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MODAR

FINAL REPORT

Submitted to

The National Aeronautics and Space Administration
Lyndon B. Johnson Space Center

Evaluation of Organic Carbon Analyzers
for Space Application
#NAS9-16675

Submitted By

MODAR, Inc.
14 Tech Circle
Natick, Massachusetts 01760

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1. SUMMARY

This report evaluates the state-of-the-art technology for organic carbon analysis in space applications. An investigation into total organic carbon (TOC) analysis has identified a variety of schemes which include different methods for: 1) separation of inorganic carbon from organic carbon and/or differentiation of inorganic carbon from organic carbon; 2) reaction of organic carbon to form a quantifiable species; and 3) detection and measurement of that species. Each method option is discussed in this report.

None of the currently available commercial instruments can be used in space as designed, primarily due to the requirement for ambient gas/liquid separation in almost every instrument. In addition, none of the instruments that have on-line monitoring capability is designed to measure volatile components of the total organic carbon, which may result in serious underestimation of the organic carbon content of a recycled water stream unless these instruments are modified. A program to develop an instrument which would be functional in space is presented.

2. INTRODUCTION

On manned space flight missions of extended duration it will become advantageous to recycle the water supply rather than replenish it periodically. The conversion of waste water into potable water will have to be carefully monitored to protect the health of personnel. The use of total organic carbon content as a measure of water purity requires a sensitive, reliable measuring device capable of extended operation in space. This evaluation has been conducted to find such a device or devices among currently available total organic carbon monitors.

3. PROGRAM OBJECTIVES

This study was initially designed with five objectives:

1. Identify organic carbon monitoring techniques, both those presently in use and those currently under development

2. Determine organic carbon measurement requirements by estimating probable levels of organic carbon in potable water and identifying composition of organics

3. Conduct analysis of monitoring techniques to determine limitations in principle or hardware design and impact in space environment

4. Perform a trade-off analysis to evaluate system complexity and consumables, power and weight requirements

5. Develop a plan to support the development of an optimum organic content monitoring system

4. ANALYSIS OF TOC MONITORING TECHNOLOGIES

Various measurement routines are employed by the different instrument manufacturers. Most routines use some variation of the following scheme:

1	2	3	4
Separation of Organic and Inorganic Carbon	Reaction of Organic Carbon to Produce a Quantifiable Species	Separation of Reactions Products	Detection and Measurement

Advantages and disadvantages of the different methods of separation, reaction and detection are discussed, and various alternative techniques which have not been commercially developed are outlined. The instruments available from each manufacturer are briefly described, along with the rationale for choosing specific instruments for further investigation.

4.1 SEPARATION OF ORGANIC AND INORGANIC CARBON

Inorganic carbon (as carbon dioxide) is present in all waters that have not been treated for its removal. If the final measurement of TOC is done by detection of CO_2 or CH_4 produced by reduction of CO_2, separation of organic carbon from inorganic carbon is necessary. The most common detectors used on TOC analyzers cannot sense total organic carbon directly, and cannot distinguish between the reaction products of inorganic and organic carbon. The most commonly used method of removing inorganic carbon is by acidification of the sample followed by sparging with neutral gas. Acidification to low pH converts inorganic carbon in the forms of carbonate and bicarbonate to CO_2. Sparging with a gas devoid of CO_2 effects rapid removal of the CO_2.

The sparging system in most on-line analyzers is composed of single or dual coils. The sparging gas forces the sample into a thin layer as it travels up the inner walls of the coil. CO_2 leaves the liquid phase and

enters the gas phase. The coil is followed by an ambient pressure gas/liquid separator. The conditions which affect the inorganic carbon removal efficiency are pH sparge time.

The major drawback to this method of inorganic carbon removal in a space application is the use of ambient gas/liquid separation, which will not function in zero gravity. In general, any of the four measurement steps which depend on ambient gas/liquid phase separations will not function in space.

Another potential shortcoming of sparging is poor efficiency. None of the commercially available on-line instruments is designed to remove high concentrations (greater than 50 ppm) of inorganic carbon from a sample containing low levels of organic carbon. In a recycled water, however, depending on the method used for destruction of organic carbon, it is conceivable that the inorganic carbon content could be considerably higher than 50 ppm. It was unclear whether this sparging inefficiency results from lack of optimization of the above-mentioned conditions which affect inorganic carbon removal or if sparging is inherently inadequate at high inorganic carbon concentration. To answer this question a laboratory experiment was designed and conducted. The results are reported in Appendix 1. It was found that sparging could be made efficient by optimizing the conditions.

The fraction of the total organic carbon which is volatile, and therefore purgeable by the inorganic removal system, is lost from the TOC in the standard sparge-oxidize-detect scheme. This is seldom of great concern in the analysis of natural waters since the system has been open to atmosphere which results in purgeables being a small fraction of the total organic carbon. In recycled water, however, the purgeable fraction of TOC cannot be assumed to be insignificant.

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Only two manufacturers of commercially available total organic carbon analyzers have incorporated systems to recover the purgeable organic carbon (POC) fraction. The Oceanography International (O.I.) 600 incorporates a purgeable organic carbon (POC) measurement in which the gas used to sparge the sample is passed through a Tenax trap. Purgeable organics are caught on the trap while the CO_2 inorganic fraction passes through to a vent. The Tenax trap is then heated and the purgeables are desorbed and carried into a reduction reactor where they are reduced to methane, and then detected by a flame ionization detector (FID). As it is presently designed, this technique suffers from the same drawback as sparging to remove inorganic carbon; it is not expected to work in zero gravity.

