CRUDE OIL COMBUSTION AT SEA: THE SAMPLING OF RELEASED PRODUCTS USING REMOTE-CONTROLLED BOATS.

M.C. Bissonnette, M.F. Fingas, R.D. Nelson, P. Beaudry and J.R.J. Paré
Environment Canada
Environmental Technology Centre
Ottawa, Ontario
K1A 0H3

BACKGROUND

Laboratory and tank scale experiments, conducted over the past several years, have shown that burning can be used as an effective means to remove crude oil from the surface of water and reduce the environmental impact of marine oil spills at sea. A management team comprising over 25 agencies conducted a large scale burn experiment 40 km off-shore Newfoundland. The experiment was called NOBE, the Newfoundland Off-shore Burn Experiment. The team monitored the chemicals and particulates released during combustion using two remote-controlled (rc) boats equipped with adapted field instruments.

Remote-control boats were used mainly to ensure the safety of personnel during the experiment. The operators were able to control the location of the sampling boats without being in the direct line of the burn. It protected personnel from the high temperatures, smoke and provided safety in case of an accidental rupture of the boom. The use of remotely operated sampling stations (rc boats) also allowed sampling at a close proximity to the burn and provided the most concentrated samples possible.

This paper deals mainly with the design, development and installation of instruments on the remote-controlled boats.

REMOTE-CONTROLLED BOATS

Four identical remote-controlled boats were built, the plan being to use two rc boats for sampling and have two as backups.

Fourteen-foot aluminum fishing boats were modified with a platform deck for the instruments. Marine grade mahogany plywood covered with varnish (Spar) was used for the deck. Each boat was equipped with a sump pump connected to a water sensor to remove any water accumulation under the deck. A cover was designed and fabricated from aluminized fabric (similar to the material used for fire resistant suits); its purpose was to reflect the heat and keep water from splashing on the instruments.

A Minn Kota electric auto pilot trolling motor was installed on the bow of each boat. A 1/4" thick aluminum bumper was fabricated and installed on the bow to protect the motor. The motor operated on two 12V batteries which provided 4 1/2 hours of

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continuous operation. The motor was controlled by a computer and a program that allowed for speeds from 0 to 9 as well as left/right manual steering. The operator sets the direction and speed of the boat via the computer, then activates the trolling motor's autopilot function. The motor has a built in compass which allows the autopilot to maintain the boat in the desired direction. Whenever the wind or current deviates the boat from its course, an automatic correction takes place. A problem arises with the rc boats as each one weighs 2000 pounds, making it difficult to control by autopilot. So much weight implies a slow response time to steering commands. The addition of a rudder at the rear of the boat allowed better control by diminishing sideways motion.

A black and white video camera with focus and zoom controls was mounted on the central mast of each rc boat and used a low power UHF television transmitter to provide an image to the television located at the master control station. The camera's function was to aid in navigating the boat directly downwind of the boom as the operator was located parrallel to the rc boat. See location of CCG 215 relative to first rc sampling boat in figure 1.

Over 500 kg of rechargeable batteries were required on each boat to power the equipment. The power requirements and instrument layout rationale is described in the next section.

Figure 2 illustrates the key components of each rc boat. The operator has the full control of the boat at the master control station which consists of a notebook computer connected to a DataRadio RF Modem (through the serial port). The station is completely contained in a portable transit case and requires a 12V power source. Another identical RF Modem on the rc boat is connected to the process control system and to the datalogger via serial ports. The process control system sends signals to the Minn Kota Auto Pilot Trolling Motor, the sampling instruments and the video camera.

A Campbell Scientific CR10 Data Logger was used to record data. The sequence of events was programmed in the computer and downloaded to the CR10 via the serial cables and RF modems. The real time data from the CR10 can be viewed directly on the computer screen and the logged data is uploaded directly from the unit. The CR10 recorded data from the instruments and batteries (i.e. current and voltage).

The four sampling boats and the two master control stations were set up in a network in which each components had its own address. All the RF modems were the same which allowed both master control stations to direct all four boats. This provided a backup in case one of the control station stopped working. See figure 3 for a schematic of the possible links between the network components.

The program used to control the rc boats was written in-house using Borland C^{++} 3.1 (Windows version). Each boat had its own window and could be operated simultaneously. The program allowed to control the Minn Kota motor, the video camera, the datalogger and the instruments. Real time status was available for CR10 information, battery current/voltage and ON/OFF status of the instruments.

SAMPLING INSTRUMENTATION

Environmental sampling was performed using a variety of field instruments, each having a specific purpose. Previous laboratory and tank testing had indicated the nature of emissions from *in-situ* burning of oil. A team composed of members from the Emergencies Science Division of Environment Canada and from the Emergency Response Team of the US Environmental Protection Agency selected the target compounds and parameters. The following table is a summary of the sampling instruments chosen for the NOBE experiment. In brackets is the number of units present on each boat.

<u>TABLE 1</u>- Instruments installed on each sampling boat.

