mg/L as C).
4. Prepare a stock solution of pyridine for recovery determinations (DOC = 1000 mg/L as C).
   a. dispense approximately 65 µL of pyridine into a tared 50-mL volumetric flask and record the exact weight.
   b. bring to volume with ASTM Type I water.
   c. acidify as instructed in section C.4.
   d. calculate the theoretical DOC of this solution:
      DOC (mg/L) = (15.18) x (mg pyridine added/0.050 L).
   e. dilute this stock solution 1:5 with ASTM Type I water (DOC = 200 mg/L as C).

F. SAMPLE ANALYSIS

1. Load the "Water Analysis" program into the HP 97S.
   a. turn off the coulometer main power.
   b. With the HP 97S calculator in RUN mode, run the program card through the HP 97S card reader.
   c. initiate the program as per the user instructions (Appendix B).
   d. turn on the coulometer main power.
2. Load samples into the 200-µL injection loop with a 1.0-mL gas-tight HPLC syringe.
   a. Rinse the syringe and sample loop with one milliliter of sample; this is required to exponentially dilute the persulfate reagent from the loop. Ensure that the injector waste line is connected to the proper receptacle.
   b. fill the syringe with a minimum of 0.6 mL of sample.
   c. insert the syringe needle into the injection valve port.
   d. position the rotary sample injection valve in the LOAD position.
   e. load the sample into the 200-µL injection loop. Leave the syringe in place to prevent introduction of air into the sample loop by capillary action.
   f. switch the rotary injection valve to the INJECT position and initiate the sample program on the HP 97S as per the user instructions (Appendix B).
   g. the syringe can now be removed from the injection port. The valve must remain in the INJECT position during sample analysis.
   h. the suggested analysis time for each sample is 5 minutes.
   i. for replicates, repeat steps a-h.
   j. check the burette water trap. This trap should be emptied between analyses so that the gas line does not become submerged in the condensate.

3. Repeat step 2 for each sample.
4. Samples should be analyzed in the following order:
   a. the sample blank; the mean DOC value from the blanks must be subtracted from the DOC value of each standard and sample. This calculation is performed automatically by the HP 97S "Water Analysis" program.
   b. the acid phthalate standards.

   NOTE: If standard recoveries deviate more than 5% from the theoretical values, check for the following in decreasing order of priority: accuracy of standard stock solution and standard dilutions; exhaustion of scrubbers; clogging of anode-cell glass frit; silver deposition on platinum wire cathode; condition of persulfate reagent; condition of UV lamp; coulometer performance.

   c. the recovery standards (phenol and pyridine).
   d. the DOC samples.

   NOTE: if a large number of DOC samples is to be analyzed, the series of standards should be analyzed at intervals throughout the DOC analyses.

   e. upon completion of the DOC analyses, the series of standards and blanks should be reanalyzed.

G. SHUT-DOWN
1. Turn off the HP 97S.
2. Turn off the main power supply to the UV lamp.
3. Drain the contents of the reactor vessel and discard.
4. Disconnect the persulfate reservoir and refrigerate.
5. Turn off the peristaltic pump after the lines have been pumped dry.
   a. disengage the platten and remove all tubing from the pump.
6. Turn off the oxygen cylinder valve.
7. Open the stopcock on the burette water trap.
8. Disassemble the coulometer cell.
   a. turn off the electrolysis current.
   b. turn off the main power.
   c. unplug the anode and cathode wires from the coulometer.
   d. disconnect the gas line at the one-way valve in-line between the coulometer cell and the nitrogen oxide scrubber.
   e. remove the coulometer cell from the coulometer.
   f. remove the silver anode, rinse with ASTM Type I water, and air-dry on a clean surface.
   g. remove the rubber stopper from the coulometer cell and rinse the anode cell with acetone; ensure that no potassium iodide deposits remain in the anode cell. Using a vacuum source and the perforated serum stopper, draw a small volume of acetone through the fritted-glass end of the anode cell.
   h. rinse the exteriors of the anode, cathode, and gas line with ASTM Type I water and air-dry on a clean surface.
   i. rinse the coulometer cell and stir bar several times with ASTM Type I water and air-dry on a clean surface.