In the Dohrmann DC-54 and DC-80, the sparge gas is passed through a lithium hydroxide trap which quantitatively traps the inorganic CO_2 and allows the purgeable organics to pass through. The purgeable organics are then routed to either a reduction reactor and FID, or an oxidation furnace and infrared detector (NDIR), for an independent POC measurement.

An alternate method of removing inorganic carbon is dialysis of CO_2 in the sample through a silicone rubber membrane into strong base where the CO_2 is continually removed by reaction with base to form carbonate and bicarbonate. This method only reduces the residual inorganic carbon to ca. 1.5 ppm (Lantz et al., 1980). This level may be too high when the required sensitivity to organic carbon is in the sub ppm range. It is unclear whether this shortcoming is a result of lack of optimization or an inherent limitation, but this technique has not been used in commercially available instruments for inorganic/organic differentiation, although dialysis of CO_2 after the oxidation step is an integral part of systems which use colorimetric detection. A method such as this for removing

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inorganic carbon which was selective for CO_2, avoided ambient sparging, and left the purgeable organics in solution, would allow a true TOC to be obtained from one measurement, rather than from separate POC and non-POC determinations.

Several detection/measurement systems such as ultraviolet absorption meters, resistivity cells and electrodes can be used without prior separation of organic and inorganic carbon. Barnstead's laboratory model TOC analyzer detects the purgeable organics along with TOC in a closed reaction and measurement system which senses the change in the conductivity of the sample solution during the oxidation. Since CO_2 need not be removed before the oxidation step, no sparge is employed.

4.2 REACTION

The reaction step generally involves oxidation of the organic carbon to inorganic CO_2, with subsequent reduction to CH_4 if detection is by flame ionization. The oxidation methods used include high temperature combustion, wet chemical oxidation and UV photochemical oxidation.

4.2.1 High Temperature Combustion

High temperature combustion is carried out at approximately $900^{\circ}C$ over an oxidation catalyst such as barium chromate, silver, palladium, cobalt oxide, copper oxide, or platinum. The sample is carried through the reaction chamber and detector by a CO_2-free carrier gas which contributes oxygen for the oxidation. Sample size is limited by the rapid combustion and expansion of the sample which can possibly cause the quartz or ceramic reaction tube to explode. This possibility is controlled by limiting the sample size, which is usually 10 to 100 ul. High temperature

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combustion has been demonstrated to produce essentially complete oxidation of a wide range of organic compounds. Those compounds for which literature data exists are listed in Table 1.

Difficulties with incomplete reaction using the high temperature oxidation of organic carbon were reported by Wolfel and Sontheimer (1974), working with tris (2-chlorethyl)-phosphate, and MacKinnon (1978) who observed that at low pH oxidation of benzoic acid was incomplete.

Problems with clogging of the sample injector and the oxidation catalyst by particulates and high salt solutions have been reported but should not present a problem in the analysis of high purity water which is, for the most part, free of salts and particulates.

4.2.2 Wet Chemical Oxidation

Wet chemical oxidation using an oxidizing agent such as dichromate or persulfate has been used extensively by researchers analyzing sea water samples (Menzel and Vaccaro, 1964, and Oppenheimer, et. al., 1963). Compounds which have been successfully recovered by wet chemical oxidation are included in Table 2. There has been much controversy regarding the efficacy of wet chemical methods (MacKinnon, 1978, Williams, 1969, Sharp, 1973, Baldwin and McAttee, 1974, Skopintsev et. al., 1976, and Gershey et. al., 1979). The discrepancies in the results of various investigators may have been largely a function of the different methods employed for sample preservation and inorganic carbon removal. One factor which has been demonstrated to affect the extent of oxidation is the presence of silver catalyst, particularly $AgSO_4$ for seawater samples, where the formation of AgCl precludes the reduction of persulphate by Cl^-, thereby maintaining the ability of the persulfate to promote oxidation in high salt samples (Skopintsev et. al., 1976, and Goulden and Brooksbank, 1975).

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Table 1

Compounds Oxidized Completely by High Temperature Combustion

pyridine	methanol	glucose	thiourea
salicylic acid	Na benzoate	urea	Na oxalate
sucrose	acetanilide	cystine	o-cresol
humic acid	thiamine HCl	Na oleate	fulvic acid
glycollic acid	tartaric acid	acetone	EDTA
trichlorophenol	phenol	n-butanol	formic acid
PAA	DMF extract	starch	KCN
quinoline	Na lauryl sulfate	1,6 hexanediol	ethanol
cis-stilbene	lignin sulfonic acid		dextrose

cyclohexane-2,4 dinitrophenyl hydrazone

Table 2

Compounds Oxidized Completely by Wet Chemical Oxidation

1-10 phenanthroline	chitodextrin	L-cysteine
acetic acid	dextrose	DL leucine
sulfanilamide		

Concentration and specific oxidant, temperature, and time of reaction have also been shown to affect the completeness of reaction.