Instrument	Air flow rate	Collection media	Sampled parameter
GMW PS-1 High volume air sampler (2)	Average 200 L/min	PUF, glass fiber filter	PAH and total particulates
Anderson 8-stage cascade impactor (1)	28.3 L/min	PUF, glass fiber filter	Particulates less than 10μ
MIE RAM-1 (2)	2 L/min	DL	Real-time total particulates
Gilian 513A pump + cyclone (2)	1.7-2 L/min	PVC, 37mm filter	Particulates less than 5μ
Gilian 513A pump (2)	185-250 cc/min	DNPH tube	Oxygenates
Gilian 513A pump + impinger (2)	90-200 cc/min	Hydrogen peroxide	Sulfur Dioxide
Gilian Aircon 2 pump (2)	2L/min	MCE, 37mm filter	Metals
Summa canisters (4)	500 cc/min & 100 cc/min	6 L	VOC and Carbon Dioxide
Armstrong CD-1 Analyzer (2)	1 L/min	DL	Carbon Dioxide
Neotronics Exotox 75 (1)	300 mL/min	DL	Sulfur Dioxide, Nitrogen Dioxide, Carbon Monoxide
Biosystems Cannonball (1)	1L/min	DL	Sulfur Dioxide, Carbon Monoxide
Sigma Streamline 800 SL water analyzer (2)	N/A	Clean glass jars	Water for chemical and biological analysis
Thermistors/thermocouples (7)	N/A	DL	Air and water temperature

LEGEND:	PUF	Polyurethane foam
	PAH	Polyaromatic hydrocarbons
	DL	Datalogger
	PVC	Polyvinyl chloride
	DNPH	Dinitrophenyl hydrazine
	MCE	Methyl cellulose ester
	VOC	Volatile Organic Compounds

Figure 4 is a schematic representation of the layout of the instruments on the top deck of a rc boat. The layout was designed to have minimum interferences from various pump rates of the instruments. Furthermore, the equipment was balanced on each side of the boat to provide stability. The PS-1 high volume samplers which have the highest pump rate (~200 L/min) were located at the rear, as far as possible from the summa canisters which only collect their samples with a maximum intake of 500 L/min. All the other instruments comprised tubing mounted at regular intervals along the arms of the mast (see figure 5). The mast also supported a small platform onto which the cascade impactor was installed. The impactor was operated at a flow rate of 28.3 L/min and was located about 2 feet away from the closest sampling line, thus not affecting the flow rates. Figure 6 is a cross section representation of the equipment installed on the boats. Note the location of the water sampling line at the bow and of the thermocouples and thermistors at the bow and on the mast.

The PS-1 High volume sampler and the cascade impactor are the only instruments which required AC power. Therefore, an inverter, powered by 8 - 6V batteries was installed under the deck. Two more 12V batteries were sufficient to provide power to the CR-10, the RF modem, the relay junction box and the process control system box. Some instruments had their own power supply: the MIE RAM-1, the Armstrong CD-1, the Exotox 75 and the Cannonball. All Gilian pumps and the Sigma 800 SL water samplers required power supplied by the 12V batteries. The latter instruments were turned on using a relay which closed the circuit providing power to the instrument. Figure 7 is a typical representation of a circuit.

The RAM and Armstrong CD-1 were connected to the CR10 datalogger. The Exotox and the Cannonball had their own internal datalogger and the data was uploaded individually from each instrument at the end of the day.

The following is detailed description of the sampling procedures and the type of analysis performed on each type of sample. This section describes the set-up of the instruments and summarizes the procedure. The analytical results are described in others papers listed in the reference section.

PAH and total particulates (during burn only)

<u>Method 1</u>

High-volume air sampling was performed using a General Metal Works model PS-1 instrument modified to be fitted on the deck of the sample boat. The PS-1 sampling heads were rinsed with hexane prior to loading the media. The sampling media consisted of 3" diameter fiber glass fiber filter and a solvent rinsed PUF - 3" thick, density 0.022 g/cm^3. The media was manipulated with powderless gloves. After the experiment, the filters and PUFs were wrapped in aluminum foil and placed in glass jars. The media were kept in coolers until ready for analysis.

The flow rate varied between 128 and 279 L/min, the lower flow rates corresponding to older instruments. The volume of air passing through the samplers during the experiment varied between 9 200 and 13 600 L.

All pre- and post- weighings of the media were conducted under constant atmospheric conditions. The PUF and fiber filter from the same sampling head were then combined to undergo soxhlet extraction and gas chromatography-mass selective detection (GC-MSD) analysis for PAH.

Method 2

A 8-stage cascade impactor by Anderson was used to collect various fractions of particulates at a constant sampling rate of 28.3 L/minute. The stages collected the following fractions: 10-9μ, 9-5.8μ, 5.8-4.7μ, 4.7-3.3μ, 3.3-2.1μ, 2.1-1.1μ, 1.1-0.65μ and 0.65-0.43μ. The device is used as a substitute for respiratory tract and reproduces the dust collecting characteristics of the human respiratory system. Each fraction of inhaled dust will penetrate the lungs to a different degree. The instrument was mounted on the mast of the rc boat and the unit was rinsed with hexane prior to the experiment.

All quartz fiber filters were weighed under constant atmospheric conditions before and after the experiment. At the end of the experiment, the filters were wrapped in aluminum foil, placed into a labelled envelope and kept in a cooler. The variations in weights were so small that all eight filters for each stack were combined to undergo soxhlet extraction and GC-MSD analysis for PAH.

