

# N89 - 20071

EVALUATION OF AVAILABLE ANALYTICAL TECHNIQUES  
FOR MONITORING THE QUALITY OF  
SPACE STATION POTABLE WATER

Final Report

NASA/ASEE Summer Faculty Fellowship Program--1988

Johnson Space Center

Prepared By: Richard D. Geer, Ph.D.  
Academic Rank: Associate Professor  
University & Department: Montana State University  
Department of Chemistry  
Bozeman, Montana 59717

NASA/JSC

Directorate: Space and Life Sciences  
Division: Medical Sciences  
Branch: Biomedical Laboratories  
JSC Colleague: Richard L. Sauer, P.E.  
Date Submitted: September 30, 1988  
Contract Number: NGT 44-005-803

## ABSTRACT

To assure the quality of potable water on the Space Station a number of chemical and physical tests must be conducted routinely. After reviewing the requirements for potable water, both direct and indirect analytical methods are evaluated that could make the required tests and improvements are suggested be make them compatible with the Space Station operation.

Of the possible analytical procedures that might be carried out on the SS, the following seem to be required to meet the water quality criteria: turbidity and color from photometric measurements, a conductivity measurement, pH by an ion selective electrode, ion chromatography for inorganic ions with set MCLs, and a total organic carbon measurement. Also required are generic methods for total phenols (MCL 1 ppb), total organic halogen compounds (MCL 10 ppb), and organic acids (MCL 500 ppb). Electrochemical methods of controlled potential amperometry and microcoulometric titrimetry may meet this need. The other PW standards for organic alcohols (MCL 500 ppb) and TOC less nontoxicants (MCL 100 ppb), are broadly defined and can only be met with either an approximate surrogate measure (example, UV absorption of aromatic compounds for "toxic TOC"), or methods that separate and measure specific compounds in those classes that are likely to be found in PW. Finally the problem of analyzing for specific toxicants that are yet to be defined will either require specific sensors (electrode or optrode), or a separation and detection system.

Each of the separation techniques evaluated appear to have special areas of applications for the SS, though supercritical fluid chromatography with CO<sub>2</sub> could probably replace gas chromatography while extending the range of analyses to nonvolatile heat sensitive compounds. Most forms of HPLC are not very compatible with the SS environment, but ion chromatography is needed for most anion and cation analyses (anodic stripping voltammetry could measure the heavy metal ions). It would be more suitable if it were converted to microbore column size. Capillary zone electrophoresis has the potential as a universal separation system, but it will require much more development in terms of buffer composition and sensitive micro volume detectors.

The most universal detector for the separation techniques is the high resolution mass spectrum detector, however its use on the SS is limited because of size, power and weight requirements associated with its high vacuum system. The need to have one on the SS seems justified only if it would be used for a variety of experiments and not just to test PW. The electrochemistry/conductivity detector appears to be the best compromise for a detector for HPLC or CZE.

Techniques are suggested for removing the interfering biocide I<sub>2</sub>/I<sup>-</sup> from water, and for carrying out chemical and electrochemical operations in microgravity where mixing and gas liquid separations are required.

## SPACE STATION POTABLE WATER

The potable water (PW) for use on the Space Station (SS) will come from the cabin air humidity condensate (HC) produced by the air revitalization system (ARS). This means the PW is in a direct recycle loop, a treatment process not previously implemented. To insure the PW remains safe for the duration of a 90 to 180 day mission, it needs to be continually monitored. This includes frequent or continuous testing of several important general or surrogate indicators that show the treatment system is operating properly. There are also a number of other specifications that the PW must continue to meet with regard to specific chemicals or classes of compounds. Table 1 gives the current criteria set for SS PW (1). The table does not include the microbiological standards, as they are not of concern to this report.

Unfortunately the majority of the organic carbon found in samples of HC from the two experiments that simulated the expected SS conditions (Space Lab and Bends) have not been correlated with specific organic compounds (2,3). Therefore, maximum contaminant levels (MCL) for possible toxic organic chemicals in PW can not be set until more specific information is obtained about the composition of the TOC in representative samples of HC from ground based tests. This, by itself, is a major analytical challenge and can influence the types of chemical analyses that are required on the SS.