With the wet chemical oxidation method a sealed ampule is usually used as the reaction vessel. Since the ampule has a restricted volume, care again must be used in sample size selection to prevent bursting of the ampule upon oxidation of the sample. In general, however, the permissible range of sample sizes is much broader than with high temperature combustion. The sealed ampule has not been adapted for on-line use by U.S. manufacturers although various instruments manufactured in West Germany use wet chemical oxidation (Bortlisz, 1976).

4.2.3 UV Photochemical Oxidation

The oxidation method which has been most often adapted for continuous TOC monitoring is UV promoted persulphate oxidation. Generally the sample passes through a coil which surrounds an ultraviolet source. Alternatively, the UV source may be immersed in the reaction solution. UV oxidation has also been employed without chemical addition, using entrained air or O_2 as the oxygen source.

The power output of the mercury lamps employed and the configuration of the coil has varied among researchers. It is generally agreed that sufficient radiation below 210 nm is required for complete oxidation of all forms of organic carbon (Wolfel and Sontheimer, 1974). The presence of the 185 nm line is critical because it is this wavelength which excites water to free radicals, which promote the oxidation reaction. Low pressure mercury lamps deliver more radiation at the lowest wavelengths than medium or high pressure lamps of equivalent power. Systems in which the UV lamp is freestanding in air may require venting for ozone formation. Xenon, argon, neon, krypton and zinc were tested as alternate

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sources of UV by Orion Research, Inc. in their TOC studies under NASA contract #NAS 9-14229. These sources of UV did not deliver sufficient power in the proper spectral region to promote oxidation.

Several different configurations are possible for the reaction chamber and UV source. The Dohrmann models DC-62 and DC-54 contain a quartz coil surrounding a 450 watt medium pressure mercury lamp. Cooling air is passed between the coil and the UV lamp for venting of ozone produced during irradiation. The Astro LTO 1800 reaction chamber is composed of 3 low pressure mercury lamps immersed in the sample. Total wattage does not exceed 500 watts, and venting is not required. Ionic's Process 5900 contains a UV source which consumes less than 20 watts. Samples must be much larger than with the hot combustion method, presumably because the reaction is slower and the H_2O is not vaporized, resulting in a slower and less concentrated release of CO_2 to the detector. Reaction efficiency is affected by excessive acidity, reaction time, and type of oxidant (Gershey et. al., 1979, Van Steenderen et al., 1979, and Collins and Williams, 1977). It has been suggested that sulfur (thio) compounds may be difficult to oxidize completely by the UV method (Gershey et. al, 1979) but this possibility has not been thoroughly investigated. Some compounds which have been completely oxidized via UV oxidation are given in Table 3.

One advantage of the UV oxidation method in which the solution flows through the cell and the water is not vaporized, is that salts and particulates are easy to handle. Another is a low and stable blank. The blank is the response of the instrument to a sample which contains no organic carbon. Since the blank establishes the background noise, it affects the detection limit and reproducibility. In general the blank

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Table III

Compounds Oxidized Completely by UV Oxidation

pyridine	sucrose	thiourea
2,2-bipyridyl	K biphthalate	saccharose
adenine	formic acid	n-butanol
ethanol	dimethylamine	formic acid
glucose	glycerol	DMF-extract
glucoseamine	humic acid	starch
acetic acid	phthalic acid	KCN
palmitic acid	glycine	1,6-hexanediol
fumaric acid	semicarbazide	cis-stilbene
salicylic acid	alginic acid	4 aminobutyric acid
benzoate	EDTA	PAA
urea	valine	1,6-hexanediol
acetamide	K oxalate	cis-stilbene
oxalic acid	acetone	4 aminobutyric acid
dimethyl sulphide	acrilonitrile	PAA
tryptophane	benzaldehyde	
methionine	glycerol	
ascorbic acid	Na lauryl sulfate	
quinnol	nicotinic acid	
malonate	acetonitrile	
casein	acetamide	
	1-glutamic acid	
	lignin sulfuric acid	
	tetra n-butyl ammonium bromide	

and also the anti-oxidants:

phenylalanine	quinine sulfate	quinoline
3,5 dihydroxytoluene	aniline	phenylacetic acid
phenylhydrazine	chlorophenol	
trichlorophenol	o,m and p toluidine	

value is higher with more reagents and sample handling. The flowing sample stream used with UV oxidation affords low blank values, possibly as a result of the complete removal of the constituents of the previous sample from the oxidation chamber before a new sample is introduced, or because the conditions of the reaction are not as severe as the other methods.

4.3 SCRUBBING AND DETECTION SYSTEM

Most detection methods used in TOC analysis are based on CO_2 detection. They include colorimetric, coulometric, resistivity, and non-dispersive infrared (NDIR) methods. Other detection methods include microwave plasma emission spectroscopy, thermal conductivity, and flame ionization detection.

4.3.1 Non-Dispersive Infrared

The most common detection method employed in TOC monitors is non-dispersive infrared (NDIR) absorption (Small, 1980, Safranko et. al., 1981, and Shaefer). CO_2 in the sample absorbs IR energy at certain wavelengths and the sample absorption is compared either to the absorption at a wavelength where CO_2 does not absorb, or to the absorption in a reference cell filled with a CO_2-free reference gas. The NDIR detectors which compare absorption at two different wavelengths can use one source, and one cell. An advantage of the single cell is that any interference with IR transmission due to corrosion of the walls or dirty windows will affect the sample and reference equally, and drift is minimized.