Particulates-real time (pre-burn, during burn and post burn)

A RAM-1 instrument was used to perform real-time aerosol monitoring and measure relative concentrations of airborne particulates. It generally responds to a physical particle size of 0.1 to 10 micrometers which correspond to respirable particulates. The flow rate of this instrument is 2 L/minute and Tygon tubing was connected from the instrument to the mast to allow sampling at 4-5 feet above deck level. The instrument was connected to a datalogger which recorded the data every minute. The data was imported in a spreadsheet program.

Particulates - less than 5 microns (during burn only)

A cyclone sampler equipped with a Gilian 513A pump was used to trap particulates smaller than 5 microns on a 37 mm diameter PVC filter placed inside a cassette (Tygon tubing connections). Tygon tubing was connected from the instrument to the mast to allow sampling at 4-5 feet above deck level. Flow rates varied between 1.7 and 2 L/min and collected air volumes between 57 and 122 L. The cassette was capped and kept in a cooler.

All filters were pre-weighed at constant atmospheric conditions and weighed at the end of the experiment under the same conditions. The filters were soxhlet extracted and analyzed for PAH content using GC-MSD.

VOC (pre-burn and during burn)

A 6L Summa canister pre-evacuated to 0.05 mm of Hg was used to collect air. Analysis was done for VOC and CO_2 concentrations to study volatile gas displacement. The flow controller (restricted orifice) was adjusted to 500 cc/min for evaporation period and to 100 cc/min for the burn. A particulate filter was connected to the restricted orifice and a stainless steel tubing extension with the end bent at 90°, going above the cover of the boat was attached. The purpose of the bent tube was to keep soot from clogging the system. A schematic representation is shown in figure 8.

Metals (during burn only)

A Gilian Aircon 2 pump was used with a 37 mm diameter cassette containing a 0.8 μ mixed cellulose ester filter to collect air for metal analysis. Tygon tubing was connected from the instrument to the mast to allow sampling at 4-5 feet above deck level. The flow rate of the pump was set at approximately 2 L/minute producing volumes of 62 to 144 L. The cassette was capped and kept in a cooler until analyzed.

All filters were pre-weighed and post-weighed under constant atmospheric conditions. The filters were digested according to a conventional method which uses acid and microwave energy, and analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The elements screened were Mo, P, Zn, Pb, Ni, Fe, Cr, Mg, V, Cu, Ti, Ba.

Oxygenates (during burn only)

A Gilian 513A was used to pump air through a DNPH (2,4-dinitrophenylhydrazine)-silica cartridge attached to a Tygon tube to obtain a sample which was analyzed for aldehydes and ketones. Tygon tubing was connected from the instrument to the mast to allow sampling at 4-5 feet above deck level. The cartridge contained 350 mg of silica coated with 1.0 mg of DNPH. The flow rate was set between 185-250 cc/min and the pumped air volumes varied between 1.1 and 18 L. The cartridge was wrapped in foil, placed in a 40 mL amber vial and kept in coolers. The samples were analyzed by GC-MSD.

CO_2 (pre-burn, post-burn and during burn)

The CD-1 Armstrong carbon dioxide samplers were used to monitor the displacement of gases around the fire and the sampling rate was 1 L/minute. Tygon tubing was also connected to the mast. Data were logged every minute and imported in a spreadsheet program.

CO, SO_2, NO_2 (pre-burn, post-burn and during burn)

The Exotox 75 was used to analyze all three gases mentioned above. It has a flow rate of 300 mL/minute. The Cannonball analyzed for carbon monoxide and sulfur dioxide only, and its flow rate was 1 L/min. Tubing was connected from the instrument to the mast and data were logged every 30 seconds and imported in a spreadsheet program.

SO_2 (during burn only)

The concentration of sulfur dioxide in the air was also measured using the impinger method. It consisted of drawing a known volume of air through a Tygon tube attached to a filter (37 mm MCE, 0.8 μ) contained in a cassette and through a midget bubbler (25 mL) containing 15 mL of 0.3N hydrogen peroxide. The bubbler was attached on the mast and the end of the tubing was connected to the mast arms. The flow rate of the Gilian 513A pump was set between 90-200 cc/min and air volumes varying between 3 and 14 L passed through the impinger.

All filters were transferred to 40 mL amber vials and kept in coolers until analyzed. Subsequent analysis was performed using NIOSH method S308 which consists of titrating the sulfuric acid (from the reaction of sulfur dioxide with hydrogen peroxide) with barium perchlorate and a Thorin indicator.

Water samples

Sigma 800SL samplers were used to collect water samples for biological and chemical analysis. There were two samplers on each boat. One sampler contained 4 x 3.78 L sterile glass bottles with teflon lined caps (biology) and the other contained 24 x 350 mL glass jars (chemistry). The samplers were located on the deck at the rear of the boat. Teflon tubing ran from the sampler to the front bumper and was attached to a pole so that sampling occured 1 meter below water surface.

All samples were collected, placed in refrigerated coolers and shipped within 24 hours of collection. The smaller bottles were sent to the Emergencies Science Division for chemical analysis and the larger bottles were sent to EVS consultants in B.C. for biological testing.