H. DATA REDUCTION

1. Calculate the mean value for each set of DOC replicates:
   a. $\bar{x}(DOC) = \Sigma(x_i - b)/n$
      where x_i = each data point in a set of replicates;
      b = the mean value of all DOC blank analyses
      n = the number of replicates per sample.
2. The HP 97S "Water Analysis" program automatically calculates $(x_i - b)$ X (dilution factor) for each data point. Therefore the mean for a set of replicates equals the sum of data outputs divided by the number of replicates (n).
3. Determine whether suspected outliers should be discarded.
   a. suspected outliers should be subjected to statistical analysis before being discarded (1).
   b. if an outlying value is known to be the result of a mechanical or operator error, it may be rejected without statistical verification.

I. MAINTENANCE

1. Record the appropriate information in the C-Analyzer Log Book, including:
   a. date and duration of usage.
   b. number of injections (retort water and total) and sample dilutions.
   c. symptoms of malfunctioning.
   d. repairs.
   e. initial all entries.

J. REFERENCES

1. ASTM
Annual Book of ASTM Standards, Part 31, Water; American Society for Testing and Materials: Philadelphia, PA, 1977; 1110 pp.

Prepared by: G.W. Langlois, B.M. Jones, R.H. Sakaji, and C.G. Daughton.

Acidification-Purge/Coulometric Titration

A. START-UP

1. Turn on the main power supply for the inorganic carbon apparatus.
   a. the main power switch controls both the air pump and the heating element.
2. The temperature control knob should be set at 60 (60 ^{0}C).
3. Increase the air flow rate to 100 cm^3/min.
   a. if foaming occurs in the KOH scrubber, add a small amount of ASTM Type I water to the KOH; if foaming persists, replace the contents with approximately 12 mL of fresh 45% KOH solution.

   NOTE: Use Analytical Reagent grade chemicals only.
4. Refill the Ag_2SO_4 scrubber.
   a. the contents can be removed with a 9-inch pasteur pipette.
   b. refill with 3 mL of saturated Ag_2SO_4 solution containing 3% H_2O_2 (vol/vol).
5. Refill the perchloric acid ($HClO_4$) reservoir-dispenser if necessary (each analysis requires 2 mL of acid).

   NOTE: Take appropriate precautions when handling concentrated $HClO_4$. (e.g., read pertinent sections in "Prudent Practices for Handling Hazardous Chemicals in Laboratories"; "Guide for Safety in the Chemical Laboratory"; and "First Aid Manual for Chemical Accidents").
   a. to prepare a 2N solution of $HClO_4$ (70%), place 100 mL of ASTM Type I water in a 250-mL volumetric flask, followed by 43.0 mL of $HClO_4$, and bring to volume.
6. Check the neoprene slip-on septum.
   a. replace the septum if signs of oxidation (i.e., from $HClO_4$) are evident (e.g., dryness, cracking).
7. Check the silicone reducing connectors on the air- and acid-delivery lines.
   a. replace these fittings if they show signs of deterioration.
8. Assemble the coulometer cell.
   a. fill the coulometer cell with 75 mL of coulometer solution.
   b. add the stir bar.
   c. position the rubber stopper on the coulometer cell such that the anode, cathode, and gas line face the back wall of the cell (that portion of the beaker containing the volume graduations).
   d. add 3 pellets of potassium iodide to the anode compartment.
   e. add anode solution to the anode compartment. The anode solution level should be slightly higher than that of the coulometer cell solution.
   f. place the silver anode in the anode compartment. Ensure that the tip of the silver anode is wetted by the anode solution.
   g. place the assembled coulometer cell in the cell holder of the instrument; the volume graduations should face the rear of the instrument.
   h. plug the anode (red) and cathode (black) wires into the coulometer.