The dual source, dual cell detectors require precise source balance adjustments to assure equivalent source output intensity, and also require a very steady voltage source.

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The differential infrared sensing is done by either a microphonic or a solid state detector. The microphonic, or "Luft" type sensing element is composed of two chambers which are filled with CO_2 and separated by a flexible diaphragm. Each chamber is in line with one of the NDIR detector cells. When CO_2 passes through the sample cell it absorbs IR, whereas the reference cell allows the IR to pass completely to the chamber. The reference cell heats up more than the sample chamber as the CO_2 absorbs the incoming radiation, causing the diaphragm to flex, producing a capacitive output. The reference cell may be filled with CO_2 instead of CO_2-free gas, causing this to be a 0% transmittance instead of a 100% transmittance reference.

The solid state detector may be either photovoltaic, as with lead selenide, or pyroelectric, as with lithium tantalate. They are not as sensitive to vibration as the microphonic detectors.

Water vapor may interfere in the IR measurement due to broad band absorption and therefore it must be removed by an appropriate scrubber assembly. At least one manufacturer requires thermal stabilization of the detector to prevent condensation in the cell. NDIR detectors which have gold foil coated cell walls to concentrate the IR energy can be corroded by the chlorine gas produced by chlorinated hydrocarbons and therefore chlorine must be removed by a scrubber. NDIR detectors are effective in the low level range of approximately .02 - .2 ug C, and detection limits reported by the TOC instrument manufacturers who use NDIR are in the 20-100 ppb range.

4.3.2 Colorimetric

Colorimetric detection also measures TOC as CO_2. The CO_2 to be measured must be in solution and therefore this method is not used in

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conjunction with high temperature combustion, No carrier gas is required to sparge the oxidation product into the detector; rather the CO_2 in solution diffuses through a gas permeable silicone rubber membrane into a buffered solution which contains an indicator. The resultant change in pH causes a color change in the indicator, which is detected by a colorimeter at 530 nm. The method is subject to interference from other dissolved gases and the membrane must be changed periodically. Several reagents are required. The detection limits as reported by several TOC instrument companies utilizing this method are around 1 ppm.

4.3.3 Coulometric

Coulometric titration is a method in which CO_2 reacts with a solvent such as triethanolamine to produce an acid, which is then titrated by an electrochemically generated base (Huffmann, 1977). A colorimeter detects the endpoint of the titration and the coulometer quantifies the amount of CO_2 which has been titrated. Other gases which may react with the solvent to form a titratable acid, such as H_2S, SO_2, NO_2, HCl, Cl_2 can interfere. The detection limit reported for this method is 50 ppb.

4.3.4 Conductimetric

The conductivity measurement is a measure of the ionic species in solution (Poirier). In this method the increase in the conductance of a solution caused by the increase in the carbonate concentration as CO_2 dissolves in the solution, is detected by a conductivity cell in one arm of a Wheatstone bridge. Other gases which may dissolve to form ionic species will interfere with the measurement. The detection limit reported for this method is 50 ppb.

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4.3.5 Microwave Plasa Emission

Microwave plasma emission spectroscopy has been investigated for the measurement of organic carbon and CO_2 at 193 nm (Mitchell et. al., 1977). The major difficulty is the requirement for a highly purified plasma gas. This method has not been incorporated into a commercial TOC instrument.

4.3.6 Thermal Conductivity

Thermal conductivity detection for TOC analysis has been commercialized only by Hoechst of Germany who reports a .05 ppm detection limit using a 100 ml sample (Bortlisz, 1976). Thermal conductivity is often used in gas chromatography and is nonspecific for all types of organic and inorganic compounds.

4.3.7 Flame Ionization

Flame Ionization Detection (FID) is employed in ultra low level TOC analyzers. The FID is commonly used as a gas chromatography detector. The FID detects hydrocarbons which are decomposed to ionic fragments and electrons in a hydrogen/O_2 or air flame. The charged species are collected at electrodes and produce an electric current. The FID senses any oxidizable carbon and thus can measure the TOC directly if it can be separated from the aqueous medium. Usually, however, the organic carbon is oxidized to CO_2 by one of the methods previously discussed, and the CO_2 is then separated from the aqueous solution and fed to a reduction furnace where it is reduced to methane before entering the flame ionization detector.

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4.4 ALTERNATIVE TECHNOLOGIES

Several other methods of measuring TOC have been tried and may be viable with further development.

Life Systems, Inc. (Army contract #DAMD17-76-C-6077) developed a breadboard on-line TOC analyzer for use in a mobile unit (Lantz et. al.). No compressed gases are required. Inorganic carbon is removed by acidification to form CO_2 from carbonate, followed by diffusion of CO_2 across a gas permeable membrane into a high pH stream. Organic carbon is oxidized by UV radiation. Measurement is accomplished by detecting the pH change in a solution when CO_2 from the sample diffuses across a gas permeable membrane into the solution; i.e., it is a gas permeable membrane electrode. All reagents are electrochemically generated and thus need not be stocked. The analysis time and detection limit (.5 ppm) may be parameters that require further refinements.