Not all planned samples were collected because of malfunction of the samplers. The instruments were factory set to contain 24 bottles, thus those samples were obtained without problem. The samplers had to be modified to collect the larger jars and the volumes collected were much lower than expected. Testing showed that the shorter arms required to collect the larger jars were not adjusted properly.

LESSONS LEARNED

A few lessons were learned during the experiment. One of them is that corrosion is inevitable at sea. Although the best care was taken to ensure that the instruments were kept dry and away from the water, the salt in the air was enough to corrode many of the metal parts. The Minn Kota motors seemed the most affected by salt since they were used directly in the water. Of all the instruments, only one pump from a cascade impactor seized because of salt air (during practice). This problem was solved by placing the pumps in plastic containers with a few holes to allow air circulation.

Salt water also had some effects on the electrochemical cells of the Exotox and of the Cannonball. The calibration performed at the Coast Guard base was not in line with that done at the dockyard before leaving. This situation was rapidly overcome by performing the calibrations on the dock where the salt content in the air is a closer match to the open sea situation.

Two of Minn Kota motors were damaged. There is a combination of two problems: corrosion by salt water and a delay during the transmission between the RF modems. The computer controls the steering of the Minn Kota trolling motors by sending "start steering" and "stop steering" commands to a process control module on board the sample boats (via the RF Modems). The process control module, which is connected to the trolling motor, uses these two commands to generate a pulse. The width of this pulse controls how much the motor turns. Occasionally the RF Modems would introduce a delay between the "start steering" and the "stop steering" commands. This delay would increase the width of the pulse generated by the process control module. If the delay in communication is 1 second, the steering may be over by a few degrees whereas a delay of more than 3 seconds can be dramatic as it produces a big change in the direction of the boat. In one instance, the delay was so long that the motor made a complete turn along its axis, forcing the motor and damaging it. This problem can be resolved by using a process control module which requires one command to generate a pulse, instead of two separate start/stop commands.

CONCLUSION

The remote-controlled boats were an effective means of collecting environmental samples in a safe and effective manner. The fact that only quality parts were used and a lot of attention paid to details made this a rugged boat which can certainly withstand rougher conditions than those it was exposed to. This design could be adapted to monitor and sample any type of chemical spill on water surfaces.

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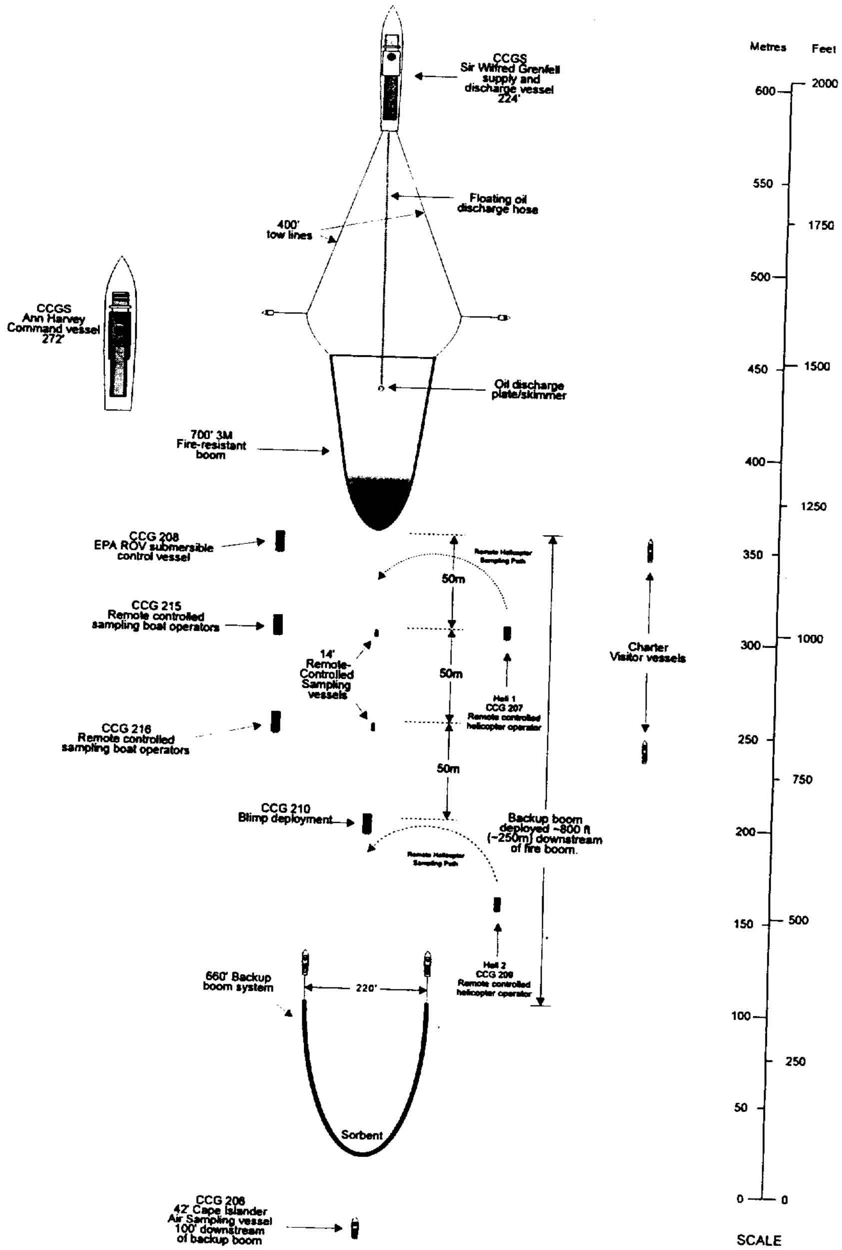

Figure 1 - This scale diagram shows an aerial view of the positioning of some of the vessels used during NOBE.

