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ANNUAL PROGRESS REPORT
submitted to
OCEAN MARGINS RESEARCH PROGRAM
OFFICE OF HEALTH AND ENVIRONMENTAL RESEARCH, ER-76
THE DEPARTMENT OF ENERGY, WASHINGTON, D.C. 20545

Development of Gas Chromatographic System for Dissolved Organic Carbon Analysis in Seawater

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Lamont-Doherty Geological Observatory
Columbia University, Palisades, NY 10964

December 1992

ABSTRACT

During the first six months of this two-year grant, we have completed the construction of the analytical portion of a prototype gas chromatograph-based system for the analysis of dissolved organic carbon in seawater. We also have begun testing the procedures to be used to cryogenically concentrate and transfer carbon dioxide from the oxidizing atmosphere of the high-temperature furnace into the reducing hydrogen carrier gas of the gas chromatograph. During the second half of the first year, we will construct the high-temperature catalytic oxidation furnace and test the entire system on laboratory-prepared aqueous solutions of various organic compounds. Also during this period, we will take part in an initial scoping study within the Cape Hatteras field area on board the R/V Gyre. This study will involve both the collection of samples of seawater for organic and inorganic carbon analysis and the measurement of surface-water pCO_2.

1. INTRODUCTION

This is a second-year continuation proposal for the two-year study "Development of gas chromatographic system for dissolved organic carbon analysis in seawater", which is funded for the period June 1, 1992 through May 31, 1993. The purpose of this funded study is to develop an alternative to the commonly used infra-red analysis of the oxidation products of dissolved organic matter in seawater and to test the system on samples collected at sea. The progress made on this project to date is described in this report.

2. PROGRESS TO DATE

Figure 1, which is taken from figure 2 of the original proposal, illustrates the proposed analytical system which was to be constructed under this grant. The heavy line divides the system into two major subsystems-- the high-temperature catalytic oxidation furnace and gas-drying components on the left and the cryogenic trapping and gas chromatograph-based analytical subsystem on the right. Assembly of the latter subsystem has been completed and initial testing has begun. As originally planned, the construction and testing of the former will take place during the second half of the first year of the grant.

Since the compact Shimadzu Mini-2 gas chromatograph which we use in our other carbon dioxide analysis systems has been discontinued, we have selected an SRI gas chromatograph (Model 8610, manufactured by SRI Instruments of Torrance, California) as the analytical component of our system. Although SRI is prepared to equip their gas chromatograph with a nickel methanization catalyst, we have extensive experience preparing and using catalysts of ruthenium and prefer them to those using nickel because of their reduced susceptibility to poisoning and their relative insensitivity to oxygen. Consequently, we have equipped our gas chromatograph with an in-house constructed catalyzer and separate temperature controller. We have further adapted the gas chromatograph to our needs by bringing the carrier gas out to the calibration and cryogenic trapping and injection modules rather than use the original syringe injection port or alternative gas sampling valve.

The 8-port 2-loop calibration gas injection valve can be located in any of several points in the various gas streams of our analytical system. With the valve located in the hydrogen carrier gas line of the gas chromatograph, it is possible to inject and analyze any of a number of calibration gases directly, without cryogenic trapping of the CO_2. This mode of operation is equivalent to that used