Development of the Electrochemical Organic Content analyzer was done under contract #DAMD17-75-C-5070 by Life Systems, Inc., and was investigated for aerospace applications under #NAS9-15402 (Life Systems, 1977, and Davenport, 1979). This is the only measurement technique which detects organics directly without prior transformation to another form. This analyzer detects the capacitance change at a platinum electrode when organic compounds are adsorbed. Different organic compounds exhibit maximum adsorption at different potentials; and therefore it is not possible to optimize performance for all organics simultaneously. This could be applied to advantage in differentiating what type of organic is present. Sub ppm measurement of organics is possible. Previously adsorbed organics are removed prior to analysis by the oxidation of the platinum surface at high electrode potential, followed by a reduction

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cycle to restore the Pt surface. Further exploration of this technology may reveal an important role in water quality monitoring for this relatively simple probe as a selective check when the identity of potential contaminants are known.

Orion Research, Inc. designed and built an instrument for space application to monitor four indicators of water quality, including TOC (contract #NAS9-14229, West et al., 1979). The on-line instrument used membrane dialysis for inorganic carbon removal, UV for organic oxidation, and a CO_2 electrode for detection. The design goal for TOC measuremt was a range of 1-100 ppm TOC; however the experimental results indicate that the lower limit of detection is greater than one ppm. Also there appeared to be some difficulty with the oxidation of phenol, but it is possible that completeness of the reaction is dependent on a variable condition of the instrument.

The air gap electrode requires only a very small sample and has increased response time as compared to membrane electrodes for gases (Fiedler et. al., 1975). Further development of the electrode for measurement of CO_2 evolution in solution may lower the detection limit of this probe to a level consistent with other TOC detectors. This would obviate the need for gas/liquid separation and scrubbing following oxidation of organic carbon.

5. CRITERIA USED FOR COMPARISON OF INSTRUMENTS

Table 4 lists the set of operating parameters which were used to compare the commercially available TOC monitors.

Table 4

Parameters for TOC Analyzer Comparison

1. Detection Limit

2. POC Recovery Capability

3. Use of Acutely Hazardous Components or Processes

4. Expendables Usage

5. Sample Size Requirements and Analysis Time

6. Weight and Power Requirements

7. On-Line Capability

5.1 Detection Limit

The total organic carbon measurement of a water sample is a non-specific measurement of organic materials which is used to indicate water contamination. A natural water might contain 15 ppm of total organic carbon as harmless acids and products of microbial decomposition. Therefore a measurement of 15 ppm TOC on a natural water sample may not indicate hazardous contamination. On the other hand, an industrial effluent stream carrying two ppm of organic carbon could be hazardous if the two ppm is made up of toxic compounds. Therefore, in an evaluation of a desirable or tolerable level of TOC, one must look at the source, the treatment process, and the intended use of the product.

In the application of the TOC measurement to a water recycling system in space, we will assume that the source of the treatment water is domestic wastes and that the intended product is potable water. It is possible that the treated water may contain a considerable amount of organic carbon without becoming a hazard. Conversely, a small TOC measurement may represent a large hazard if it is a result of:

1. toxic chemical compounds entering and surviving the waste treatment system

2. buildup of a toxic component of human waste which is not removed by the treatment system.

To determine the buildup of toxic materials possible with continued recycling of water in prolonged manned spaceflight would require an individual study of the capabilities of each candidate water treatment system with respect to all known components of human waste. This is beyond the scope of the present study. The rationale for the TOC measurement requirements used in this study is discussed below.

It would be impractical to attempt to monitor organic contaminants in recycled water as individual compounds. Therefore, it is necessary to set

a maximum allowable TOC content for potable water based on the most toxic compound that could be present. This maximum allowable TOC would most likely be in the low ppm range. In order for this concept to be workable, the water treatment system employed would have to be capable of removing organic materials down to extremely low levels. An increasing TOC measurement would then signal loss of treatment efficiency.

The TOC levels in treated wastes vary widely. For example, in one study of the wet oxidation process on feces and urine under varying conditions, the TOC content after oxidation ranged from 194 to 1475 ppm (Lockheed Missiles and Space Co., 1977). Vacuum distillation of the effluents reduced these TOC contents to 9 to 150 ppm, and further treatment of three of the six original samples by charcoal filtration reduced the TOC to 10 to 20 ppm. Hyperfiltration of synthetic washwater reduced TOC from as high as 250 ppm to final values of 21 to 52 ppm (Lockheed Missiles and Space Co., 1981).

The efficiency of waste destruction systems is continually being studied and improved, and these examples are presented only to illustrate the order of magnitude of TOC that may remain after waste processing, which as previously stated is critical to the understanding of TOC as a water quality parameter for any system. The MODAR, Inc. supercritical water oxidation system has demonstrated virtually complete destruction of organic materials (Modell et al., 1982). A waste destruction system capable of this kind of efficiency would be necessary if the TOC measurement were to be used to detect entrance of hazardous levels of toxic organics into the treatment system effluent.

The detection limit on the TOC monitor should be lower than the maximum allowable TOC so that declining purification ability of the system

could be detected as soon as possible. Since some organic substances in the source may be volatile compounds, the TOC monitor should also have the capability to measure the purgeable organic carbon (POC).