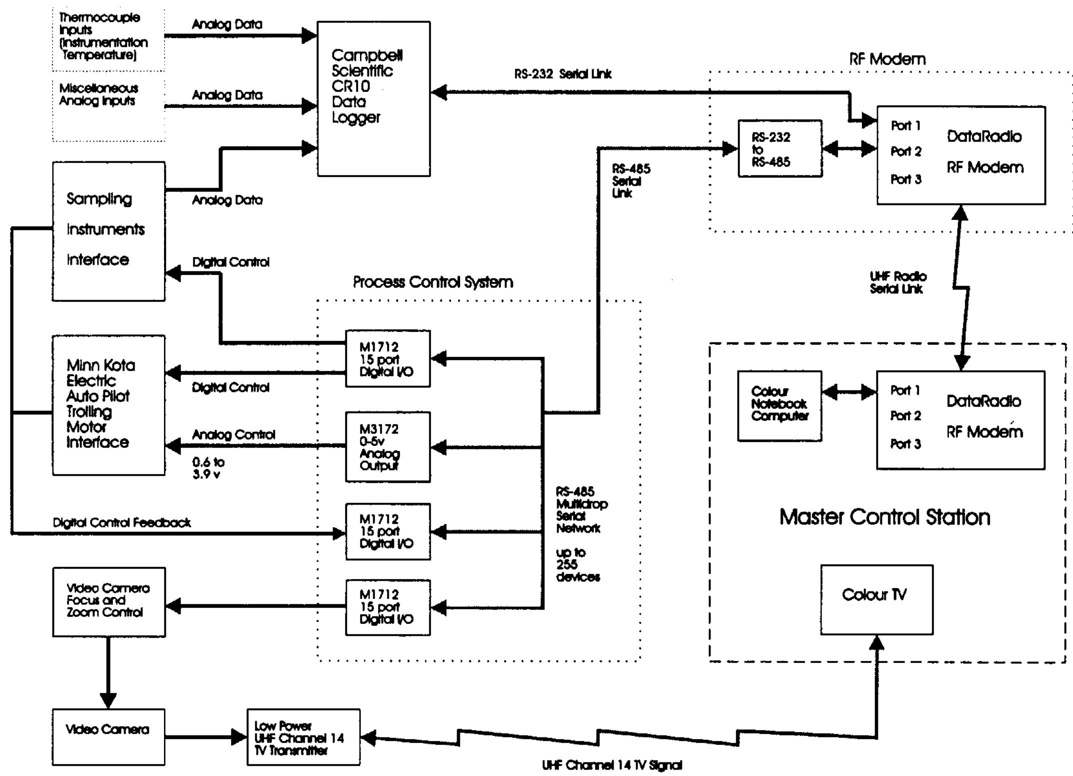

Figure 2 - Sample boat system block diagram.