This report will attempt to evaluate the kinds of on-board analytical procedure that will be required and also look at alternate methods that accomplish the same ends and/or add valuable data for determining PW quality. Modifications of procedures needed to meet the required sensitivity and potential interferences will be suggested along with ideas for efficient operation within the limitations of the SS environment. First the direct analytical methods which allow continuous on-line monitoring of the PW will be discussed, then the indirect methods which require discrete samples will be considered. These later methods require chemical reaction or separation and are the more sophisticated and complex analytical techniques.

## SPACE STATION OPERATIONAL LIMITATIONS

There are four rather severe limitations on the analytical chemistry procedures that can be used on the SS.

1. The biggest limitation is microgravity which does not allow the automatic phase separations of immiscible fluids. That is, gases and liquids do not separate without an external applied force. They can be separated by diffusion, but that is slow and inefficient. However, in zero G convection does not occur due to small density differences, this can be helpful for processes like electrochemistry or capillary zone electrophoresis (CZE) that will be discussed later.

TABLE 1.- SPACE STATION POTABLE WATER QUALITY REQUIREMENTS, MAXIMUM CONTAMINANT LEVELS (1).

Physical Parameter Limits

Total Solids (mg/l)	100	pH	6.0-8.0
Conductivity ( $\mu$ mhos/cm)	-	Turbidity (NTU)	1
Color, true (Pt/Co units)	15	Dissolved Gas (free at 35 C)	None
Taste & Odor (TTN/TON)	3	Free Gas (@ STP)	None

Inorganics mg/l (ppm)

Ammonia	0.5	Cyanide	0.2	Mercury	0.002
Arsenic	0.01	Fluoride	1.0	Nickel	0.05
Barium	1.0	Iodine		Nitrate	10.
Cadmium	0.01	Total	15.	Potassium	340.
Calcium	30.	Iron	0.3	Selenium	0.01
Chloride	250.	Lead	0.05	Silver	0.05
Chromium	0.05	Manganese	0.05	Sulfide	0.05
Copper	1.0	Magnesium	50.	Sulfate	250.
				Zinc	5.0

Organics	$\mu$ g/l (ppb)	Aesthetics	(mg/l)
** Total Organic Carbon (TOC)	500.	Cations	30
TOC (Less Nontoxicants)	100.	Anions	30
Generic Classes		CO <sub>2</sub>	15
Acids	500.		
Alcohols	500.		
Halogenated Hydrocarbons	10.		
Phenols	1.		
** Specific Toxicants	TBD		

\*\* Note, less than half the TOC from Space Lab humidity condensate samples have been associated with specific organic compounds.

2. Mission personnel will not be specifically trained in chemistry and their time will be limited for chemical or instrumental manipulations. This requires careful consideration of analytical techniques in terms of in-flight serviceability, frequency of instrument reconfiguration, recalibration or component failure, and consumable servicing.

3. Due to health and weight considerations, limits will be set on both the amount and toxic nature of consumable chemicals used in analytical procedures or instruments. There is special concern with toxic volatile waste chemicals that could get into the cabin atmosphere.

4. The SS will have limited amounts of power and space available for any operation, so these factors as well as weight will influence the choice of analytical instruments. Modularity and interchangeability of components between different instruments should be a goal in order to reduce the inventory of spare parts and improve serviceability.

#### DIRECT METHODS

Direct methods are able to continuously monitor the PW stream without personnel involvement. They have a specific response to the parameter of interest and should not respond to other substance. The methods we will consider are conductivity, photometry, and electrochemistry. These methods are most useful for monitoring general or surrogate parameters relative to the function of the PW purification system, though some are applicable to specific substances.

##### Conductivity

This is the basic test for total ion concentration in the water and increasing conductivity indicates the ion exchange resins need renewing, or there has been a malfunction and excess ions are entering the PW system from some source.

Usual equipment: Two platinum electrodes (with Pt black coating) with a fixed area and spacing, energized with a constant small amplitude sine wave voltage and read with a Wheatstone bridge circuit. The output is either in conductivity (units  $\mu\text{S}/\text{cm}$ , previously  $\mu\text{mhos}/\text{cm}$ ) or its reciprocal, as resistivity (ohms cm or megohm cm).