5.2 POC Recovery Capability

The fraction of the TOC which is volatile and therefore purgeable by the inorganic removal system is lost in the standard sparge-oxidize-detect scheme. Since a malfunctioning water treatment system may release POC, it is important to be able to detect this component of the TOC. A method which would measure POC along with non-POC, allowing a true TOC to be obtained from one measurement, would be ideal. Most available TOC instruments either do not handle POC measurement or incorporate it through a separate measurement scheme.

5.3 Use of Acutely Hazardous Components or Processes

According to West et al. (1979) mercury is an unacceptable material in spacecraft instrumentation. Instruments using ultraviolet oxidation of organic carbon would receive a heavy penalty if the ultraviolet source was a mercury vapor lamp.

5.4 Expendables Usage

The expendables usage depends on the specific analysis scheme of the instrument. Separation of organic and inorganic requires addition of acid. Combustion requires a dry catalyst which is periodically recharged, and the UV and wet chemical methods require oxidation promoting reagents. All of the instruments except the Barnstead Analyzer require a carrier gas for the reaction, detection, and/or gas/liquid separation steps.

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5.5 Sample Size and Analysis Time

The limits for these parameters are dependent on the operational requirements of the water treatment system which is being monitored.

5.6 Weight and Power Requirements

Weight and power requirements should be minimized.

5.7 On-Line Capability

The operator time required for continuous water quality monitoring using a laboratory instrument would be prohibitive. If a laboratory instrument surpassed all available on-line instruments in the other criteria, the possibility of adaptation for on-line continuous monitoring should be investigated.

6. Analysis of Organic Carbon Analyzers

Table 5 lists all commercially available TOC analyzers which were located, as well as some pertinent information about their operation. Low detection limit, POC recovery capability, and on-line capability were considered to be major requirements for a TOC analyzer to be used in a space operation center. Most instruments were not considered further unless they had at least two of these capabilities. Other pertinent criteria have been listed in Table 4.

All of the commercially available instruments require gas/liquid separation at ambient pressure and will require major modifications to function in a space operation center. Therefore steps which require gas/liquid separation were not used as a basis of comparison.

The UV and hot combustion methods of reaction are both inherently efficient. The UV method can handle salts and particulates well and

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Table 5

Commercially Available On-Line Total Organic Carbon Monitors

Company	Model	Laboratory (L) or On-Line (OL)	Reaction	Detection	Sensitivity	POC Recovery	Expendables	Response Time, Min.	Sample Volume	Weight (lbs)
Astro Resources Corp.	1800	OL	UV	NDIR	20 ppb	no	H_3PO_4;$K_2S_2O_8$ O_2 or air	5		200
	1850	L	UV	NDIR	10 ppb	by difference				
Barnstead Company		L	UV	Resistivity	50 ppb	yes	H_3PO_4; $H_2S_2O_8$ air	15	10 ul–100 ml	110
Beckman Instruments	915B	L	hot comb.	NDIR	50 ppb	no	H_3PO_4 O_2 or air	3	1	
Carlo Erba	TCM 480	OL	hot comb., reduce	FID	100 ppb	no	H_2;N_2; Air HCl	3–5		
Coulometrics, Inc.		L	UV or hot comb. or wet ox.	Coulometry	50 ppb	no	HCl;O_2;KI pri.soln. WO_3	10		
Dohrmann Envirotech	DC 54	L	UV	FID	several ppb	yes	H_2;He;Air trap;catalyst	8.5	10	10-50
	DC50A/52A	L	hot comb., reduce	FID	1000 ppb	yes		5		
	DC 60	OL	hot comb.	NDIR	500 ppb	no		5		
	DC 62	OL	UV	NDIR	500 ppb	no	H_3PO_4;$K_2S_2O_8$ N_2 or O_2	4 ml/min		272
	DC 80	L	UV/hot comb.	NDIR	100 ppb	yes		5	4 ml	
Ionics, Inc.	1258	L	hot comb.	NDIR	200 ppb	no	HCl, N_2, air	5		200
	1270	L	hot comb.	NDIR	200 ppb	no		5		200
	5800	OL	hot comb.	NDIR	1000 ppb	no	HCl	5	50-1K	
	5900	OL	UV	NDIR	100 ppb	no		6.5	50-1K	
Oceanography, Int'l	524-ATO	L	wet ox.	NDIR	100 ppb	no	ampules H_3PO_4			
	524-DIH	L	hot comb.	NDIR	5000 ppb	by difference				
	525	L	hot comb.	NDIR	1000 ppb	by difference		2		
	600	L	trap, reduce	FID	several ppb	yes	H_2;N_2;trap air	5	1-10	
Scientific Instruments Corp.		OL	UV	colorimetry	1000 ppb	no				
Technicon	650	OL	UV	colorimetry	2000 ppb	no	H_2SO_4 $K_2S_2O_8$	7		150

UV=ultraviolet oxidation
hot comb.=hot combustion oxidation
wet ox.=wet chemical oxidation

NDIR=non-dispersive infrared
FID=flame ionization detector

affords a low and stable blank. In general, however, the UV method consumes a chemical reagent not needed for hot combustion, requires a much larger sample and has a longer response time than hot combustion. Additionally the mercury vapor lamp UV source may be disallowed in space operations. Therefore an instrument which uses hot combustion, although it may have higher power consumption, is a better candidate for adaptation for space application.

The non-dispersive infrared (NDIR) detector has an adequate lower limit of detection and uses no expendables, and therefore would be preferred over other detection methods which require expendables. NDIR detectors which function with one source, one cell and solid state detection would be preferred for increased stability.

