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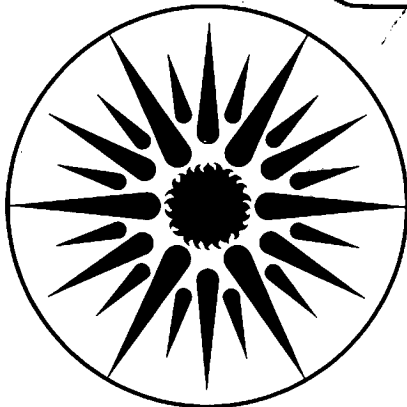
QUANTITATION OF CARBON IN OIL SHALE PROCESS
WASTEWATERS: COULOMETRY COUPLED WITH
UV-PEROXYDISULFATE AND HIGH-TEMPERATURE OXIDATION

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

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Quantitation of Carbon in Oil Shale Process Wastewaters:
Coulometry Coupled with UV-Peroxydisulfate and
High-Temperature Oxidation

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ABSTRACT: Wastewaters from the production of synfuels, in particular oil shale retort waters, present several major problems to various instrument configurations designed for carbon analysis. A carbon analyzer was fabricated from commercially available oxidation and detection units. Carbon oxidation occurred in an ultraviolet photochemical reactor using acid peroxydisulfate; quantitation of the evolved carbon dioxide was accomplished with an automatic coulometric titrator. This new design eliminated 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. infrared detection), and (iii) frequent detector calibration (viz., infrared and flame ionization detection).

The UV-persulfate/coulometric titration carbon analyzer was compared statistically with an ASTM-approved high-temperature combustion system on the basis of (i) the accuracy and precision of recovery of total dissolved carbon (TDC) and dissolved organic carbon (DOC) for nitrogen heterocycles, which were of primary interest because of their preponderance in oil shale process waters and their reported resistance to certain oxidation methods and (ii) the precision of TDC and DOC determinations for nine oil shale process wastewaters. Several qualitative considerations are discussed for both analyzers, including ease of operation, instrument downtime, and maintenance costs.

KEY WORDS: oil shale wastewaters, retort water, carbon analysis, coulometry, UV-persulfate oxidation, high-temperature combustion, nitrogen heterocycles

INTRODUCTION

Oil shale process wastewaters are complex aqueous mixtures of dissolved and suspended organic and inorganic compounds. These wastes present numerous problems when quantifying the "total" amount of solutes or quantitating the degree of contaminant removal effected by a waste treatment process. Methods that are specific for given compounds or for entire chemical classes 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 the sample matrix. Two methods commonly employed to estimate the total concentration of organic solutes in wastewaters are biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [1]. Neither of these methods can distinguish organic compounds from certain inorganic compounds (ammonia and thiosulfate will yield BOD and COD values, respectively), and neither is able to detect compounds that are refractory to the respective means of oxidation.

One of the most widely employed element-specific methods is "carbon analysis," which can be used to quantitate inorganic and organic carbon. 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) [2,3], and these compounds also have proved resistant to certain methods of oxidation used for organic carbon measurements [4,5].

There are eight major classes 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 comprises total organic carbon (TOC) and total

inorganic carbon (TIC). The term 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 centrifugation or filtration), 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., 0.20 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 [6] by various 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. 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 [7]; this problem can be partially solved by the use of tangential-flow filtration apparatus. The chemical sorption or precipitation of solutes by electrostatic [8] or chemical interactions of the

solution with the membrane surface also can effect removal of dissolved solutes. In addition, the partitioning of solutes into the immobilized, retained particulate phase has been hypothesized [9]. 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 CO₂ 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 [10]. From our experience, polycarbonate membranes offer the best compromise of features for the filtration of oil shale wastewaters; they are hydrophilic and yet have fewer extractables and smaller dispersion in nominal pore diameter than other filters, and they permit collection of larger volumes of filtrate from oil shale process waters.

There are two major rationales for distinguishing between dissolved and total carbon. First, dissolved carbon is the major form of carbon available to microorganisms in waste treatment. Second, error during subsampling of liquids that contain large quantities of both particulate and colloidal forms of carbon is minimized when the particulates are removed. For these reasons, this study was restricted to the determination of dissolved species of organic and inorganic carbon.

The quantitation of carbon generally requires two steps: (i) the liberation of each organic or inorganic carbon atom as an identical C-1 molecule that is not influenced by the covalent bonding in the parent compounds and (ii) the detection and quantitation of these carbon units. The first step usually involves conversion of covalently bound carbons to a

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 indirect or direct method [11]. The indirect method involves the separate determination of total dissolved carbon and dissolved inorganic carbon; dissolved organic carbon is then calculated by difference. The direct method requires the removal of inorganic carbon prior to the determination of the remaining dissolved carbon; TDC then becomes equivalent to DOC. Removal of DIC can be accomplished by (i) precipitation with barium hydroxide or (ii) acidification followed by either purging with an inert gas or boiling [12]. For the latter method, acidification converts inorganic carbon to carbonic acid which subsequently hydrolyzes to H_2O and CO_2 . Purging is the most widely accepted approach to direct DOC analysis [3,13].

The direct method using acidification can result in the precipitation of organic compounds such as higher-molecular-weight fatty acids with the concomitant occlusion or partitioning of organic solutes by these precipitates; subsequent purging of the CO_2 can volatilize lower-molecular-weight organic solutes, especially carboxylic acids [14]. The indirect method requires the least sample manipulation, but lengthens the sample-throughput time because two analyses are required for each sample DOC determination.

Quantitation of inorganic carbon can be accomplished at a low temperature (60°C) by conversion of mineral carbon species to CO_2 via acidification. Oil shale wastewater inorganic carbon is almost exclusively carbonate and bicarbonate. 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.

This report briefly discusses the advantages and disadvantages of various instrumental techniques for determining organic and inorganic carbon in highly contaminated waters such as those from oil shale retorting; a more general review of carbon analysis procedures is reported by Golterman [15] and Kübler [16]. A new approach to organic carbon analysis is presented. This analyzer is a hybrid of two commercial carbon analyzers; it combines their strengths and avoids their weaknesses. The performance of this instrument in quantitating dissolved carbon in oil shale process wastewaters and in standard solutions of pure reference compounds is compared with that of an ASTM-approved carbon analyzer [17].

BACKGROUND

Carbon Analysis

The conversion of carbonaceous species to CO_2 for carbon analysis is generally accomplished by one of four methods: high-temperature combustion, chemical oxidation, UV oxidation, or UV-enhanced chemical oxidation.