Suggested improvements for SS operation: The commercial equipment can be used "as is" with the only interference coming from gas bubbles in water. However, the system can be improved by using a bipolar pulse detector circuit (4) which allows simple rugged electrodes of materials like stainless steel to be built into the water line (example, ring electrodes separated with Teflon insulating rings). This method is very sensitive and responds rapidly to conductivity changes. It is used in many modern instruments, often with micro cells. The electronics are simple and interface readily to computer control. In principle, one bipolar pulse circuit could be multiplexed to all the conductivity detectors and other resistance devices (like thermistors) on-board. If several units are used they would have the advantage of interchangeability.

##### Photometry

This is a group of methods including turbidimetry, spectrophotometry, and fiber optic sensors (optrodes), all based upon sensing the amount of light that is absorbed or scattered at one or more wavelengths.

Turbidimetry is a required water quality measurement related to the amount of light scattered from particulate matter suspended in water. If the scattered light is actually measured the method is called

nephelometry and is more sensitive for low light scattering. On the SS, increasing turbidity will generally indicate the presence of bacterial growth in the system or breakdown of the activated carbon or ion exchange resins. Detergent molecules, which form micelles, and gas bubbles will also scatter light. This permits the detection of unallowed gas bubbles in the PW as their size, and thus turbidity, is pressure sensitive.

Spectrophotometry is required for the PW "color" requirement. It is also being considered as a surrogate measurement for total organic carbon (TOC) in PW. However, individual organic compounds vary considerably in the amount of light absorbed at a specific wavelength, with most aliphatic compounds only weakly absorptive ( $\epsilon < 40$ ) above 200 nm. The method, if carried out at several specific wavelengths, may give a reasonable measure of aromatic compounds, as they strongly absorb ( $\epsilon > 8000$ ) in the region of 200 to 350 nm. If one makes the assumption that aromatic containing chemicals are the most hazardous, this measurement would be closer to a surrogate response for the "TOC less nontoxicants".

Usual equipment: Photometric processes require either laser or broad band, highly stable, light sources (with monochrometers or filters to select the desired wavelengths) and an optical train free from unwanted stray light and vibrations. The detectors need to be very sensitive with a wide dynamic range of response. This means they need very well regulated power supplies, often with either high voltage or current output capability.

Suggested improvements for SS operation: If several optical measurements are to be made, it may be possible to combine them, using only one or two light sources (UV and Visible) and one monochromator, with fiber optics used to pick up specific wavelengths and distribute them to the sample cells. Also, absorption measurements for contaminants of PW requires 10 cm or longer path length cells. For a typical aromatic compound at 100 ppb, with a molar absorptivity of  $8 \times 10^4$ , a 10 cm cell would give only an absorbance of 0.01 units (only 2.3% of the light absorbed). Other problems for photometric measurements on the SS come from absorbance due to added biocide (forms of  $I_2/I^-$ ), this may need prior removal (see section on "Silver Bullet"), and need to correct for scattering due to gas bubbles or turbidity. Finally to circumvent these problems the use of "optrodes", optical sensors equivalent to electrodes, may be used for some specific determinations. Optrodes have a reagent immobilized on the end of a double fiber optic that gives a color or fluorescence with the species of interest. Light is sent down one fiber and returned up the other and does not enter the solution (5).

### Electrochemistry

Direct measurements with electrochemistry include potentiometry, using ion and molecular selective electrodes (ISE and MSE) and oxidation reduction potential (ORP) electrodes, and some applications of controlled potential amperometry (CPA).

An ISE for pH determination is required for PW, and the activity of several other specific ions could be measured, examples  $I^-$  and  $F^-$ , however many other ISE suffer interference problems. MSEs could be used to measure  $O_2$ , and perhaps  $CO_2$  and  $NH_3$ . They also have the possibility for determining biochemical molecules through immobilized enzymes (6). The problem with most of these ISE and MSE is their need for frequent recalibrations. While not required, an ORP electrode (made of Pt or Au) would be useful for monitoring the redox potential of PW, which would indicate the level of  $I_2$  and/or  $O_2$ . A more negative trend in the potential may indicate anaerobic bacterial growth in the system.