Referring to Table 5, the Astro LTO 1800 TOC analyzer was chosen as a model for further consideration because it is an on-line instrument and has a very low limit of detection of 20 ppb. Additionally it uses a solid state NDIR with single source and cell. It does not recover purgeable organics, and it employs UV oxidation. Other Astro instruments were more limited and were not considered further.

The Barnstead Analyzer is not considered adaptable to space due to high sample consumption at the lower limit of detection. Inorganic carbon removal is not required and purgeable compounds are recovered in this unique instrument. The sample to be analyzed is circulated between the measurement chamber and the reaction chamber until the resistivity reading is constant. Then UV irradiation takes place in the reaction chamber and the resistivity change is monitored as organics are oxidized to CO_2.

The Beckman 915B was not included in further consideration because it is a laboratory instrument and does not recover purgeable organics.

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The Carlo Erba TCM 480 high temperature total carbon monitor is an on-line instrument with a .1 ppm limit of detection and therefore was considered for adaptation to space although it does not recover purgeable organics. In its favor, the 480 uses hot combustion. In its disfavor, a reduction reactor and FID are used for detection.

Coulometric's TOC instruments were not considered for adaptation to space because they are laboratory instruments and do not recover purgeable organics. Since the coulometer has a .01 ug C limit of detection it would appear that development of the TOC reaction and treatment would increase the viability of this method for ultra low TOC analysis in space.

Dohrmann division of Xertex markets a variety of TOC analyzers. The DC-62 was chosen for further consideration because it is an on-line instrument. It does not recover purgeable organics, and the .5ppm limit of detection is not necessarily sufficient, but the model has a low level adaptation which extends TC detection to approximately 20 ppb. The DC-54 was also considered because it has a unique process which recovers purgeable organics and has an extremely low limit of detection. The DC-80 was included because it has an acceptable detection limit and recovers purgeable organics. The other Dohrmann instruments were more limited and were not considered further.

The Ionics 5900 was chosen for further consideration because it is on-line and has an acceptable limit of detection. Purgeable organics are not recovered. The 5900 oxidizes TOC by UV irradiation and uses NDIR detection. Other Ionics instruments were laboratory instruments or had an inadequate limit of detection and were not considered further.

The Oceanography International (O.I.) TOC 600 has a very low limit of detection and also recovers POC, and therefore, despite the fact that it

is not an on-line instrument, it was given further consideration. The other O.I. instruments were more limited and therefore were not considered for space application.

Scientific Instruments Corporation has an on-line instrument which uses UV oxidation followed by detection of CO_2 by colorimetry. The detection limit is 1 ppm which is comparatively high, and purgeable organics are not recovered, and therefore it was not considered adaptable for space.

The Technicon 650 is also an on-line analyzer which uses UV and colorimetry. The detection limit is comparatively high, and purgeable organics are not recovered, and therefore the 650 was not considered further.

7. Conclusions and Recommendations

Table 6 lists the instruments which were chosen for possible modification for space application. Considering the fact that none of the instruments comes considerably closer to application in space than any other instrument, and also because all of the instruments would require major modification for application in space, it will be more productive to discuss feasible modification schemes than to conduct a numerical trade-off analysis.

The first scheme involves the integration of the Astro 1800 and the O.I. 600, an instrument with auto sampling, and an instrument with POC recovery, respectively. Scheme 2 involves modifying the O.I. 600 to include auto sampling and inorganic carbon removal. Scheme 3 is the addition of POC recovery to the Astro 1800. A LiOH trap would be put in the "gas" line after gas/liquid separation to entrain CO_2 before returning to the main stream. Scheme 4 is the integration of the Dohrmann

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Table 6

Instruments Selected As Candidates for Modification for Space Application

Instrument	OL, L	Reaction	Detection	Detcn. Limit	POC Recovery
Dohrmann DC-80	L	UV/hot comb.	NDIR	.1 ppm	yes
Dohrmann DC-60	OL	hot comb.	NDIR	.5 ppm	yes
Dohrmann DC-62	OL	UV	NDIR	.5 ppm	no
Dohrmann DC-54	L	UV	FID	several ppb	yes
Ionics 5900	OL	UV	NDIR	.1 ppm	no
Astro LTO 1800	OL	UV	NDIR	20 ppb	no
Erba 480	OL	hot comb.	FID	.1 ppm	no
O.I. 600	L	trap, reduce	FID	several ppb	yes

OL = on-line instruments

L = laboratory instrument

DC-60 and the O.I. 600, an instrument with auto sampling, and an instrument with POC recovery, respectively.

Additionally, the Dohrmann DC-80 would fulfill the major requirements if it were adapted for on-line analysis.

None of these schemes is adequate as is. Wherever gas liquid separation is involved, modification will have to be made for operation in zero gravity. One approach may be to replace sparging components with dialysis membranes. Typically, the residual inorganic carbon remaining after dialysis is in the 1 mg/l range. This may be somewhat high if the upper limit of organic carbon acceptable in drinking water is less than 1 mg/l.

Sparging could also be replaced by trapping of organic carbon directly from the liquid stream while allowing inorganic CO_2 to pass through. To accomplish this, a trapping material would have to be found which would retain both volatile organic carbon and larger organic molecules. It may also be possible to develop a trap specific for CO_2 in the aqueous samples which would allow organic carbon to pass through. Neither of these options is currently commercially available and both would require development.