Of these four oxidation/combustion methods, only high-temperature combustion and UV-enhanced persulfate oxidation were suitable for the routine determination of organic carbon in oil shale process waters. The alternative methods, chemical and UV oxidation, were not applicable to these waters because of reported incomplete oxidation of certain organic compounds and lengthy analysis times. The persulfate oxidation procedure described by Menzel and Vaccaro [18] yields incomplete recoveries of polycyclic aromatic and long-chain hydrocarbons. Persulfate oxidation, in general, gives significantly lower recoveries (by 10 percent) than either combustion or photooxidation methods [5,19]. Although UV oxidation compares favorably with combustion for the recovery of organic carbon from natural waters [5,20], it is incapable of complete mineralization of many of the nitrogen- and

sulfur-containing organic compounds [4,5] that typify oil shale process waters. The effects of extensive UV irradiation of these waters have been reviewed by Jones et al. [21].

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 infrared (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, significant problems were encountered with each. High-temperature combustion units were subject to frequent and unpredictable downtimes because of damaged combustion tubes and fouled catalysts. Infrared detectors exhibit substantial drift, requiring frequent standard curve determinations; even then, relative standard deviations for the direct method approach 10 percent [22].

The ASTM-approved analyzer used in this study was obtained from Coulometrics, Inc. (Model #5020; 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 (Dohrmann Division, Xertex, Inc., Santa Clara, CA) 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 (Fig. 2) oxidizes both organic and inorganic carbonaceous compounds. Samples are introduced to a

quartz combustion tube by direct injection with a 200- μ L syringe, e.g., Hamilton (Reno, NV) CR-700 "constant rate" carbon analyzer syringe. The syringe and injection port form a gas-tight Luer-slip union. The combustion tube, successively packed with a WO_3 -coated quartz wool plug, barium chromate catalyst, and 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 through 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-percent potassium hydroxide 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 converts organic and inorganic carbon to CO_2 and produces acidic gases (e.g., SO_x 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 potassium dichromate/manganese dioxide for removal of contaminative acidic gases. The gas stream, now theoretically containing only CO_2 and O_2 , then enters the coulometric titration cell where the CO_2 is absorbed.

High-temperature combustion of organic compounds provides the most complete oxidation within a short time period 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 content of 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 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; this aids in the rapid oxidation of carbonates and prevents the formation of sodium carbonates, which are more thermally stable [17]. In addition, the sample introduction method is somewhat unsatisfactory. The constant-rate syringe lacks precision and accuracy for measuring repetitive sample volumes; this necessitates volume corrections for each data point. Sample analysis time is increased because the syringe must remain in the injection port throughout the analysis period; this prevents preparation of the subsequent sample for injection.

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 eliminates 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 UV lamp surrounded by a silica coil, a common configuration for other photochemical reactors [20,23]; 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 percent).

The photoreactor unit (Fig. 3) was assembled from parts that were purchased from Dohrmann (Xertex Inc., Santa Clara, CA). A low-pressure six-port injection valve (e.g., model #50-20, Rheodyne, Berkeley, CA) incorporates a calibrated 200- μ L 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- μ L 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 [24]. 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 oxygen that is introduced to the bottom of the reactor through a fritted-glass impinger. A portion of the reactor fluid is withdrawn for recycle from a sidearm at the mid-portion of the reactor; this fluid is combined at a tee fitting 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 waste fluid is drawn off from the top horizontal section of the glass loop. The upward flow of the impinged oxygen creates a downward flow of reactor fluid through the loop; this ensures that

any 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 rate and removing the waste from a set surface level. The upper rate for wastage is limited, however, by careful consideration of the amount of reactor headspace that is also removed; since the carrier gas flow rate is $200 \text{ cm}^3/\text{min}$, a wastage rate of up to $2 \text{ mL}/\text{min}$ would result in loss of nearly 1 percent of the evolved CO_2 , depending upon the volume of gas that enters the waste line. The gaseous oxidation products are swept by the oxygen carrier gas through the effluent line connected to the reactor cap.

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; this resulted in high background carbon counts ($10 \text{ mg-C}/\text{L-min}$), most likely caused by plasticizers and unreacted oligomers. Overnight preconditioning of tubing in a hypochlorite solution could only temporarily (e.g., for several days) reduce the background ($3.3 \text{ mg-C}/\text{L-min}$). Collins and Williams [23] reported the need for tubing preconditioning and observed a decreased background 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 $3.2 \text{ mg-C}/\text{L-min}$) without preconditioning. The disadvantages of Viton tubing are its higher cost and

reduced elasticity, which necessitates more frequent replacement (lifetime = 50 to 80 hours of operation). The recirculation pump tube (0.063-inch 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-inch 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 radicals, two powerful oxidants [25,26]. Ultraviolet energy also can cause excitation of organic compounds, facilitating their oxidation to CO_2 by sulfate and hydroxyl radicals. The oxidation of retort water organic solutes by hydroxyl radical has been discussed by Jones et al. [21]. High chloride ion concentration in a sample can interfere with the mineralization of organic analytes by competing for oxidant [25]. This interference could possibly be minimized by complexing the excess chloride ions with mercuric ion [26].

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

Inorganic Carbon Determination

The Coulometrics carbonate-carbon apparatus (model #5030) uses the acidification/purge technique (Fig. 4). The sample is injected into the

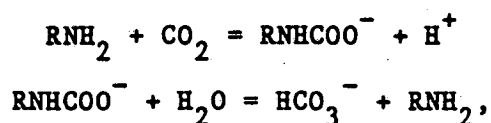
reaction tube with a 200- μ L gas-tight syringe fitted with a septum-piercing needle (e.g., Unimetrics TP 4250S with repetitive volume adjustment). A repipette (e.g., 5-mL Dispensette, Brinkmann Instruments Co., Westbury, NY), connected to the top of the reactor tube with Teflon tubing and unions, is used to dispense 2.0 mL of 2N perchloric acid. Ambient air, scrubbed through an aqueous solution of potassium hydroxide, sweeps the acid and sample down to the bottom of the reactor tube where the mixture is maintained at 60°C. The CO₂ that evolves from the carbon oxides is swept through a silver sulfate/H₂O₂ scrubber for removal of interfering acidic gases (e.g., SO_x 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.