The use of CPA with large area inert electrodes could be valuable for monitoring the concentrations of several classes of organic compounds present in PW, Table 2. In aqueous solutions the range of potentials available for CPA, before  $H_2$  or  $O_2$  formation occurs, is about +1.0 to -1.0 volts. The method might be used as a surrogate method for phenols (MCL of 1 ppb) and halogenated hydrocarbons (MCL of 10 ppb). With porous electrodes CPA could be used to remove the interfering  $I_2/I^-$  from PW before the trace organics are measured and to regenerate  $I_2$  from  $I^-$ .

TABLE 2.- POTENTIALLY DETECTABLE ORGANIC FUNCTIONAL GROUPS BY CONTROLLED POTENTIAL AMPEROMETRY (7).

Oxidizable Groups	Potential (V vs SCE)	Reducible Groups	Potential (V vs SCE)
Azines	> +1.2	Halogens	+0.2 > -0.2
Hydrocarbons	> +1.0	Nitro compds	-0.2 > -0.5
Amides	> +0.5	Diazo compds	-0.2 > -0.6
Amines	+1.0 > +0.5	Ethers	-0.6 > -1.4
Quinolines	+0.6 > +0.2	Esters	-0.8 >
Phenols	+0.5 > 0.0	Aldehydes	-1.1 >
		Ketones	-1.4 >
		Olefins	-1.7 >

(Note: This list represents general trends, as it is by no means complete nor totally accurate based upon my experience. RDG)

Usual equipment: For potentiometric measurements an indicator electrode and a reference electrode are needed, one reference electrode would work for several indicator electrodes if they are in close proximity. A very high impedance potentiometer, equivalent to a pH meter, is needed to sense the voltage without disturbing the measurement. For controlled potential amperometry usually separate reference, counter and working electrodes are needed, the latter two would be made of either Pt or Au. A three electrode potentiostat is usually needed to control and monitor the potential and current.

Suggested improvements for SS operation: Commercial equipment can be used, one precaution is the need for gel filled reference electrodes to avoid bubble formation between the electrode and the salt bridge

junction. All the indicator electrodes could be multiplexed thru one output console if each electrode has its own very high impedance operational amplifier. The problems to overcome in potentiometry are the stability of the electrodes and a means of cleaning and recalibrate them during a mission. If the electrodes are used in-line with the PW, a bypass loop to one or more special calibration solutions might be required. The CPA instrumentation is simple and should be interface thru a computer for digital control of potentials and currents. The electrodes may be subject to long term fouling if bacteria are present and may need periodic cleaning and exchange between missions.

#### INDIRECT METHODS

Indirect methods usually involve periodic sampling with chemical treatment, or sample separation followed by determination of the species of interest. The reaction processes to be discussed are TOC and two electrochemical techniques, anodic stripping voltammetry and micro-coulometric titrimetry (an insitu titration method). Also discussed are a semi-micro, zero G reaction system and a method for removing the interference of  $I_2/I^-$ . The separations methods of gas chromatography (GC), supercritical fluid chromatography (SFC), high performance liquid chromatography (HPLC), and CZE will be discussed briefly along with their detectors and required interfaces suitable for microgravity operation.

#### Chemical reactions

The TOC method oxidizes the organic carbon present in a PW sample and measures the  $CO_2$  released. This is an important surrogate measure of the organic quality of PW and should be carried out routinely on the SS.

Usual equipment: Organic matter in water samples (<10 ml) is oxidized in a reactor either by photochemical or thermal decomposition of persulfate, or by some other oxidation catalyst. The  $CO_2$  produced is measured by conductivity or IR, usually after trapping the  $CO_2$  in molecular sieves and purging it to the detector. The methods have problems with incomplete oxidation of refractory organic molecules. High temperature persulfate oxidation appears to give superior results and will be the method discussed. Inorganic carbon,  $HCO_3^-$ , interferes and is removed by prior  $N_2$  purging of the acidified sample. This causes some volatile organics to be removed and they must be trapped and oxidized to  $CO_2$ . These separate measurements of  $CO_2$  are called TIC and TVOC respectively.