Appendix I - INVESTIGATION OF INORGANIC REMOVAL EFFICIENCY

Removal of inorganic carbon from samples for measurement of the residual organic carbon is achieved by acidifying the sample to convert carbonate and bicarbonate to CO_2 and H_2O, and then driving the CO_2 off with a CO_2-free gas. This process takes place either in a sample vial with a sparging tube or in a sparging coil through which the sample passes. There are a few exceptions to this scenario. Astro uses a variation of the sparging coil which works on the same principle. O.I. has developed a proprietary trap which will retain organic carbon from an aqueous stream while allowing inorganic carbon to pass through. This trap will not retain volatile organic compounds, however, so sparging is still used to recover the volatiles on a Tenax trap. The Barnstead analyzer does not require inorganic carbon removal prior to organic carbon measurement.

The Astro method removes up to 50 ppm of inorganic carbon with 99.8% efficiency. The Technicon sparge coil can reduce 1000 ppm of inorganic carbon to 2 ppm, the detection level of the instrument. Other companies report percentage decreases of the inorganic content such as 99% or 99.9%.

In speaking with representatives of various manufacturers it was apparent that there is little known about the efficiency of the inorganic removal procedure when applied to a sample containing high levels of inorganic carbon. This question is also not addressed in the scientific literature.

Since a water recycling system in space may produce highly carbonated water, it is of interest to investigate its removal for the determination of low levels of TOC.

The first part of our experiment tests the effect of sparging time on the decrease of inorganic carbon. The second part of the experiment tests the effect of the inorganic removal process on recovery of small spikes of organic carbon.

Inorganic carbon samples were made by combination of sodium carbonate and sodium bicarbonate. Organic carbon additions were made up with potassium hydrogen phthalate. A Beckman model 915B Tocamaster was used for total carbon analysis, with a calibration scale of 2 ppm using 90 ul injections. The 915B accessory sparging unit was used for inorganic carbon removal. Approximately 10-20 drops of 6N HCl were added to the 20 ml samples in 40 ml vials to bring the pH below 2 before the samples were attached to the sparging unit. Sparging times were varied systematically.

Duplicate samples were usually run. The lack of consistency in some results of duplicates was most likely due to two different factors. The first is a component of the experiment - the sparging rate. The sparging rate was initially measured as 160 ml/min. with a soap bubble flow meter held against the sparging unit, and is a rough approximation of the flow. However, the error in this measurement may be as large as 100%. When the sample vial is attached to the sparging unit it opens the air flow valve. The flow rate cannot be measured with a vial in place, nor can one be sure that putting the vial in place opened the air valve exactly as much as when the flow meter was in place. Control over the flow rate was exercised by screwing the vials in place until the bubbling rate appeared to be the same in all samples. It is logical that higher flow rates would be most effective in the inorganic removal process, and thus it may be that differences in the duplicates are the result of differential sparge rates. The second factor is a natural pitfall of measuring TOC in the ppm range. Extreme caution must be taken to avoid contamination. Some

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sources of potential contamination are CO_2 from the air, organic contamination in the acid addition, unsparged sample from the upper wall of the sparging vials, the injection syringe, and lint from the air or analyst.

The experimental data are presented in Table 7. The results of the first part of the experiment, in which samples containing high levels of inorganic carbon were acidified and sparged, indicate that the five minute sparge time recommended by the manufacturer is not sufficient for removal of all the inorganic carbon in highly carbonated samples. Extended sparging time does, however, decrease the inorganic carbon to the detection limit of the instrument (within $\pm$ .1 ppm experimental error). It appears that though 10 minutes of sparging may be sufficient for some samples (possibly dependent upon sparge rate), additional sparging to 15 minutes assures total removal of inorganic carbon.

The second part of the experiment tested the effect of the inorganic carbon removal process on recovery of small spikes of TOC. Spikes of 1.3 and 1.0 ppm were added to 10000 and 500 ppm inorganic carbon. After 10 minutes of sparging it appears that the inorganic carbon has been driven off. Neither 10 minutes nor longer sparging times brings the total carbon values to lower than the TOC spike added. This part of the experiment demonstrates that prolonged sparging for inorganic removal will not interfere with the TOC measurement, insofar as potassium hydrogen phthalate is representative of the TOC components of the sample of interest.

Table 7

Results of Sparging Efficiency Experiments

IC (ppm)	TOC (ppm)	no sparge no acid	acid only	30 sec	1 min	2 min	5 min	10 min	15 min	20 min
								Total Carbon Remaining (ppm) After Sparging Period		
1000							35	9.0	0.0	
							26	.2	.2	
								.2	.1	
								2.0		
500						19	30	.8		
						18		0.0		
								.5		
								.2		
100					36	13	.8			
							.2			
10			3.8	2.4	.1	.4				
					.5	.2				
0		0.0	.1							
			0.0							
1000	1.3							1.3	1.3	
1000	1.0							1.2*	1.1*	1.0*
								1.5*	2*	1.1*
500	1.3							1.3	1.3	
500	1.0						2.3*	1.0*		
							1.1*	1.2*		
0	1.0	1.0							1.0*	

*corrected for drift in calibration

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