Coulometric Titrimetry

The automatic CO₂ 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 CO₂, the coulometer cell is filled with approximately 75 mL of a proprietary monoethanolamine solution that 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 glass tube with a fritted-glass end and contains potassium iodide pellets, a proprietary anode solution, and a silver electrode, which is connected to the coulometer circuitry. The anode solution is most likely a saturated potassium iodide solution that acts as a salt bridge. 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 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 value of 30 percent at 612 nm) is approached [27]. 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 (RNHCOOH; Fig. 5). Dissociation of the acid yields one hydrogen ion per molecule of CO₂ absorbed. The transient carbamate is hydrolyzed by water, producing bicarbonate and regenerating MEA. The equilibrium reactions occurring in the bulk solution are [28,29]:



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

Absorption of CO₂ 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 (Fig. 5). 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 CO₂ 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 CO₂ absorption), regenerating water. As the CO₂ concentration decreases during titration, the increase in pH causes dissociation of the indicator to the colored form. When all of the CO₂ 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. Although the dried carrier gas continually evaporates liquid from the coulometer solution, thereby decreasing the transmittance possibly beyond the endpoint, small quantities of CO₂ serve to continuously readjust the transmittance; problems with reproducibility have not been encountered after extended operation.

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 CO₂ seems particularly well suited for analysis of carbon in oil shale process waters because of the wide range of concentrations of inorganic and organic carbon. An occasional problem of sample over-titration, however, has been observed; this problem appears to be related to the rate at which CO₂ enters the coulometer cell and the response lag-time for the high-to-low titration trip-point.

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 accuracy and precision of recovery of 17 pure reference compounds in standard solution were also determined. Of the organic solutes present in oil shale process wastewaters, nitrogen heterocycles were of primary interest because

they are purported to be responsible for much of the difficulty in waste treatment processes [30] and also because they resist many oxidation schemes. A series of water-soluble, methyl-substituted pyridines, reported to occur in synfuel wastewaters [31,32] was selected for recovery studies. Acetonitrile and cyanuric acid were selected because they are resistant to complete and rapid oxidation by photochemical methods [26,33]. Several other water-soluble aromatic and nitrogen-heterocyclic organic compounds also were included in this study because of their possible resistance to complete mineralization. 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 instrument.

The nitrogen heterocycle standards (Noah Chemical, Farmingdale, NY; Jewel Nero Consulting, Sun Valley, CA) and potassium acid phthalate were analytical reagent grade. The acetonitrile was HPLC grade. A solution of each compound was prepared with acidified, CO₂-free ASTM Type I water. This minimized the uptake of atmospheric CO₂ and precluded the need to purge the standards prior to analysis for DOC. The possibility of loss of carbon from volatilization was therefore minimized, and the TOC and DOC of these standards were equivalent. The mass of compound added to a class A 50-mL volumetric flask was determined with a semi-micro Mettler analytical balance (model HL52). The theoretical carbon concentration for each standard solution was calculated. Standard solutions and diluted samples were stored at 4°C in 25-mL glass scintillation vials with Teflon-lined screwcaps. Ten single-operator replicate injections of CO₂-free water (blanks) were analyzed on each instrument to determine the background during a 5-minute analysis time. Ten single-operator replicates of each standard were then analyzed for TDC concentration (in this instance synonymous with DOC) on each carbon analyzer.

Samples of nine oil shale process wastewaters (Table 1) were pressure filtered (0.4- μm pore-diameter polycarbonate membranes; Bio-Rad Laboratories, Richmond, CA) 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 (120 cm^3/min). This represents less than a one-percent dilution error, and the final DOC values were not corrected. It is important to note that the procedural order (i.e., filtration, dilution, and acidification) and the rate of acidification may affect the dissolved 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 process water sample were analyzed on each system for both TDC and direct DOC.

For the determination of direct DOC, the extent and precision of the purging operation were also determined. High purity helium (99.995 percent) was delivered through Teflon tubing to a purge station consisting of a six-place aluminum manifold; the flow rate through each outlet was 120 cm^3/min . The time-course removal of volatile carbon (presumably DIC) was followed for a wastewater that was composed of equal volumes of nine process waters (Table 1); this composite water was chosen to moderate possible idiosyncrasies of the individual waters. Duplicate samples of the composite water (filtered, diluted, and acidified) were purged for each of nine time intervals up to 15 minutes and then analyzed for TDC (i.e., what normally would be DOC if purging of DIC were complete) with three replicate determinations for each duplicate; the duplicates were purged at separate times using the same manifold station to eliminate variability from

differences in flow between manifolds. The imprecision of purging was determined by purging replicate samples at five stations for 10 minutes each; five carbon determinations were completed for each replicate, and the study was repeated so that each purge station had a duplicate sample.

All statistical analyses were based on the appropriate sections in Rohlf and Sokal [34] and Sokal and Rohlf [35]. Detailed operating protocols for all instruments used in this comparison study have been reported [36].

RESULTS AND DISCUSSION

Pure Compounds: Recovery and Reproducibility Comparison Study

The theoretical concentrations and the observed recoveries of pure compound solutions from the high-temperature combustion unit are presented in Table 2. Complete recoveries were obtained for all compounds except pyridine (95 percent) and acetonitrile (97 percent). The degree and position of alkyl substitution for the N-heterocycles did not affect the recoveries. The relative standard deviation (rsd) values were less than one percent for most compounds, and they did not exceed three percent for any compound. Recovery of the potassium acid phthalate standards deviated slightly from linearity at the lowest concentration (100 mg-C/L); a similar deviation was also noted for the UV-persulfate system. 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 3) as reported by others [26,33]. The recovery of pyridine (95 percent) was identical to that from the high-temperature system; this may indicate that the pyridine contained impurities that reduced its overall carbon concentration. The oxidation of acetonitrile was incomplete after the five-minute analysis

period; higher recoveries (i.e., 100 percent) were obtained by increasing the analysis time to 10 minutes. Cyanuric acid, an s-triazine, was completely resistant to UV-persulfate oxidation, regardless of the analysis time. Similar findings were reported for cyanuric acid and melamine by the manufacturer of the UV reactor [33]. It is not known whether other triazines present a similar problem, but these compounds have not been reported in oil shale process waters. With the exception of cyanuric acid, the rsd values for sample recoveries were less than two percent for most samples and did not exceed four percent for any sample.

The close agreement between analyzers for the recovery of all the pure compounds, except cyanuric acid, is illustrated in Figure 6. The pattern of small range deviations above and below 100-percent recovery was similar for both analyzers; this was probably the result of impurities in the stock reference compounds and errors in sample preparation. The ranges of percent recoveries suggested 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_g) for the variability between analyzers was 1.23, which was less than the critical F-value (F_α) of 4.41 at $\alpha = 0.05$. Therefore, there was no significant difference ($P > 0.05$) between carbon analyzers for the recovery of carbon from solutions of pure compounds.

Because of the anticipated problems with the ability of the UV-persulfate oxidation system to completely oxidize acetonitrile and cyanuric acid, the mean recoveries of these compounds were tested by a priori comparisons between analyzers. There was no significant difference ($P > 0.05$) between analyzers for the recovery of acetonitrile: $F_g (< 1) < F_{.05} (4.41)$.