   DO NOT TURN ON THE ELECTROLYSIS CURRENT.

9. Connect the HP 97S to the coulometer interface cable.
   a. turn on the HP 97S.
   b. with the calculator in the RUN mode, load the "background" program as per the user instructions (Appendix A).

   NOTE: Analyses may be conducted without the HP 97S.
10. Turn on the coulometer main power supply. Allow a warm-up period of several minutes.
11. Adjust the coulometer cell transmittance.
   a. rotate the coulometer cell until a maximum transmittance is obtained.
   b. adjust the transmittance to 100% using the "100% adjust" knob.
   c. connect the coulometer cell gas line to the one-way valve in-line from the $AgSO_4$ scrubber.
   d. check that the gas flow into the coulometer cell does not deflect the 100% transmittance setting. If a deflection occurs, reposition the gas line to eliminate this interference; disconnect the gas line and repeat steps a-d.

   NOTE: The gas line must be submerged in the coulometer solution.
12. Turn on the electrolysis current and initiate the background program.
   a. allow several minutes for the titration of endogenous CO_2 in the coulometer solution.
   b. following this initial titration, check the coulometer stability. A stable background count of 1.0 to 1.2 mg/L per minute should be obtained when the range plug is set to display mg/L. Stabilization may take as long as 30 minutes.

B. SAMPLE PREPARATION -- DISSOLVED INORGANIC CARBON (DIC)
1. Filter all samples through 0.4-µm pore diameter polycarbonate membrane filters.
2. Dilute sample filtrates with ASTM Type I water to yield DIC concentrations between 100 and 500 mg/L.
3. Prepare a DIC sample blank; a 10-mL sample of ASTM Type I water should be processed with the DIC samples.
4. Refrigerate samples until analysis time.

C. PREPARATION OF STANDARDS
1. Prepare a stock solution of sodium carbonate (DIC = 1000.00 mg-C /L).
   a. weigh 4414.5 mg of dried sodium carbonate and quantitatively transfer to a 500-mL volumetric flask.

   NOTE: Glassware should be acid-washed.
   b. bring to volume with ASTM Type I water.
2. Prepare working standards of 100, 250, and 500 mg/L.

   NOTE: additional standard concentrations should be made if the sample DIC concentration is expected to be outside of this range.
   a. 100 mg/L : pipette 1.0 mL of stock solution into a 10-mL volumetric flask and bring to volume with ASTM Type I water.
   b. 250 mg/L : pipette 2.5 mL of stock solution into a 10-mL volumetric flask and bring to volume with ASTM Type I water.
   c. 500 mg/L : pipette 5.0 mL of stock solution into a sample vial.

   NOTE: Use air- or positive-displacement pipettes.

D. SAMPLE ANALYSIS

1. Load the "Water Analysis" program into the HP 97S.
   a. turn off the coulometer main power.
   b. with the HP 97S in the RUN mode, run the program card through the HP 97S card reader.
   c. initiate the program as per the user instructions (Appendix B).
   d. turn on the coulometer main power.
2. If a gas-tight syringe (e.g., Unimetrics) is used, check that the constant-volume adaptor is set for 200 µL. Recheck frequently during sample analysis.
3. Rinse the syringe 10 times with the sample to be analyzed.
   a. insert the syringe needle through the septum injection port.
   b. inject the sample and withdraw the syringe.
   c. depress the plunger on the perchloric acid resevoir and initiate the program loop as per the user instructions (Appendix B). The repipette should be set to deliver 2.0 mL of acid.
   d. the suggested analysis time for each sample is 3 minutes.
   e. for replicates, rinse the syringe twice with the sample to be analyzed and repeat steps a-e.