Suggested Improvements for SS operation: Since  $CO_2$  is sparged from the reactor with  $N_2$  or air, the commercial method needs adaptation to work in microgravity. The method also consumes sodium persulfate and phosphoric acid solutions that should be considered hazardous in the SS environment. An "orbital reactor" (see indirect electrochemical methods) could be used to handle the gas-liquid separation problem and to conduct the persulfate high temperature oxidation. The acid and persulfate could be generated by standard electrochemically reactions within the reactor to avoid the need for consumables other than a sodium sulfate solution.



Microcoulometric titrimetry of the  $\text{CO}_2$  collected by purge and trap methods would allow for smaller water samples, down to 0.1 ml, than the current IR detector system. The reaction could be carried out in a 0.5 ml cell that would require less heat and smaller volume of consumables. These changes effectively convert the TOC determination to an electrochemical method.

**Electrochemical techniques** often require the removal of interferences due to  $\text{I}_2/\text{I}^-$  and  $\text{O}_2$  at the concentrations expected in PW, as they give appreciable reduction currents at small electrode potentials. I would suggest a pair of porous silver/silver iodide electrodes separated with a Nafion ion exchange membrane that can reduce iodide to very low levels, base upon the applied potential and the AgI solubility product of  $1.5 \times 10^{-16}$  at 25 °C. This "silver bullet" (SB) works on the principle that as the required water passes thru one electrode,  $\text{I}_2$  will react spontaneously with Ag to form AgI and  $\text{I}^-$  and further anodic oxidation of Ag will form more AgI on the electrode. Meanwhile, as a small amount of water passes thru the other electrode, its coating of AgI is reduced to Ag and  $\text{I}^-$  is released (this concentrated iodide solution can be collected for re-use in the PW loop after oxidation to  $\text{I}_2/\text{I}^-$ ). The relative amount of  $\text{I}^-$  in the two water streams is controlled by the applied voltage, with 350 mV giving a ratio of  $10^6$ .

Note, the SB method can be readily scaled up to remove  $\text{I}^-$  from PW for end uses. PW at 1 liter per minute would need a maximum current of 190 mA (27 mA nominal, 3 ppm  $\text{I}_{\text{total}}$ ). In this use the SB would have three connection positions, then as the AgI builds up on one electrode and is depleted on the other they can be interchanged so the opposite water streams flow thru the electrodes and their functions are exchanged. The third position would allow bypassing the electrodes to periodically disinfect the terminal portion of the water system with biocide.

Removal of  $\text{O}_2$  from water can also be accomplished by electrochemical reduction in similar flow cells with Pt electrodes, or by sparging the solution with pure nitrogen or argon. An "orbital reactor" (OR) is suggested as a microgravity method for the mixing and sparging of solutions required for chemical or electrochemical reactions. The OR is a platform holding a reaction vessel that is given a orbital motion while its orientation remains fixed, the only moving parts associated with the reactor are the connecting wire leads and tubing. These need to flex with the motion of the OR and their position and composition must be selected to reduce stress fatigue. The reaction cells can be of numerous sizes and shapes, but for electrochemistry a disk or washer shaped cell of 0.5 ml to 5 ml should work well. For example, a washer shaped cell 0.25 mm thick with radii of 1 and 2 cm, the volume would be 0.5 ml and with an orbiting rate of 212 rpm the force would be 0.5 and 1 G at the inner and outer surfaces respectively. For purging the OR cell, gas would be introduced at the periphery of the cell and it would move to the center in a spiral motion. The shear of moving water by the gas inlet would cause the bubbles to be small and well separated, giving very efficient sparging. The optimum amount of G force needs to be

determined, as little as 0.1 to 0.2 G may be sufficient for these operations. The flat shape and large area of these OR cells allows the placement of a variety of sensors in the same cell, for example, conductivity, large area, micro, reference, counter, and thin layer electrodes of several different materials, as well as optrodes and thermistors. Divided electrochemical cells for microcoulometric titrations, where the reagent is generated in situ, can be made by splitting the OR reactor horizontally with an ion exchange membrane.