There was a highly significant difference ($P < 0.001$) between analyzers for the recovery of cyanuric acid despite the nonsignificant overall anova:

$$F_s(19.24) > F_{.001}(15.4).$$

Process Wastewaters: TDC and DOC Reproducibility Comparison Study

Results from the purge time-course study are presented in Figure 7. The rsd values for the three replicate determinations of each duplicate were less than 1.0, except for one sample. A one-way anova conducted on these data indicated a highly significant variance component ($P < 0.001$) for purge time: $F_s(46.5) >> F_{.001}(8.96)$. Results of the Student-Newman-Keuls step-wise multiple comparison test indicated that there was a significant difference ($P < 0.05$) between means for purge times of 0.0, 0.5, and 1.0 minutes; there was no significant difference between purge times of 1.0 and 15 minutes ($P > 0.05$). Since oil shale wastewaters differ greatly in DIC concentrations, they may require more or less purging than the composite water used in this study. The results for this composite water showed that 10 minutes was a more than sufficient purge time for DIC removal from the nine waters used in this study. This study, however, did not address the question of whether volatile organic compounds also are lost during purging.

Results of the purge precision study (Table 4) indicated that the variability between purge stations was small. A one-way anova conducted on these data showed no significant difference ($P > 0.05$) among stations:

$$F_s(3.91) < F_{.05}(5.19).$$

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 5. There was close agreement between the two analyzers (each labeled "A" or "B" in Table 5) for TDC and DOC determinations for each water. 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 [5], it therefore can be concluded from these results that UV-enhanced persulfate oxidation of oil shale process waters yielded 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.

The rsd values for the recovery of TDC and DOC by either analyzer were less than three percent and generally less than two percent. To determine if a significant difference existed between carbon analyzers for the recovery of TDC, a two-way anova was conducted on square-root transformed data. There was no significant difference ($P > 0.05$) between analyzers for TDC recovery: $F_s(4.88) < F_{.05}(5.32)$. There was a significant interaction effect between analyzers and wastewaters $F_s(3.99) > F_{.05}(1.94)$, but the results of Tukey's test indicated that an insignificant portion was due to nonadditive effects, $F_s(0.21) < F_{.05}(5.59)$, and therefore did not violate the assumptions of the statistical model. The additive interaction between treatments (i.e., between wastewaters and analyzers) obviously resulted from the wide range in TDC values between wastewaters.

A two-way anova was conducted on square-root transformed DOC data with similar results. There was no significant difference ($P >> 0.05$) between carbon analyzers for the quantitation of DOC: $F_s(0.98) < F_{.05}(5.32)$. The interaction term was significant but additive. For each carbon analyzer, the direct and indirect DOC data for the nine process waters (Table 5) were compared by a two-way anova on log-transformed values. There was no significant difference ($P >> 0.05$) between direct DOC and indirect DOC measurements for either high-temperature combustion or UV-persulfate

oxidation: $F_g (<1) < F_{.05}$ (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. These observations are in agreement with indirect versus direct carbon determinations for oil shale wastewaters reported by Fox et al. [11]; it should be noted, however, that extensive volatilization may have already occurred in all of these waters because they had been stored for long periods. The imprecision of the indirect DOC method was greater than that of the direct method, as shown by its larger rsd values (Table 5). Since indirect DOC is the difference between TDC and DIC, its associated rsd contains the propagated error from both the TDC and DIC analyses.

The discrepancies between some of the paired direct and indirect DOC values possibly resulted from problems with determining DIC values which were required for calculation of indirect DOC. For S-55, Omega-9, 150-Ton, and Oxy-6 gas condensate (Table 5), TDC values 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 values for DIC were less than two percent (Table 5), several of the process waters exhibited TDC values that were lower than values obtained in previous analyses. The following are offered as possible origins of this problem. (i) Samples containing DIC greater 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 this same stock gave 100-percent recovery. It is unknown whether this was a problem with inadequate acidification/purging or with inefficient

absorption of large dosages of CO_2 by the coulometer solution. The latter was not a problem when the same amount of CO_2 was generated by the high-temperature or UV-persulfate units, where the CO_2 is presumably released over a longer time interval. (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°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 solutions of 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).

Recalcitrant compounds could probably be more effectively oxidized by using ozone/oxygen for the carrier gas through the photooxidation unit. This would promote formation of hydroxyl radical [21]. A problem would be selectively removing residual ozone from the carrier gas stream prior to its entry to the coulometer.

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 μ L; 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; maintenance was limited to replacement of worn pump tubing and replenishment of persulfate reagent. One of the few disadvantages was that the 200- μ L 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 also can be easily automated.

A cost comparison of the UV-persulfate system and the Coulometrics high-temperature total-carbon analyzer showed that the UV-persulfate system (\$8,500) was slightly less expensive than the Coulometrics analyzer (\$9,200). The photochemical system was 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; combustion tube and catalyst lifetimes are a function of the concentration and number of process water sample injections.

Based on recoveries of the potassium acid phthalate standards (Tables 2 and 3), 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 titration system for analysis of oil shale wastewaters on the basis of ease of operation, downtime, and maintenance costs, while maintaining accuracy and precision of sample recovery.

A major question that has not been addressed relates to the analysis of total carbon (TC). This involves both dissolved and suspended forms; the latter includes particulate and colloidal forms. The major problem with determining TC (TOC and TIC) is representative subsampling. Particulate sampling is biased when a syringe is used for high-temperature combustion, but the combustion process itself should not be a problem. Particulate analysis with the UV-persulfate oxidation system may not be possible because the particulates will float to the surface of the reactor fluid or sink to the bottom. Two possible approaches to the subsampling problem are (i) collection of suspended materials on quartz filters followed by introduction to the combustion furnace tube with a ladle or boat assembly and (ii) homogenization of the sample by ultrasonication followed by syringe subsampling for either combustion unit.

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TABLE 1--Origins of oil shale process wastewaters used in comparison study.

Process Water	Water Type	Retort/Process	Shale Source	Retorting Atmosphere	Maximum Retorting Temp. (°C)	Operator/Collection Date
<u>Field In-Situ Retorts</u>						
Oxy-6 RW	RW ^a	retort #6/MIS ^b	Logan Wash, CO	air/steam	unknown ^c	Occidental Oil Shale Inc., 1979
Oxy-6 GC	GC ^d	retort #6/MIS	Logan Wash, CO	air/steam	unknown	Occidental Oil Shale Inc., 1979
Geokinetics	RW	retort #9/TIS ^e	Book Cliff, UT	air	unknown	Geokinetics Inc., 1978
Omega-9	RW	site #9/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
<u>Field Surface Retorts</u>						
Paraho	RW	Paraho direct mode	Anvil Points, CO	air/re-cycle gas	750	Development Engineering, Inc., 1977-1978
TV (TOSCO V)	RW	TOSCO HSP ^f	Colony Mine, CO	inert gas	500	TOSCO, March 1981
<u>Simulated In-Situ Retorts</u>						
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

^aRetort water. ^bModified in-situ. ^cRetorting temperatures for MIS field retorts are not accurately known; temperatures may reach 1000°C. ^dGas condensate. ^eHorizontal true in-situ. ^fHydrocarbon solids process.