   NOTE: If analyses are conducted without the HP 97S, a stopwatch should be used to measure the analysis time. The coulometer should be reset at the start of the analysis time.
4. Repeat step 2 for each sample.
5. Samples should be analyzed in the following order:
   a. the sample blank; the mean DIC value from the blanks must be subtracted from the DIC value of each standard and sample. This calculation is performed automatically by the HP 97S "Water Analysis" program.
   b. the sodium carbonate standards.

   NOTE: If standard recoveries deviate more than 5% from the theoretical values, check for the following in decreasing order of priority: accuracy of standard stock solution and standard dilutions; exhaustion of scrubbers; clogging of anode-cell glass frit; silver deposition on platinum wire cathode; contamination of reactor tube; coulometer performance.

   c. the DIC samples.

   NOTE: if a large number of DIC samples is to be analyzed, the series of standards should be analyzed at intervals throughout the DIC analyses.

   d. upon completion of the DIC analyses, the series of standards and blanks should be reanalyzed.

E. SHUT-DOWN

1. Turn off the HP 97S.
2. Turn off the inorganic carbon apparatus.
   a. remove the reactor tube and rinse thoroughly with ASTM Type I water.
3. Disassemble the coulometer cell.
   a. turn off the electrolysis current.
   b. turn off the main power.
   c. unplug the anode and cathode wires from the coulometer.
   d. disconnect the gas line at the one-way valve in-line between the coulometer cell and the Ag_2SO_4 scrubber.

e. remove the coulometer cell from the coulometer.
f. remove the silver anode, rinse with ASTM Type I water, and air-dry on a clean surface.
g. remove the rubber stopper from the coulometer cell and rinse the anode cell with acetone -- ensure that no potassium iodide deposits remain in the anode cell. Using a vacuum source and the perforated serum stopper, draw a small volume of acetone through the fritted-glass end of the anode cell.
h. rinse the exteriors of the anode, cathode, and gas line with ASTM Type I water and air-dry on a clean surface.
i. rinse the coulometer cell and stir bar several times with ASTM Type I water and air-dry on a clean surface.

F. DATA REDUCTION

1. Calculate the mean value for each set of DIC replicates:
   a. $\bar{x}(DIC) = \Sigma(x_i - b)/n$
      where x_i = each data point in a set of replicates;
      b = the mean value of all DIC blank analyses
      n = the number of replicates per sample.
2. The HP 97S "Water Analysis" program automatically calculates $(x_i - b)$ X (dilution factor) for each data point. Therefore the mean for a set of replicates equals the sum of data outputs divided by the number of replicates (n).
3. Determine whether suspected outliers should be discarded.
   a. suspected outliers should be subjected to statistical analysis before being discarded (1).
   b. if an outlying value is known to be the result of a mechanical or operator error, it may be rejected without statistical verification.

G. MAINTENANCE

1. Record the appropriate information in the C-Analyzer Log Book, including:
   a. date and duration of usage.
   b. number of injections (retort water and total) and sample dilutions.
   c. symptoms of malfunctioning.
   d. repairs.
   e. initial all entries.

H. REFERENCES

1. ASTM
Annual Book of ASTM Standards, Part 31, Water; American Society for Testing and Materials: Philadelphia, PA, 1977; 1110 pp.

2. Lefevre, M.J.
First Aid Manual for Chemical Accidents; Dowden, Hutchinson and Ross, Inc.: Stroudsburg, PA, 1980; 218 pp.

3. Manufacturing Chemists Assosciation
Guide for Safety in the Chemical Laboratory; Van Nostrand Reinhold Company: New York, NY, 1972; 505 pp.

4. National Research Council
Prudent Practices for Handling Hazardous Chemicals in Laboratories; National Acadamy Press: Washington, D.C., 1981; 291 pp.

Prepared by: G.W. Langlois, B.M. Jones, R.H. Sakaji, and C.G. Daughton.