**Anodic stripping voltammetry** is a common method for measuring trace (to sub ppb) levels of the heavy metal ions including Cd, Cu, Pb, Hg, Ni, Ag, Fe, Zn, and possibly Cr, Mn, and As in water. This method would replace most of the water analyses done by ground based graphite furnace atomic absorption. This method concentrates the metals by plating them out on an inert electrode, held at a sufficiently negative potential, from a uniformly stirred solution for a specific period of time. After this time the stirring is stopped and when the solution comes to rest the metals are removed by a positive voltammetric sweep. The amount of charge required to remove each metal at its specific redox potential corresponds to the metals concentration in solution. Often the metals are plated into a co-deposited mercury film and the procedure may require the addition of supporting electrolyte.

**Microcoulometric titrimetry** of the acid and base content of PW can be carried out in a divided OR cell which allows the production of either  $H^+$  or  $OH^-$ , in the PW sample, depending upon the electrode polarity. By applying constant current pulses of short duration, specific amounts of acid or base are generated, and with the use of a sensitive bipolar pulse conductivity detector, the total acid and base content of the PW can be determined from titration curves. The detection limits should, in theory, be at the sub ppb level for acid and base compounds, as a  $1 \mu A$  pulse for 100 msec is equivalent to 0.1 microcoulomb or 0.2 ppb for a 100 molecular weight acid or base in 0.5 ml. This technique might be developed to give a surrogate measure of organic acids, bases and possibly phenols in PW. It might also be used for measuring  $CO_2$  and  $NH_3$  in the PW and overcoming their analytical interference. As mentioned earlier the technique could be adapted to do the TOC analysis. The method could also be used in other SS chemical analyses where a needed titrant can be generated microcoulometrically.

### Separation Techniques

There are four general types of high resolution separation techniques that may be considered for identifying and quantitating components (mainly organic) of PW and other samples on the SS. Three are based upon pressurized fluid elution: GC, generally using nitrogen gas, SFC, using  $CO_2$  above its critical pressure ( $>1100$  psi), and several variations of HPLC, using aqueous/organic solvent mixtures or aqueous buffers (to pressures of 6000 psi). The other one, CZE, uses very high electric field driven elution and comes in several variations. For analyzing trace organics in PW these techniques will probably require concentration

of samples using some arrangement of purge and trap.

The GC technique is excellent for separating volatile heat stable organic compounds and interfaces well to a variety of detectors. It is considered the main tool for cabin atmosphere monitoring and could be useful for some specific FW analyses.

Usual equipment: The method requires a source of high pressure gas (100 psi) a sample injection system (sampling loop and valve), a temperature programmable oven (to 350 °C), a long silica capillary column with a bonded stationary phase (several may be needed) and an interface to a detector.

Suggested improvements for SS operation: Most commercial equipment would be compatible with the limitations of the SS environment. The small N<sub>2</sub> requirement can be met by using cabin make-up gas if properly purified, or generated electrochemically from hydrazine sulfate (toxic). The standard flame ionization detector (FID) should be readily interfaced to the column if a premix H<sub>2</sub>/O<sub>2</sub> micro burner is used to avoid microgravity effects. Otherwise a phototization detector (PID) might be adequate. A fourier transform infrared detector (FTIRD) should work directly, but the electrolytic conductivity detector (ElCD) that is excellent for halogen compounds would need modification of its gas/liquid reactor. The mass spectra detector (MSD), which will be discussed later, would interface easily.

The SFC technique is still developing and currently is able to separate heat sensitive compounds which are non-volatile, if they are not too polar, as well as the compounds handled by capillary GC. The technique falls between GC and HPLC in its applications and interfaces to most of the detectors used for GC.

Usual equipment: The equipment is usually a modification to either GC or HPLC instruments, and requires high pressure pumps (often the syringe type), usually a column oven for temperature up to 150 °C and an interface to a detector.

Suggested improvements for SS operation: Of the three chromatographic techniques this is the most compatible with SS operation since it uses CO<sub>2</sub> (which is recycled on the SS and is non-hazardous) and has modest power requirements. An advantage of supercritical CO<sub>2</sub> is its ability to purge traps of all but their most polar organic compounds. The eluting ability of CO<sub>2</sub> can be modified by changing its density (pressure) and by saturating it with water or polar organics. SFC has about the same detector limitations as GC.