TABLE 2--Recovery study: High-temperature combustion carbon analyzer.

Compound	DOC Concentration (mg/L)			
	Theoretical (T)	Observed ^a (O)	(O/T) X 100	rsd ^a
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

^an=10 for each standard solution.

TABLE 3--Recovery study: UV-persulfate carbon analyzer.

Compound	DOC Concentration (mg/L)			rsd ^a
	Theoretical (T)	Observed ^a (O)	(O/T) X 100	
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- <u>n</u> -propylpyridine	435.4	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

^an=10 for each standard solution.

TABLE 4--Precision of the purge operation for determining direct organic carbon in a composite sample of nine oil shale process waters.

<u>Purge Station</u>	<u>DOC^a (mg/L)</u>	<u>rsd</u>
1	6244	0.70
	6291	0.50
2	6369	0.69
	6361	0.54
3	6364	0.51
	6328	0.35
4	6369	0.32
	6394	0.19
5	6310	0.45
	6385	0.16

^aeach duplicate is the mean of 5 single-operator replicates.

TABLE 5--Comparison of carbon analyzers: Direct/indirect organic carbon (mg/L)^a in oil shale wastewaters.

Wastewater	DOC (direct)		DOC (indirect) (TDC-DIC)		TDC	DIC	rsd
	rsd	rsd	rsd	rsd			
Paraho							
A (high-temperature)	41809	1.4	43205	0.55	43415	209.8	1.3
B (UV-persulfate)	42066	1.1	42470	0.66	42680		0.66
150-Ton							
A	3147	0.58	2925	1.4	4857	1932	1.8
B	3259	0.46	3128	1.4	5060		0.53
Oxy-6 retort water							
A	2829	0.80	2832	1.6	3817	984.9	1.0
B	2942	0.40	2967	0.79	3952		0.54
Geokinetics							
A	1627	1.1	1680	3.0	3674	1994	0.67
B	1656	0.55	1688	1.3	3682		0.45
TV							
A	2651	0.23	2545	0.81	3370	824.8	0.54
B	2726	0.61	2661	1.3	3486		0.97
Oxy-6 gas condensate							
A	651.7	2.6	522.0	3.7	2735	2213	0.38
B	641.0	0.51	653.0	2.4	2866		0.47
S-55							
A	2213	0.40	2256	2.1	2595	339.5	1.6
B	2285	0.34	2294	0.63	2633		0.51
Omega-9							
A	694.7	0.34	732.0	6.5	2119	1387	1.3
B	718.4	0.44	787.0	2.5	2174		0.29
Rio Blanco sour							
A	206.3	1.4	191.3	2.7	555.6	364.3	1.4
B	207.0	1.3	183.8	3.0	548.1		0.47

^amean of 10 single-operator replicates.

Figure Captions

FIG. 1--Terminology for carbon classifications used in carbon analysis.

FIG. 2--Schematic of high-temperature combustion apparatus.

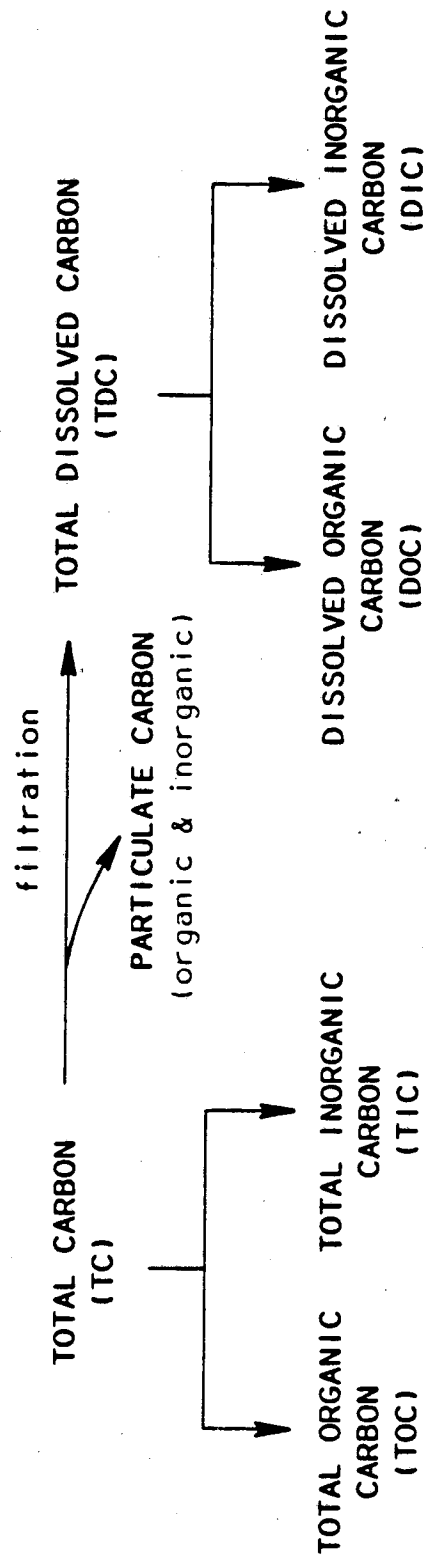
FIG. 3--Schematic of UV-peroxydisulfate low-temperature oxidation apparatus.

FIG. 4--Schematic of acidification/purge apparatus for inorganic carbon.

FIG. 5--Coulometric titration of carbon dioxide; proposed scheme.

