Principle of Operations

The detector works by converting all organic carbon to carbon dioxide and then detecting the carbon dioxide. The conversion is accomplished by oxidizing an acidified sample using peroxydisulfate and ultraviolet light. (The sample is acidified to shift the CO2 (aq) bicarbonate equilibrium to CO2(aq)). The sample is then passed to a gas transfer module. The module consists of two spiral channels separated by a micro-porous Gortex membrane. One channel has a flow of de-ionized water and the sample travels through the other channel. As a CO2 peak passes through the module a fraction of the CO2 is transferred across the membrane to the deionized water stream. The CO2 then is hydrated and carbonic acid is formed. The carbonic acid is then detected using a flow through conductivity cell. The conductivity signal is used to calculate the amount of CO2 in the deionized water. This will be proportional to the amount of CO2 in the sample stream.

Detailed Description

The sample enters the instrument and ammonium persultfate(13 wt. %) and phosphoric acid(6M) are added to the sample stream. (Refer to Figure 1) The flow of each is 2uL/min. This flow may need to be adjusted depending on the total flow, concentration of organic and buffer strength of the eluent.. Two syringe pumps are used to control the addition.

There have been two methods to introduce the sample. The first is to draw a small amount of the column effluent into the instrument using the peristaltic pump. The other method is to allow the total effluent of the column to flow through the detector. Namguk is using the later method. (Figure 1 shows only the peristaltic pump method)

The sample then passes through an inorganic carbon removing module. This is installed to remove any inorganic carbon contained in the original sample. The inorganic carbon was found to elute with the low molecular weight organics. The module is a tube and shell design. The tubes are polypropylene with an inside diameter of 380um, a length of 5in and a pore size of less than 0.2um. There are approximately 50 tubes per module. On the shell side a vacuum of 20 in of Hg is maintained. The vacuum pump is a small diaphragm pump.

The sample then enters the UV reactor. This is a coil of Suprasil quartz tube (0.1in OD and 0.05in ID) with a low pressure mercury lamp in the center of the coil. The lamp envelope is also made of Suprasil. The coils have an ID of 0.4in and the coil is 2.5in long. The internal volume of the reactor is 1mL. The reactor converts all organic carbon to CO2.

The gas transfer module is constructed of two stainless steel discs with a spiral channel machined into one of the faces of each disc. The two discs bolt together with a membrane separating the two matching channels. The deionized water flowing on one side of the module is controlled by the peristaltic pump. This water then flows through a conductivity cell.

The deionized water loop is a 150mL reservoir and small centrifugal pump and a mixed bed ion exchange resin. The water in the loop is circulated at a flow of ca 300mL/min and

the resin is contained in a PVC tube 1in ID and is 8 in long. The water from the conductivity cell is returned to the loop.

The inorganic carbon removing module, the reactor and transfer module are very unique components that took some time to develop. I can imagine that the other components could be found either in the lab or easily purchased, however these parts would be difficult to substitute.

Differences From Production Unit

Most all the components are contained in a stock Model 800 instrument and the conversion is mainly replumbing the instrument. Figure 2 contains a schematic of the original plumbing configuration. Much of the plumbing change is to disconnect the inorganic measurement components, add the IC removing module, change membranes, change the sample flow direction through the transfer module, connect the effluent of the conductivity cell to the sample peristaltic pump. (This is no longer done—the sample flow is controlled by the HPLC pump and restrictors are used to control the DI flow)

Much of the plumbing is done on what we call the 'DI Loop.' Many of the components are contained on this assembly. Figure 3 is a drawing of this assembly. What follows are steps to change the instrument

1. The membrane in the transfer module needs to be changed. The stock membrane is solid Teflon. A micro-porous membrane needs to be used to obtain a good signal. I used 0.45um pore Gortex however Celgard polypropylene might also be adequate. The DI loop assembly will have to be removed and the transfer module removed from the assembly. The transfer module is unbolted. The most convenient method to install the membrane is to hold it in an embroidery hoop. The hoop is laid on the bottom half of the module and the top is place over it. There are positioning holes that help line up the two halves. Poke holes through these and place pins in them. Then install the bolts. Tighten opposite bolts like a car wheel until all are very snug. Section 6 of document DIN00026 contains detailed instructions on how to remove the DI Loop.