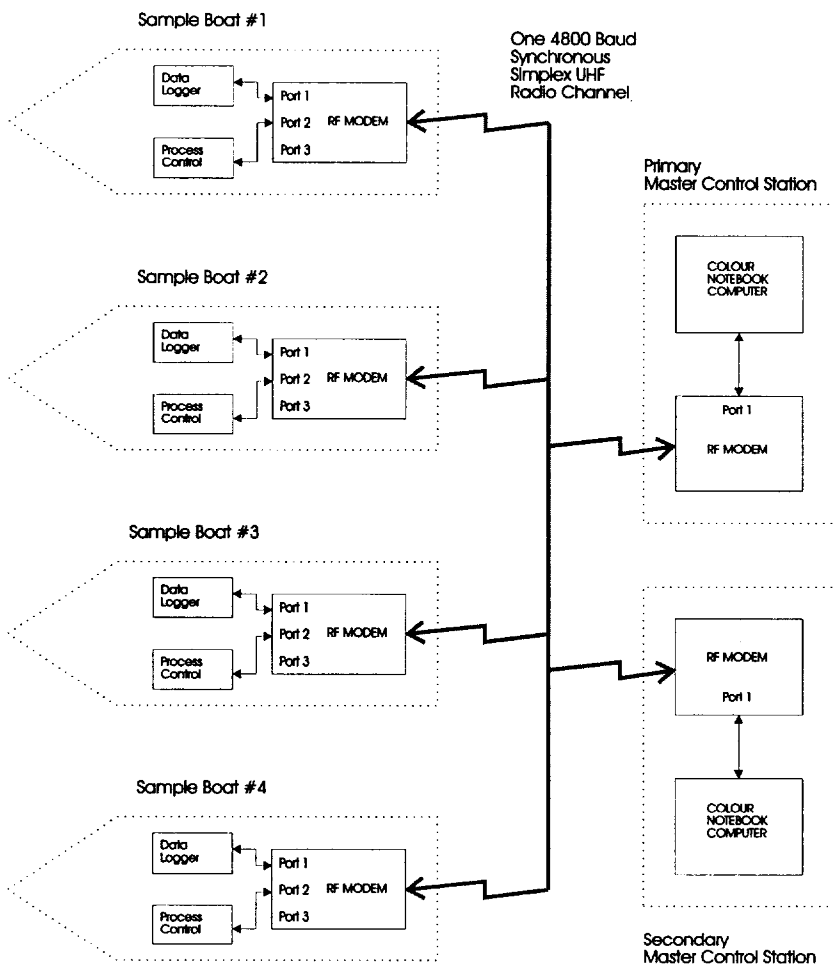

Figure 3 - Sample boat radio network block diagram.

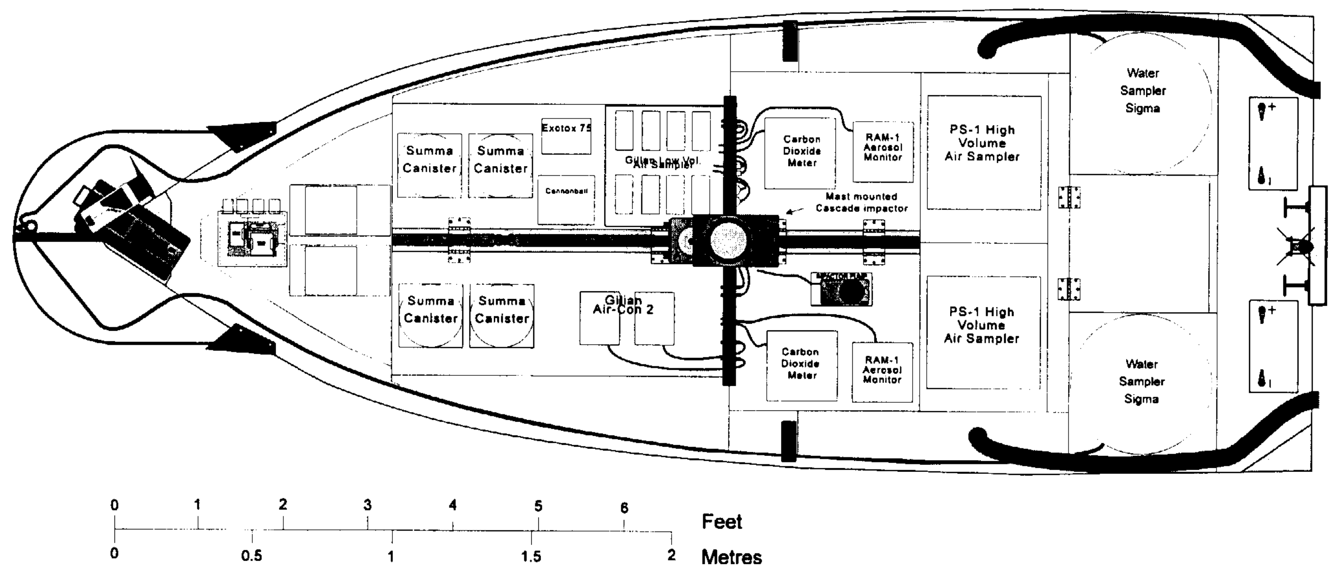

Figure 4 - Schematic representation of the layout of the instruments on the remote-controlled boat.