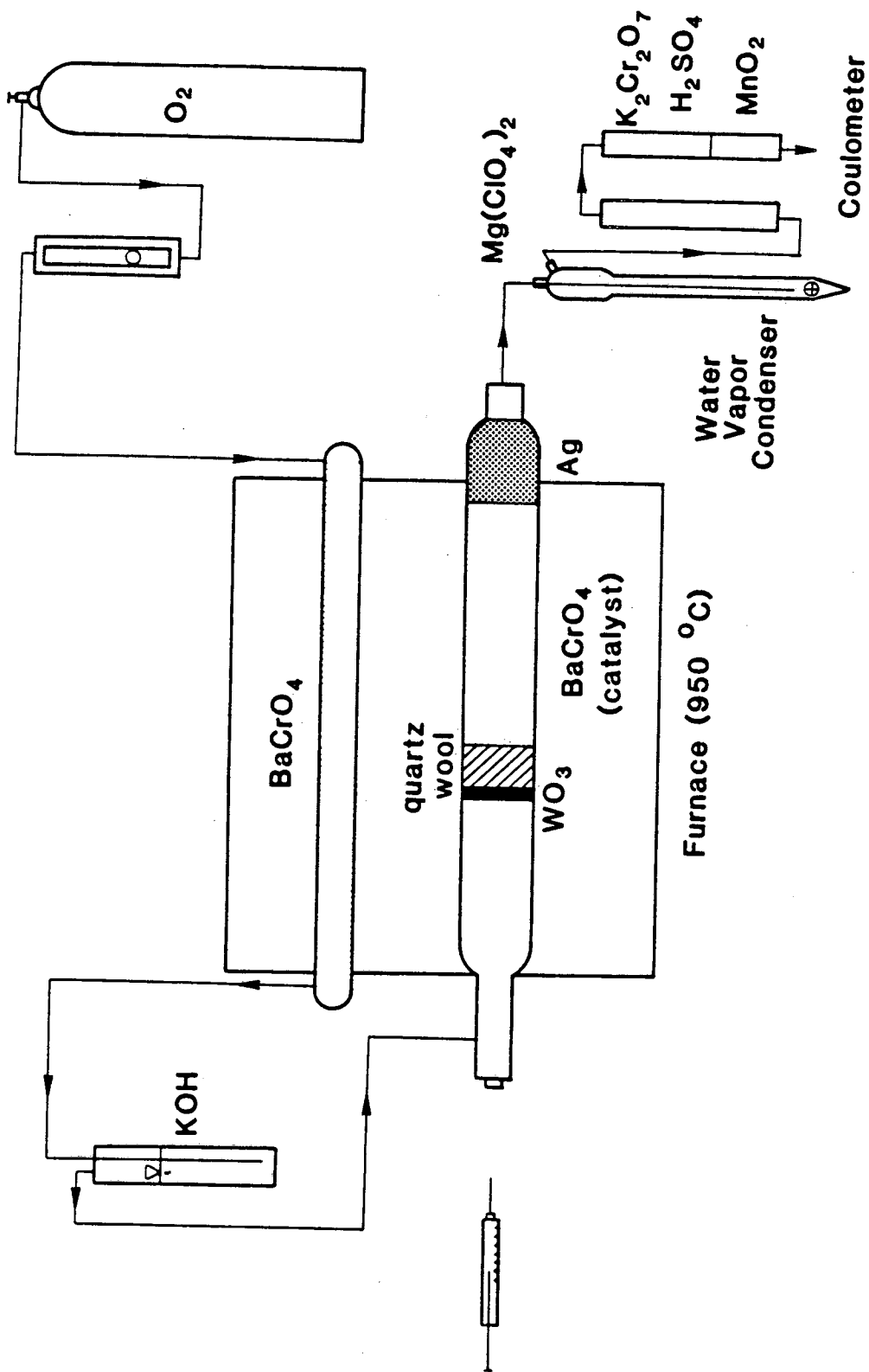
FIG. 6--Comparison of percent recovery means (X) and ranges (---) for standard solutions; concentrations of compounds are identical to those presented in Tables 2 and 3.

FIG. 7--Time-course purge study for direct organic carbon determination.