2. The connections to the transfer module have to be swapped. Disconnect the tube from the UV reactor to the transfer module this tube will have to be bent a little to reconnect it to the other port. The other port has a straight piece of stainless steel tube with pump tubing slipped over it. If the entire effluent from the column is sent to the instrument then this tube needs to be disconnected from the peristaltic pump. If this is not done the system will overpressure and component damage will occur.
3. The pump tubing connected to the sample outlet of the IC transfer module is removed and connected to the brown PEEK tube coming from the DI outlet of the TC transfer module after the PEEK tube is removed from the solenoid valve. The front panel of the instrument is removed to gain access to the tube connecting to the valve. The outlet of the pump then needs to be connected to the fittings on top of the bubble trap.

4. The tee connecting the reactor inlet tube needs to be removed. The inorganic carbon removing(ICR) module needs to be installed before the reactor. The normal configuration of the ICR is pump and fiber module integrated in a package. Using it for this application one has to be concerned with band broadening. So the fiber module is placed close to the reactor. The general principle is to use the shortest length of tubing with the smallest ID. I used 0.03in ID tubing. This seemed to be adequate for the column efficiencies observed by Namguk. (We were making changes on the fly and the plumbing got a little messy.)
5. The other end of transfer module is connected to the cross where the outlets of the syringe pumps are connected.
6. The external pressure regulator is bypassed and the column effluent can be connected directly to the cross.

The instrument is operated using Turbo software. This software samples the conductivity cell once every 3 seconds. The instruments analog output was connected to the data acquisition system that performed peak integration.

Some notes on operation

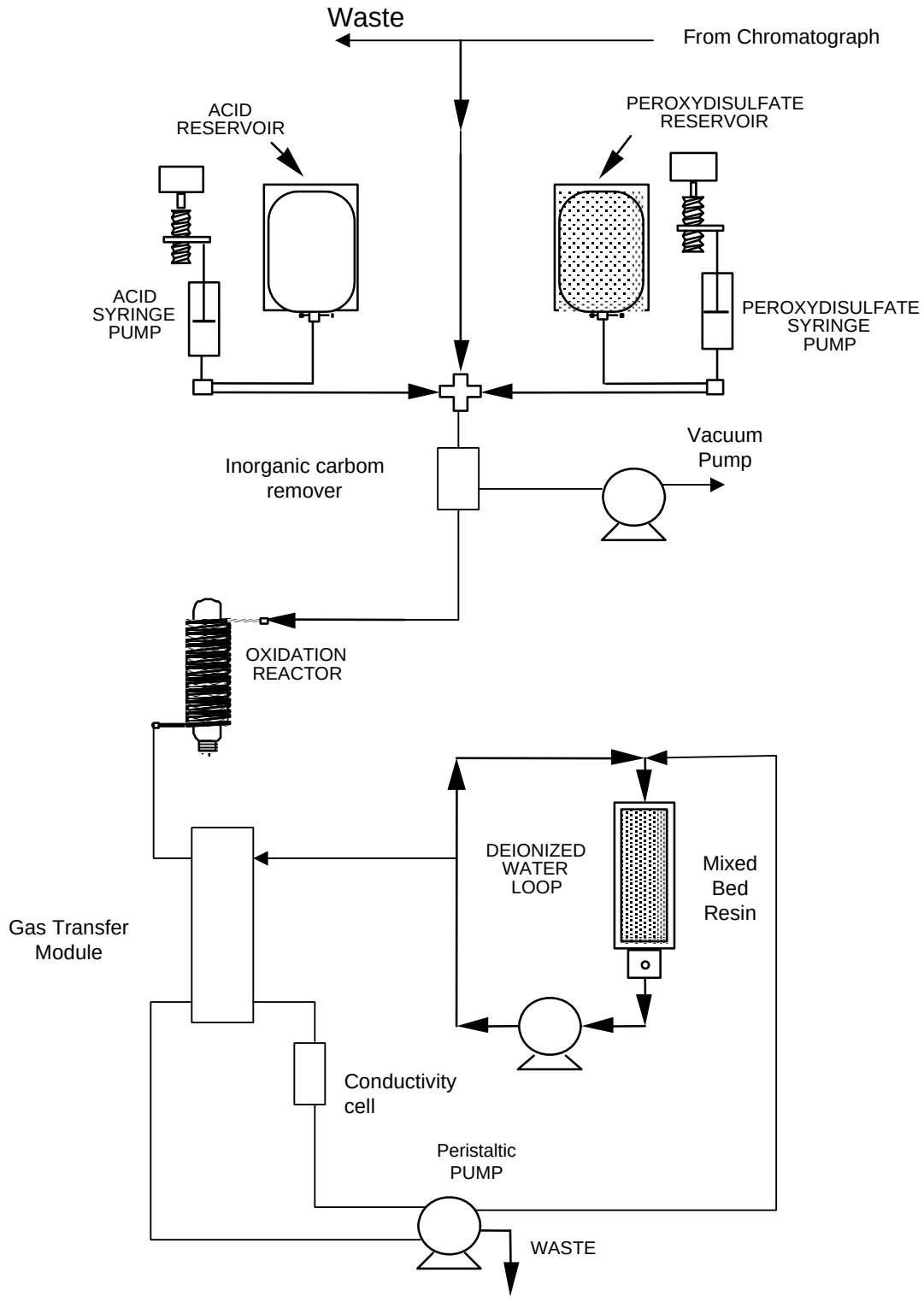
There have been times when the syringes have been exhausted during the course of an analysis. The operator has to keep track of this.