APPENDIX A. **User Instructions**

1 C-ANALYZER: BACKGROUND COUNTS PROGRAM 2

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
1	LOAD PROGRAM: calculator in RUN mode, PRINT in manual position, coulometer turned off.				
2	PRESS"E": display will go to 0.0			E	
3	PRESS "R/S": display will go to 0.			R/S	
4	ENTER NUMBER OF DATA INPUTS FROM COULOMETER (e.g., 20 inputs at 15 sec intervals = 5 min analysis time).	"n"			
5	TURN COULOMETER ON.				
6	PRESS "R/S": prints number of inputs, spaces 2 lines, begins data acquisition loop.			R/S	"n"
7	When data input is completed (i.e., after the "n"th data input) the system background for the selected analysis time is printed; the data acquisition loop is automatically reentered.				Background value
8	PRESS "R/S" to terminate the program.			R/S	
9	To change the value for number of data inputs turn off the coulometer, PRESS "f" "e" and repeat instructions beginning at step 4.		f	e	

STEP	KEY ENTRY	KEY CODE	COMMENTS
001			
001	*LBLE	21 15	
002	CF3	16 22 03	
003	R/S	51	
004	SF3	16 21 03	
005	*LBLe	21 16 15	
006	SF3	16 21 03	
007	DSP0	-63 00	
009	0	00	
009	R/S	51	
010			
010	PRTX	-14	
011	SPC	16-11	
012	SPC	16-11	
013	1	01	
014	+	-55	
015	STOC	35 13	
016	R/S	51	
017	*LBLD	21 14	
018	DSP0	-63 00	
019	0	00	
020			
020	RCLC	36 13	
021	STOI	35 46	
022	DSP1	-63 01	
023	SF0	16 21 00	
024	PSE	16 51	
025	*LBLB	21 12	
026	CF3	16 22 03	
027	CF0	16 22 00	
028	R/S	51	
029	*LBLA	21 11	
030			
030	1	01	
031	0	00	
032	÷	-24	
033	DSZI	16 25 46	
034	GTOB	22 12	
035	CF3	16 22 03	
036	PSE	16 51	
037	SF3	16 21 03	
038	PRTX	-14	
039	GTOD	22 14	
040			
040	R/S	51	
050			

STEP	KEY ENTRY	KEY CODE	COMMENTS
060			
070			
080			
090			
100			

LABELS

A DATA INPUT LOOP	B DATA LOOP	C	D INITIATE DATA LOOP	E INITIATE PROGRAM
a	b	c	d	e MANUAL DATA INPUT
0	1	2	3	4
5	6	7	8	9

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C # DATA INPUTS	D	E	I COUNTER FOR DATA INPUTS

APPENDIX B. **User Instructions**

1 WATER ANALYSIS PROGRAM: TDC, DOC, and DIC 2

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
1	LOAD PROGRAM: calculator in RUN mode, PRINT in manual position, coulometer turned off.				
2	PRESS "E": display will go to 0.0			E	
3	PRESS "R/S": display will go to 0.000			R/S	
4	ENTER STABILITY FACTOR (e.g., 0.990).	Value			
5	PRESS "R/S": prints stability factor, display goes to 0.			R/S	Value
6	ENTER BLANK VALUE	Value			
7	PRESS "R/S": prints blank value, display goes to 0.			R/S	Value
8	ENTER NUMBER OF DATA INPUTS FROM COULOMETER (e.g., 20 inputs at 15 sec intervals = 5 min analysis time).	"n"			
9	PRESS "R/S": prints number of inputs, spaces 3 lines, displays 0.			R/S	"n"
10	TURN COULOMETER ON.				
11	ENTER SAMPLE NUMBER (integer only)	Value			
12	PRESS "R/S": prints sample number, displays 0.0			R/S	Value
13	ENTER DILUTION FACTOR (e.g., "10" for a 1:10 dilution).	Value			
	NOTE: THE FOLLOWING STEP INITIATES THE DATA ACQUISITION LOOP; THE LOADED SAMPLE MUST BE INJECTED AT THIS STEP.				
14	INJECT SAMPLE, PRESS "R/S": prints dilution factor, starts analysis time.			R/S	Value