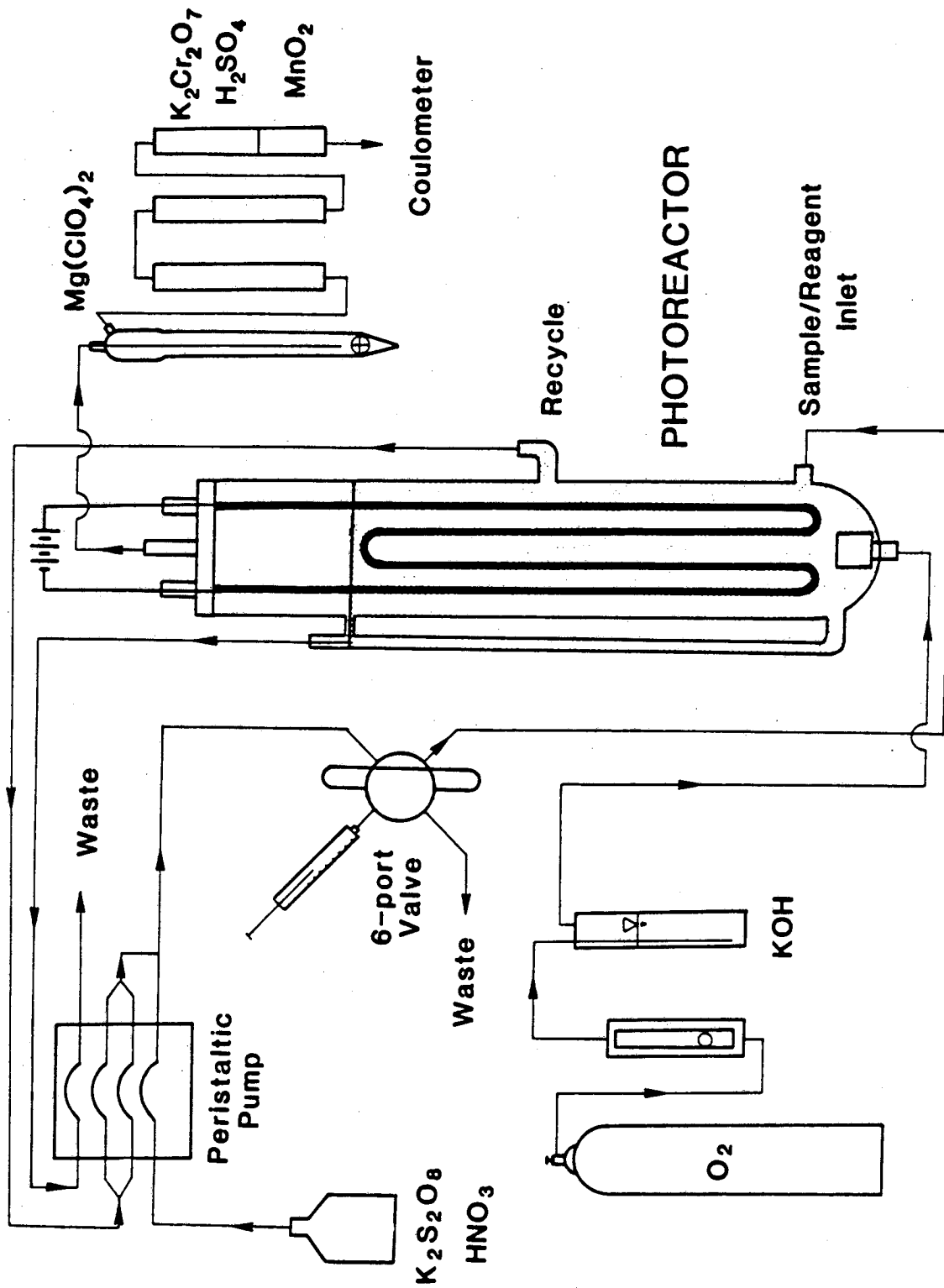
XBL 832-8330

FIG. 1



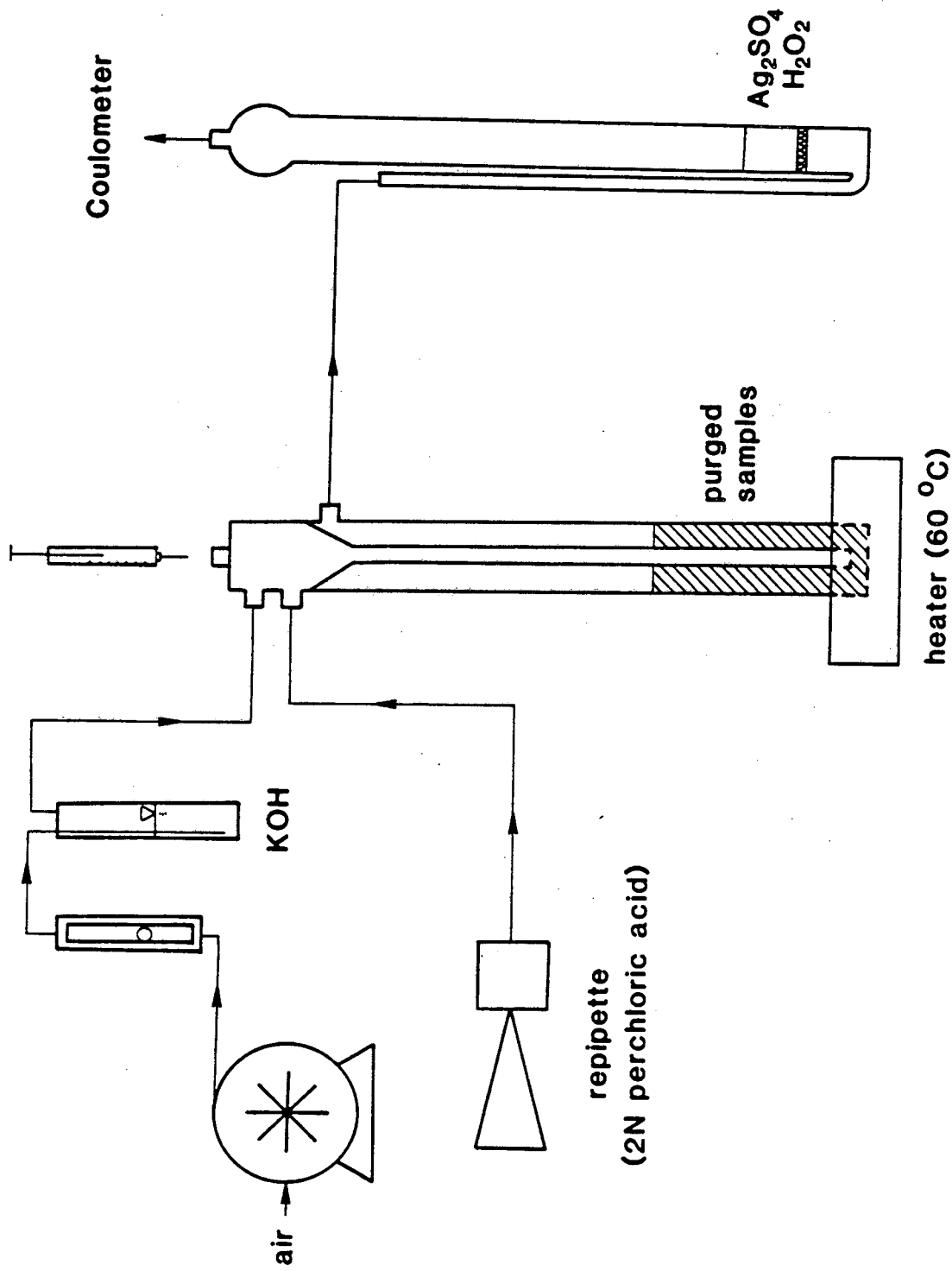
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FIG. 2



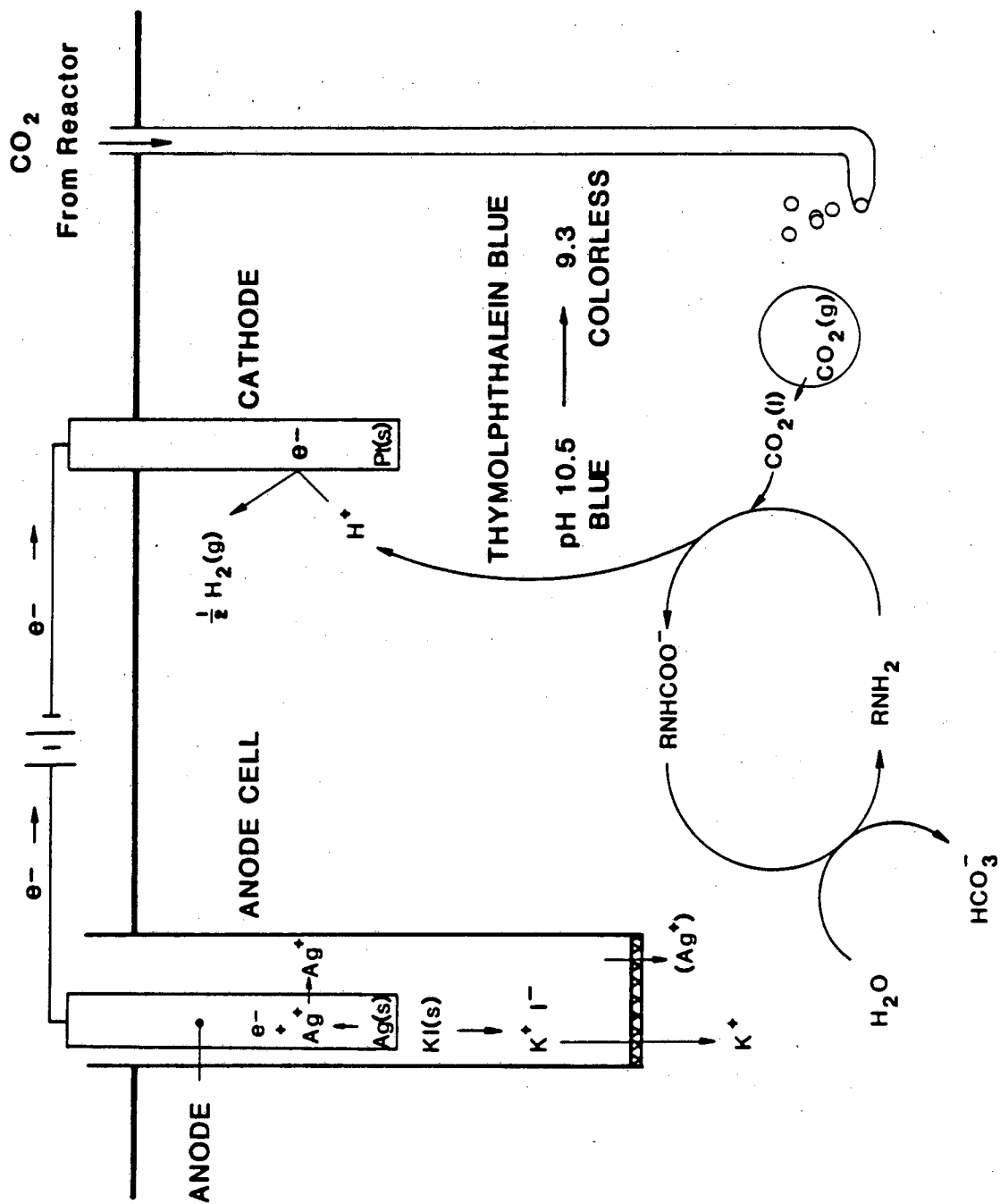
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FIG. 3