It was found that ppm concentrations of nitrate interfere. It appears that nitrate is photolysed to produce some nitric oxide. The nitric oxide crosses the membrane and is oxidized to nitrite and or nitrate on the DI side to produce a signal. This has not been fully investigated.

I can't say which configuration is better. The entire column effluent or a small amount would be better. Both have been used and Namguk has decided that the entire is better.

The transfer module channels are different sizes on the two halves. The sample side is twice as wide. This means that for the lowest band broadening the sample side should flow should be double of the DI so the velocities are identical. If peaks are multi-minutes wide this will not be a concern.

Many other operational notes can probably be gathered from Namguk.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ACID
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PUMP
PEROXYDISULFATE
SYRINGE
PUMP
Inorganic carbom
remover
Vacuum
Pump
OXIDATION
REACTOR
DEIONIZED
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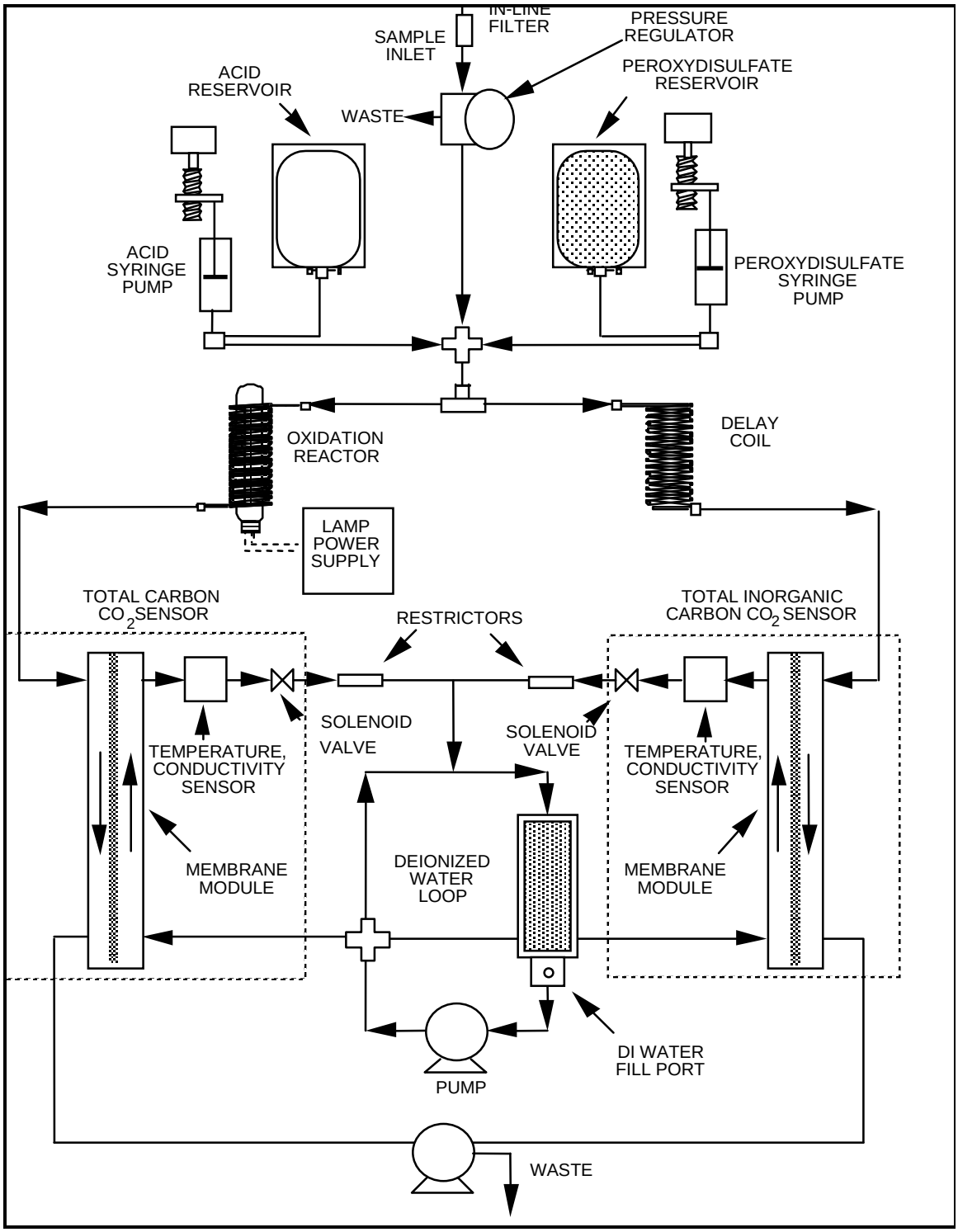
Resin
Gas Transfer
Module
Conductivity
cell
Peristaltic
PUMP
WASTE