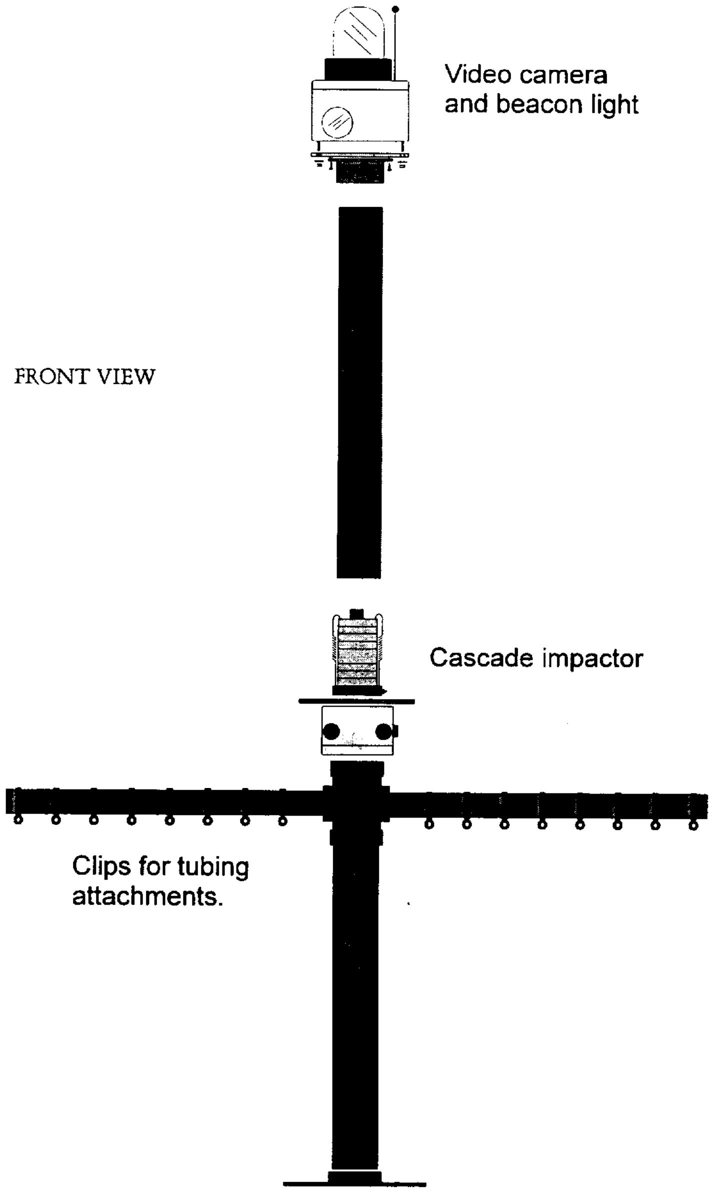

Figure 5 - Mast assembly.

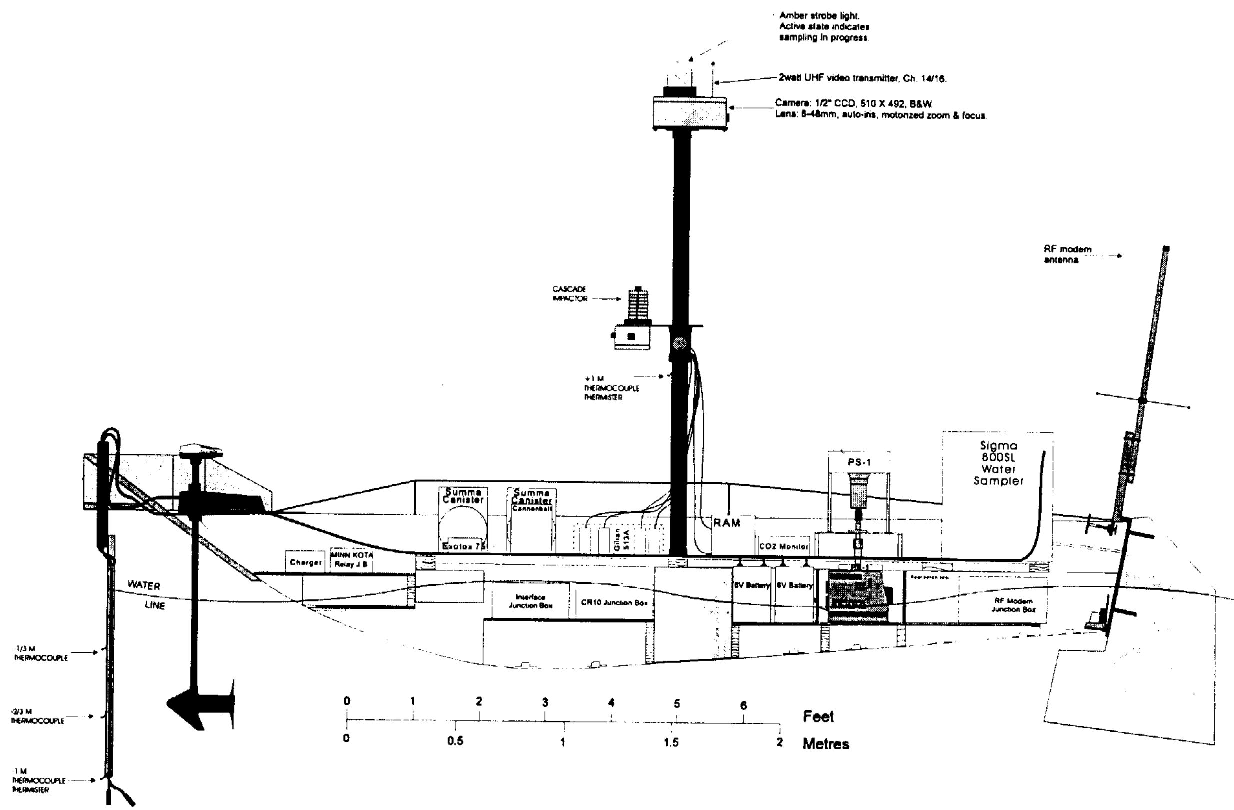

Figure 6 - Right side cross section of the remote-controlled boat.