The HPLC techniques have reached a high degree of sophistication and the ones of interest are normal and reverse phase partitioning for organics (NPP & RPP), ion pairing for ionic and ionizable organics (IP), and ion exchange, mainly for inorganic ions, called ion chromatography (IC). In combination these techniques have the ability to separate most mixtures

of organic compounds including the most polar and non-volatile, though the resolution is not as high as with GC or SFC.

Usual equipment: The methods all require special very high pressure pumps and controllers to push eluent solutions rapidly thru short (10 cm) small bore columns packed with special very small diameter particles designed or coated for the particular application. This means that either dedicated instruments are needed for each application or columns and eluent systems must be changed for different analyses. For each sample the NPP and RPP systems use about 10 to 15 ml of a complex eluent mixture, often containing acetonitrile or methanol as a major component. The IC requires several aqueous ionic buffer combinations and ion exchange columns to separate the different sets of ions effectively with a sub ppb level of sensitivity. The IP technique is a combination of the previous two and requires an organic solvent with ionic buffer and separation of organic ion pairs is usually on RPP columns. The detectors for these methods are generally ones that operate well with solutions, for example, conductivity, electrochemical (often CPA), and various photometric methods. Recently, by means of a complex interfaces, several types of mass spectra detectors (MSD) have been successfully used with HPLC (see the section on detectors).

Suggested improvements for SS operation: The large amount of consumable buffers and their waste, some of which are toxic, may limit the use of HPLC in the SS. The amount of eluent can be reduced about 80 fold by using "microbore" columns (8). However, the IC which is the most important for PW analysis apparently does not have the extra small particle ion exchange resins needed for microbore modification at this time.

The CZE techniques are very new and hold much promise as a universal separation technique (9). They use the principle of electroosmotic force to move buffer solutions down small bore (<100  $\mu\text{m}$ ) while at the same time using the electrophoretic mobility to separate charged species. Besides zone electrophoresis itself, there are two variant techniques, isotacophoresis that uses a discontinuous ionic buffer to focus and separate analyte ions, and electrokinetic chromatography that uses an ionic micelle buffer to separate neutral organic molecules.

Usual equipment: No commercial equipment is currently available, but the apparatus is simple to build. The methods requires a 30 kV DC at 10  $\mu\text{A}$  power supply, a 0.5 to 2 m length of fused silica capillary tubing, a very small volume of aqueous buffers, and an interface to a detector. Sample size for CZE is about 10 nl, and the resolution is about equivalent to capillary GC. Because of the small sample size and column diameter it requires very sensitive and high resolution detectors.

Suggested improvements for SS operation: The techniques are very compatible with the SS environment, with small weight, volume, power and consumables (non-hazardous) requirements. However, considerable development is needed to find the right buffer protocols to accomplish

the required separations. For convenience of SS operation, several columns and buffer setups may be required that can be switched between one power supply. It may be necessary to change capillary columns frequently due to plugging or other failure and replacements with easy means of installation is needed. Samples of PW will have to be concentrated for use with these techniques. For the required sub  $\mu$ l sized samples, this might be accomplished without loss of too many volatile organics by diffusion of water out thru a membrane.

#### Detectors

A number of detectors are available for the separation methods just discussed, and some were commented upon in that section. The mass spectra detector (MSD) in its several variations is close to the universal detector, giving nearly absolute identification of unknown components, requiring very small samples, having very high sensitivity, and interfacing easily to GC and SFC. The interface to HPLC and CZE is more difficult because the the eluent is a liquid. Several techniques have been developed, but there are problems with getting all analyte species ionized and into the MSD with equal efficiency. Electrochemical and conductivity detectors interface readily to the HPLC and CZE columns and are very sensitive and can be made with very small volume cells. There are several other detectors which may be useful but will not be discussed: photoionization, UV absorption, fluorescence and infrared.

The MSD methods include the low resolution units (Ion Trap, Mass Sensitive Detector and related ion drift methods) that give only the parent mass/charge ion of unit resolution, and the high resolution mass spectra systems (quadrupole units are the smallest and simplest) that give a complete molecular formula and often an unambiguous structure. Except for the ion drift method, the detectors all require a very good quality vacuum ( $10^{-7}$  Torr) and need high velocity pumping for interfacing to HPLC or CZE. The requirements of complexity, weight, volume, and energy consumption make the MSD the least compatible of the analytical techniques for SS, however their advantage may be worth the effort to develop a workable system. The most likely candidates would be an ion drift, or ion trap detector. The ion trap is the smallest detector, excluding the turbomolecular pump, it is about 64 cubic inches, while the ion drift unit works with a plasma at atmospheric pressure.