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FIG. 4



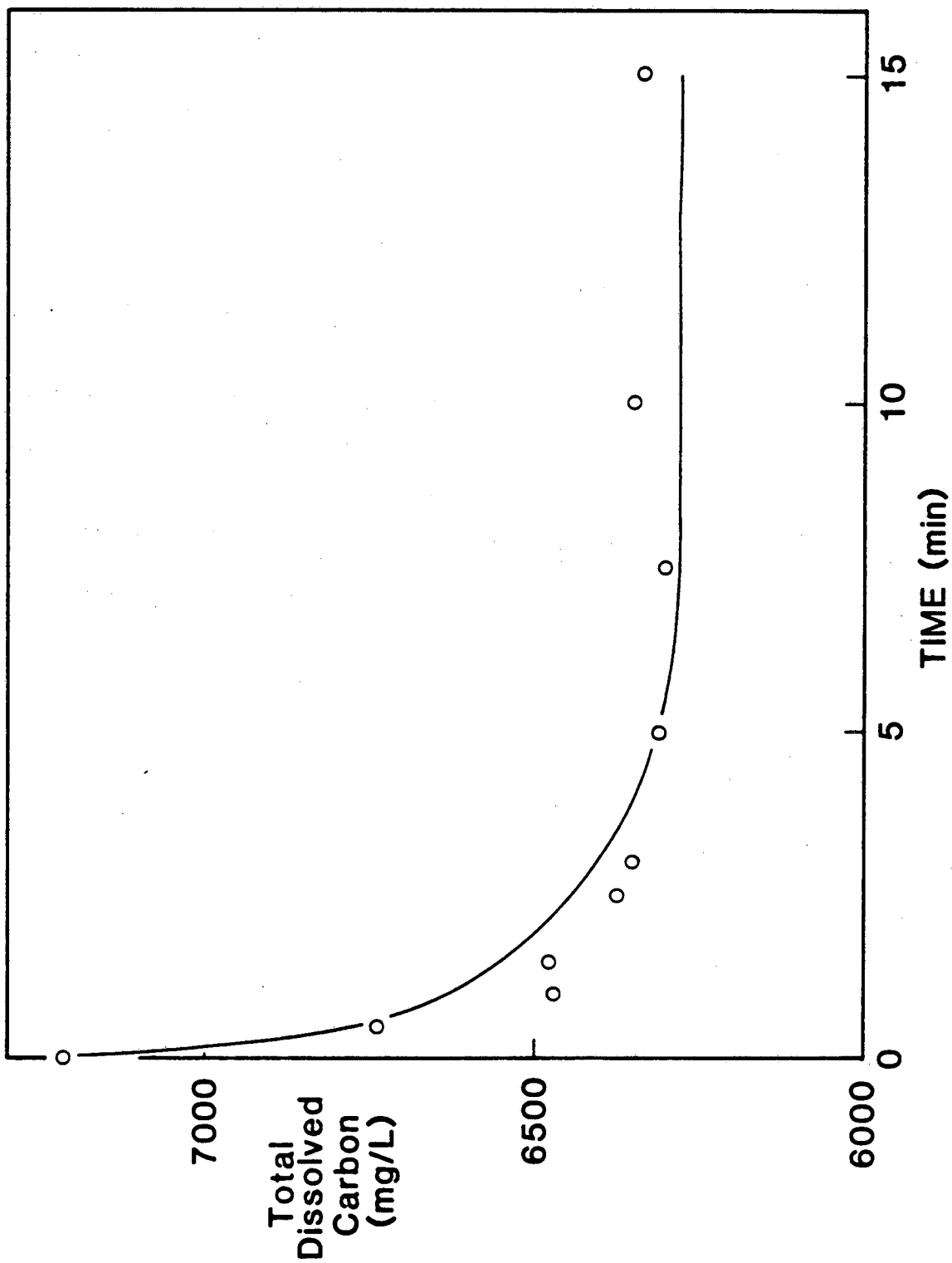
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FIG. 5

Compound	UV-Persulfate Unit			High-Temperature Unit		
	85	100	115	85	100	115
potassium acid phthalate	X-----	X---
potassium acid phthalate		X			X	
potassium acid phthalate		X			X	
phenol		X			X	
acetonitrile	X-----		---X---
3,5-dimethylpyrazole	X	X
pyridine		X			X	
2-methylpyridine		X			X	
4-methylpyridine		X			X	
2,4-dimethylpyridine	X	X
2,6-dimethylpyridine		X			X	
2,4,6-trimethylpyridine		X			X	
2,3,6-trimethylpyridine		X			X	
2-ethylpyridine		X			X	
3-ethylpyridine	X	X
3-ethyl-4-methylpyridine		X			X	
2-n-propylpyridine		X			X	
2-methylpyrazine		X			X	
cyanuric acid (0.2 - 9.5) <<					X	

XBL 833-8773

FIG. 6



XBL 832-8328

FIG. 7

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