Figure 1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PEROXYDISULFATE
SYRINGE
PUMP
OXIDATION
REACTOR
DELAY
COIL
LAMP
POWER
SUPPLY
TOTAL CARBON
CO2 SENSOR
RESTRICTORS
TOTAL INORGANIC
CARBON CO2 SENSOR
SOLENOID
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Figure 2

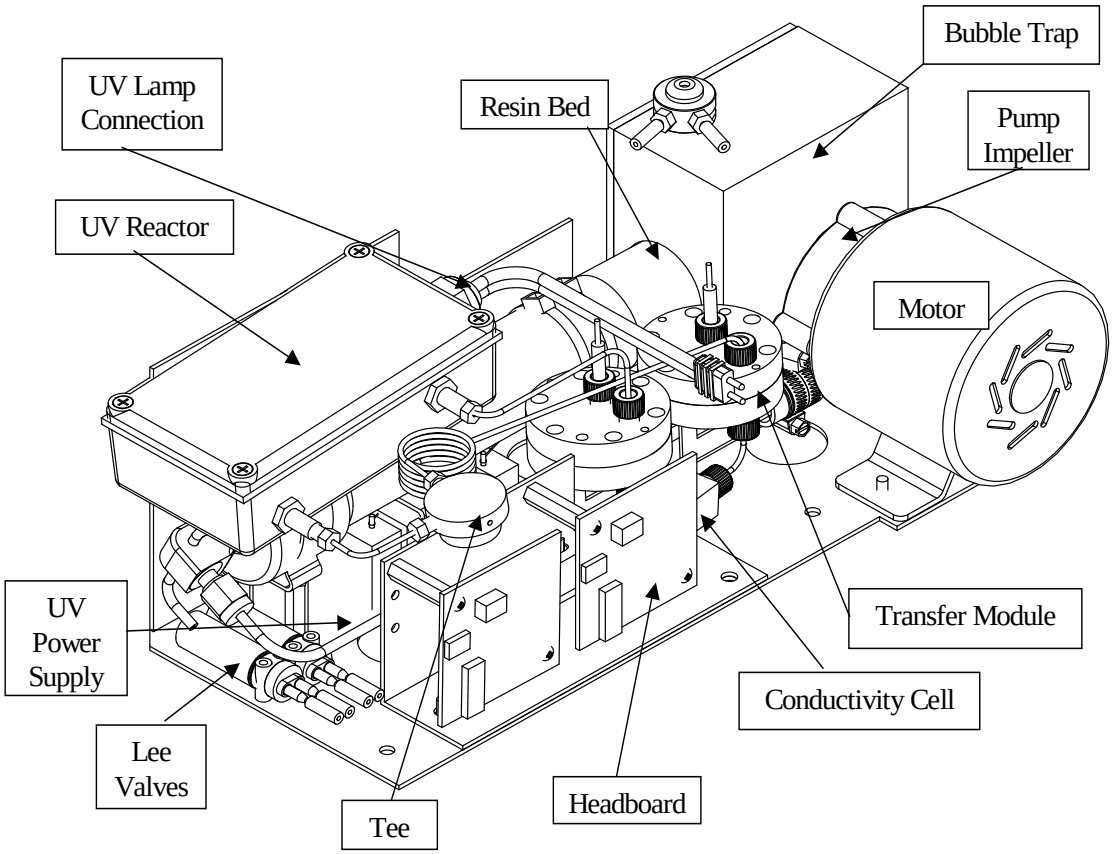
Bubble Trap
UV Lamp Connection
Resin Bed
Pump Impeller
UV Reactor
Motor
UV Power Supply
Transfer Module
Conductivity Cell
Lee Valves
Headboard
Tee

Figure 3