The MSD interface requires removing the volatile part of the eluent stream from the analyte species and converting them to "dry" ions while introducing them into the mass/charge detector system. Two interfaces currently in use are electrospray that uses high voltage to nebulize and ionize the droplets and theromospray that uses rapid heating of the effluent containing special buffers (usually  $\text{NH}_4\text{HCO}_3$ ) to produce ionization under these conditions. The removal of solvent is aided by a rapid flow of dry  $\text{N}_2$  in front of the MSD inlet. There is still a need for research on these interface methods and a combination of the two may be needed for the special conditions on the SS.

Electrochemical and conductivity detectors can both use the same microcell and electrode design to interface efficiently to HPLC and CZE systems. The conductivity detector would use the same bipolar pulse circuit that has been indicated for other conductivity measurements. The electrochemical detector would normally operate as a controlled potential amperometer (CPA), but could be used for rapid scan cyclic voltammetry for unknown identification. The micro volume cell that would fit directly on the end of either microbore HPLC or CZE columns could be constructed in sandwich fashion from thin Pt or Au foils (0.01 mm) between thin Teflon films (0.03 mm). A hole to match the inside diameter of the column (0.1 mm or less) would be punched or laser drilled through the layers to make a set of thin ring electrodes. The volume of the cell would be about 0.3 nl and would not degrade the resolution of a CZE column. Except for identifying unknowns, where accurate mass and structural information is needed, these detectors would work very well for most HPLC or CZE separation on the SS.

#### RECOMMENDATIONS

A variety of suggestions have been made throughout this report to improve the analytical techniques for SS operation. The most important recommendations are:

- (1) The silver/silver chloride electrode (SB) method of removing  $I_2/I^-$  biocide from the water, since it may interfere with analytical procedures for PW and also its end uses (page 13-10).
- (2) The orbital reactor (OR) method of carrying out chemistry and electrochemistry in microgravity by using a disk shaped reactor on an orbital table to impart artificial G force to the contents, allowing solution mixing and separation of gases and liquids (page 13-10).
- (3) A simple ultra low volume highly sensitive electrochemical/-conductivity detector for use with a capillary zone electrophoresis apparatus (page 13-15).

It is also recommended, since several different conductivity and resistance measurements are made during the analysis of PW, that the bipolar pulse measuring circuit be used in all these applications for maximum compatibility and redundancy of equipment (page 13-5).

#### REFERENCES

1. Space Station Program Definition and Requirements Document. NASA SST 30000. Rev D., 1987, Table 2-34.
2. Shrader Analytical and Consulting Laboratories Report of Analytical Services: Space Lab 3 ARS Humidity Condensate. SL 12352, 1985.
3. Sorbert Purification Testing of Air Revitalization Condensate. JSC 19170-SS-089 (CSD), 1985.
4. Johnson, D. E. and C. G. Enke: Bipolar Pulse Technique for Fast Conductance Measurements. *Analytical Chemistry*, vol. 42, March 1970, pp. 329-335.
5. Seitz, W. R.: Chemical Sensors Based on Fiber Optics. *Analytical Chemistry*, vol. 56, January 1984, p. 16A.
6. Rechnitz, G.: Bioanalysis with Potentiometric Membrane Electrodes. *Analytical Chemistry*, vol. 54, September 1982, p. 1194A.
7. Skoog, D. A.: *Principles of Instrumental Analysis*, third edition. Saunder College Publishing. 1985, p. 797.
8. Isco Application Lab Staff: Enhanced Mass Sensitivity and Resolution in Microbore LC by Improvements in Detection and Liquid Flow Path. *Isco Applications Bulletin*, No. 44, March 1985, p.4.
9. Smith, R. D.; Olivares, J. A.; Nguyen, N. T.; Udseth, H. R.: Capillary Zone Electrophoresis-Mass Spectrometry Using an Electrospray Ionization Interface. *Analytical Chemistry*, vol. 60, March 1988, pp.436-441.