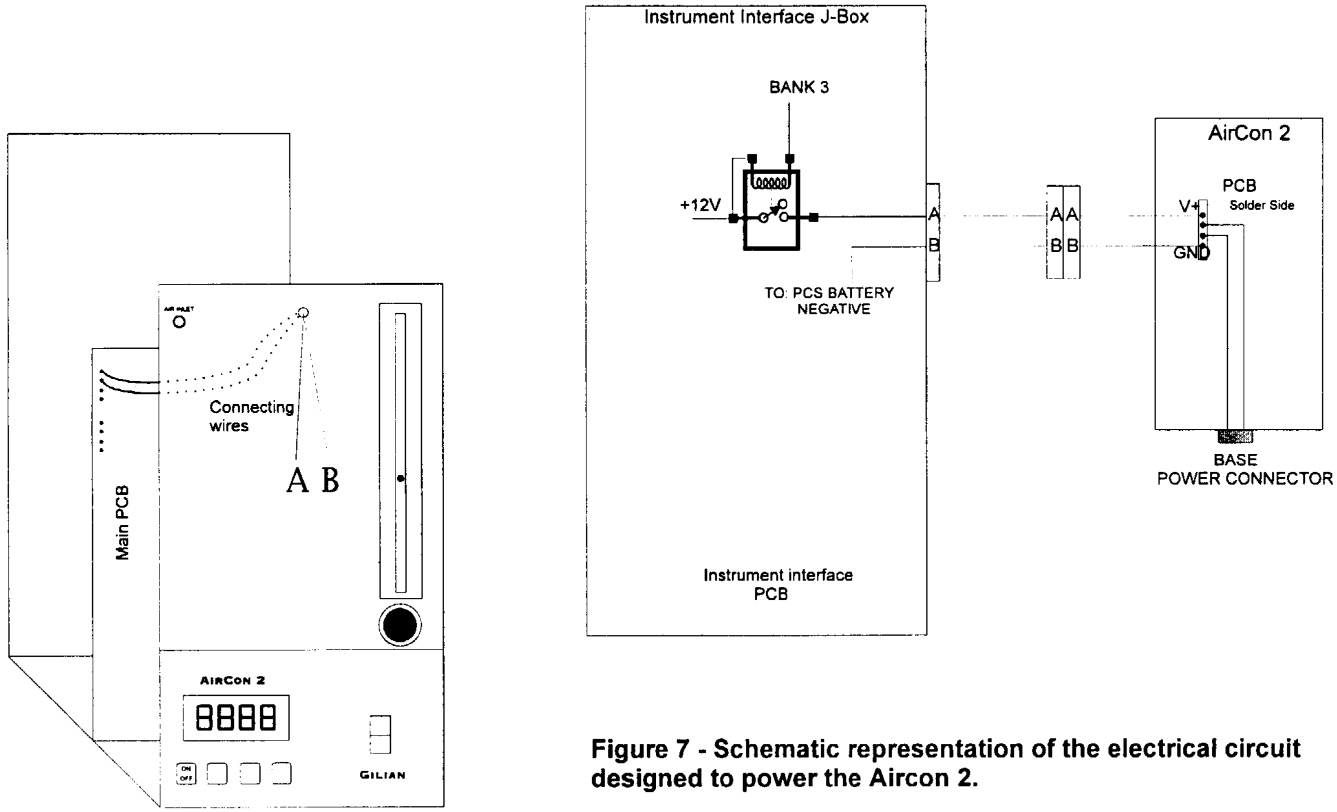

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Figure 7 - Schematic representation of the electrical circuit designed to power the Aircon 2.

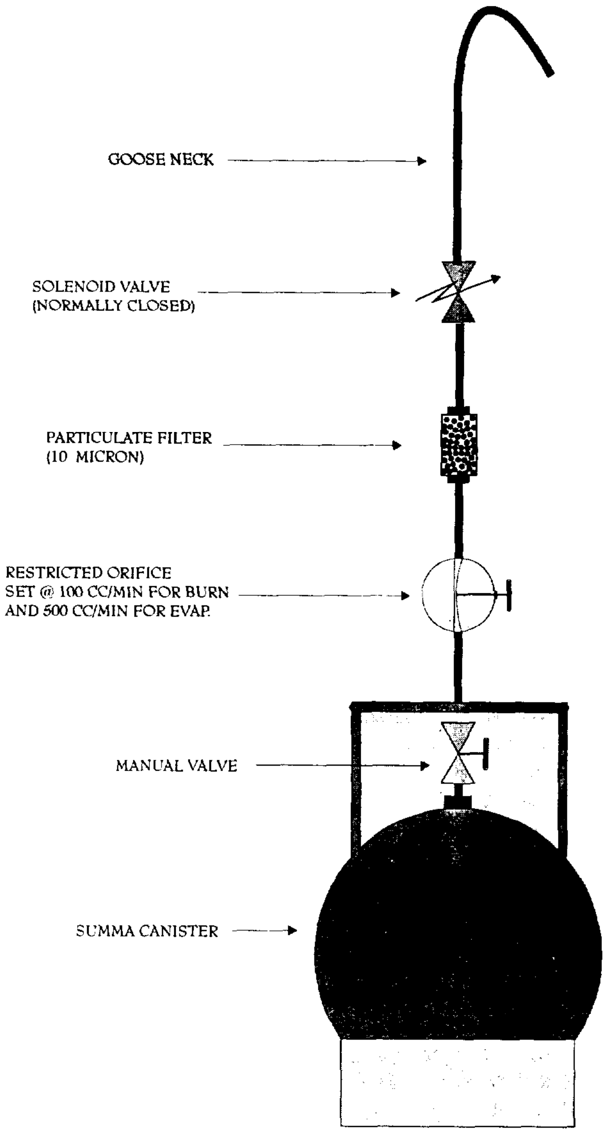

FIGURE 8 - SUMMA CANISTER, INTAKE CONFIGURATION