User Instructions

1 WATER ANALYSIS PROGRAM (continued) 2

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
15	When data input is completed (i.e., after the				Final Value minus blank,
	"n"th data input) the final value minus the				multiplied
	blank is printed; this value is multiplied by				by the dilution factor
	the dilution factor and printed.				
16	To analyze the next sample repeat steps 11-14.				
17	To change the STABILITY FACTOR, BLANK, or		f	e	
	NUMBER OF DATA INPUTS, turn off the coulometer,				
	PRESS "f" "e", and repeat instructions				
	beginning at step 4.				

STEP	KEY ENTRY	KEY CODE	COMMENTS
001 001	*LBLE	21 15	
002	CF3	16 22 03	
003	R/S	51	
004	SF3	16 21 03	
005	*LBLe	21 16 15	
006	SF3	16 21 03	
007	DSP3	-63 03	
008	0	00	
009	R/S	51	
010 010	PRTX	-14	
011	STOA	35 11	
012	DSP1	-63 01	
013	0	00	
014	R/S	51	
015	PRTX	-14	
016	STOB	35 12	
017	DSP0	-63 00	
018	0	00	
019	R/S	51	
020 020	PRTX	-14	
021	SPC	16-11	
022	SPC	16-11	
023	SPC	16-11	
024	1	01	
025	+	-55	
026	STOC	35 13	
027	1	01	
028	-	-45	
029	RCLB	36 12	
030 030	X⇄Y	-41	
031	÷	-24	
032	STO2	35 02	
033	*LBLD	21 14	
034	DSP0	-63 00	
035	0	00	
036	R/S	51	
037	PRTX	-14	
038	DSP1	-63 01	
039	0	00	
040 040	R/S	51	
041	PRTX	-14	
042	STO1	35 01	
043	RCLC	36 13	
044	STOI	35 46	
045	1	01	
046	-	-45	
047	STO3	35 03	
048	DSP1	-63 01	
049	SF0	16 21 00	
050 050	PSE	16 51	
051	*LBLB	21 12	
052	STOE	35 15	
053	CF3	16 22 03	
054	CF0	16 22 00	
055	R/S	51	
056	*LBLA	21 11	

STEP	KEY ENTRY	KEY CODE	COMMENTS
057	1	01	
058	0	00	
059	÷	-24	
0 060	DSZI	16 25 46	
061	GTOB	22 12	
062	CF3	16 22 03	
063	PSE	16 51	
064	SF3	16 21 03	
065	STOD	35 14	
066	RCLA	36 11	
067	×	-35	
068	RCLE	36 15	
069	-	-45	
0 070	RCL2	36 02	
071	-	-45	
072	X>0?	16-44	
073	GTOC	22 13	
074	DSP1	-63 01	
075	RCLD	36 14	
076	ENT↑	-21	
077	RCL2	36 02	
078	ENT↑	-21	
079	RCL3	36 03	
0 080	×	-35	
081	-	-45	
082	PRTX	-14	
083	RCL1	36 01	
084	×	-35	
085	PRTX	-14	
086	SPC	16-11	
087	GTOD	22 14	
088	*LBLC	21 13	
089	ISZI	16 26 46	
090	RCL3	36 03	
091	1	01	
092	+	-55	
093	STO3	35 03	
094	RCLD	36 14	
095	GTOB	22 12	
096	R/S	51	
100			

LABELS

A Data Input Loop	B Data Loop	C Reset for Add. Data	D Initiate Data Loop	E Initiate Program
a	b	c	d	e Manual Data Input
0	1	2	3	4
5	6	7	8	9

REGISTERS

0	1 Dilution Factor	2 Blank, Increment.	3 # Data Inputs	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A Stability Factor	B Blank Value	C # Data Inputs	D Final Data Input Value	E Previous Data Input Value	I Counter for Data Inputs

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720