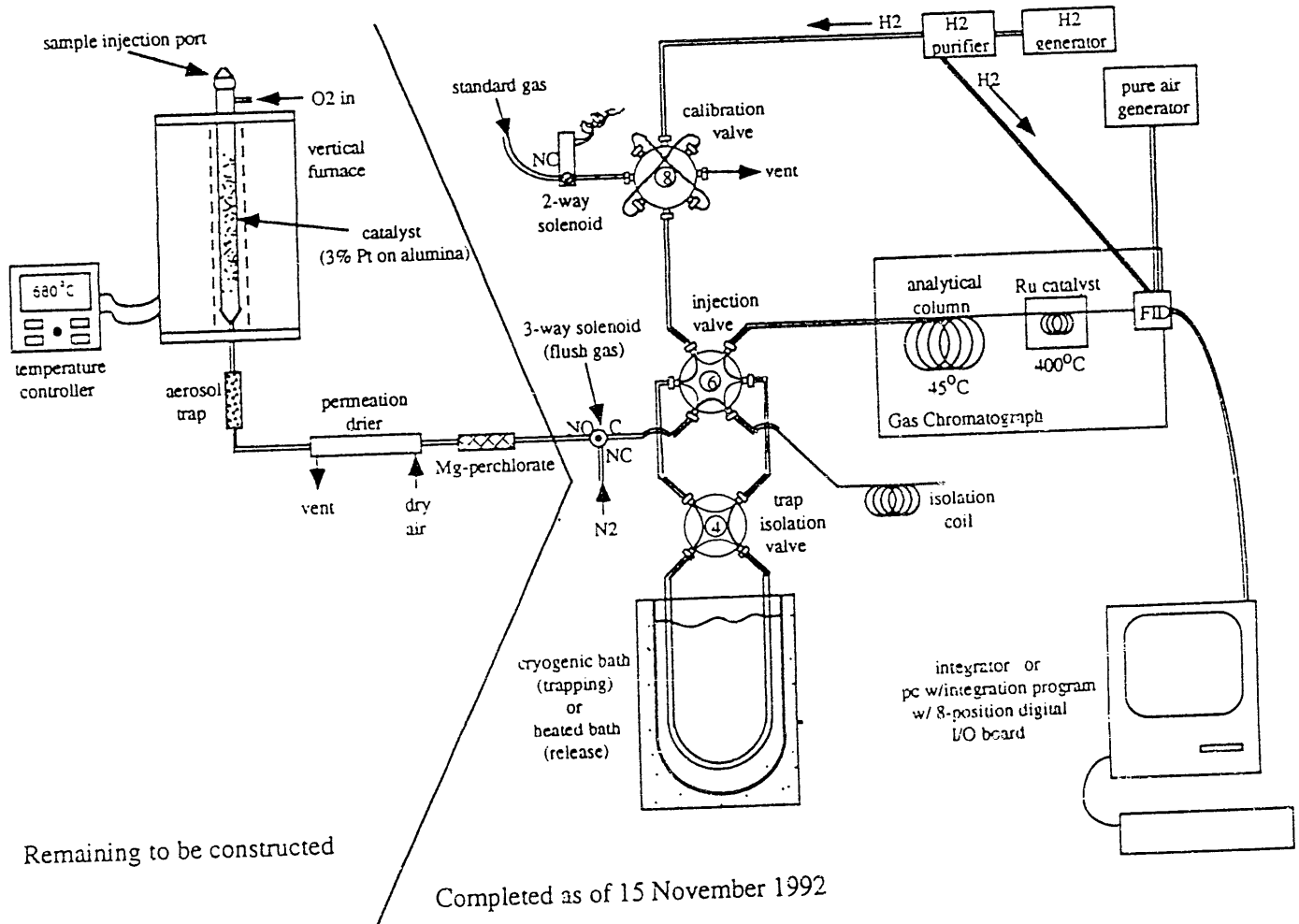

Figure 1. Gas chromatograph-based system for the analysis of dissolved organic carbon in seawater. During the first six months of the grant, the analytical portion of the system, to the right of the heavy diagonal lines, has been constucted and is currently undergoing testing. The high-temperature catalytic oxidation furnace will be constructed during the second half of the first year of the grant.

in our gas chromatograph-based system for the analysis of partial pressure of CO_2 in seawater and atmospheric samples. When operated in this mode, the SRI gives a reproducibility (one r.m.s. deviation of the raw CO_2 peak area) of +/- 0.02%, which is slightly better than that which we have normally attained using the Shimadzu Mini-2. It thus appears that high-precision analyses will be possible with the new analytical system, although this precision will be reduced somewhat when the cryogenic trapping of the CO_2 is used to transfer the CO_2 from the oxidizing atmosphere of the furnace to the reducing atmosphere of the gas chromatograph.

In order to test the efficiency of the cryogenic trapping, we have temporarily relocated the calibration valve to the line which provides nitrogen flushing gas to the trap. In this configuration, the calibration runs are made by sweeping the calibration gases (approximately 1 or 0.5 ml of air-CO_2 mixtures) onto the chilled trap, where the CO_2 is retained while the nitrogen sweeps the oxygen and methane from the trap through the isolation coil. The trap can then be isolated using the 4-port valve, heated to release the carbon dioxide, and connected to the carrier gas of the gas chromatograph for analysis. In this configuration, precisions of approximately 0.1% have been attained, and it is anticipated that computer controlled timing of the operation of the valves may improve this value. Ultimately, the calibration valve will be relocated to a position upstream of the furnace, so that calibration runs will duplicate as nearly as possible the oxidation of organic matter in the samples.

3. OTHER ACTIVITIES TO DATE

One or both of the PIs have attended two meetings relating to the Ocean Margins Program. The first, held in July at Woods Hole Oceanographic Institution, was to introduce the biogeochemical participants in the program to the other PIs and to the overall plan for the field program, and was attended by one of us (DWC). The second meeting, held at Brookhaven National Laboratory in September, was attended by both of us. At this meeting the various participants in the OMP worked together to better define the approach to be taken in the field program and to coordinate preliminary studies in the field area. As a result of this meeting, we have arranged to join an expedition to the Cape Hatteras area on board the R/V Gyre in April/May 1993 (Rick Jahnke, Chief Scientist). In addition to collecting water samples for shore-based analysis of DOC and DIC, we plan to operate a discrete seawater-air equilibrator for the determination of surface water pCO2.

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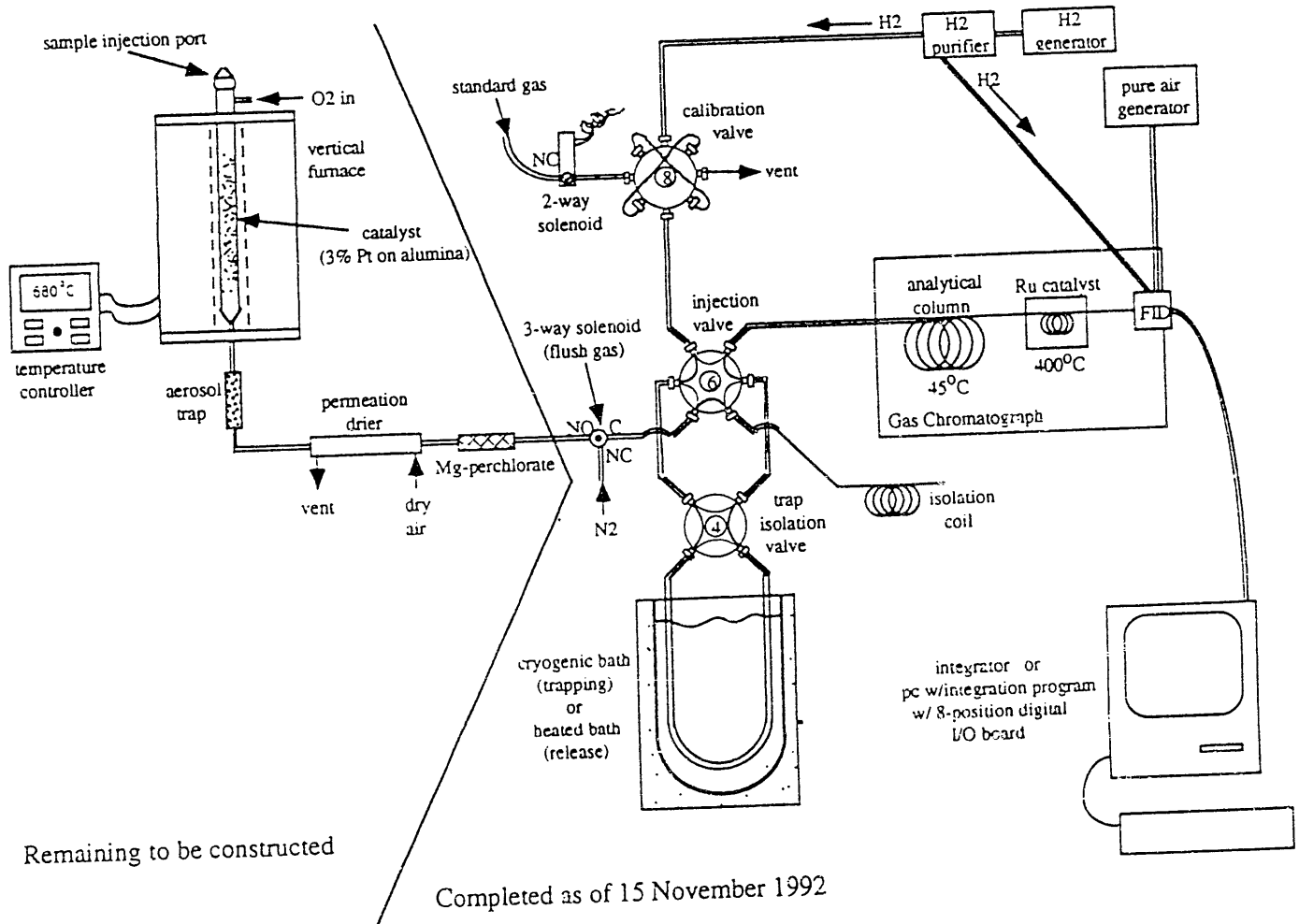

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