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# Analysis of water from the Space Shuttle and Mir Space Station by ion chromatography and capillary electrophoresis

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# Abstract

Drinking water and condensate samples collected from the US Space Shuttle and the Russian Mir Space Station are analyzed routinely at the NASA-Johnson Space Center as part of an ongoing effort to verify water quality and monitor the environment of the spacecraft. Water quality monitoring is particularly important for the Mir water supply because approximately half of the water consumed is recovered from humidity condensate. Drinking water on Shuttle is derived from the fuel cells. Because there is little equipment on board the spacecraft for monitoring the water quality, samples collected by the crew are transported to Earth on Shuttle or Soyuz vehicles, and analyzed exhaustively. As part of the test battery, anions and cations are measured by ion chromatography, and carboxylates and amines by capillary electrophoresis. Analytical data from Shuttle water samples collected before and after several missions, and Mir condensate and potable recovered water samples representing several recent missions are presented and discussed. Results show that Shuttle water is of distilled quality, and Mir recovered water contains various levels of minerals imparted during the recovery processes as designed. Organic ions are rarely detected in potable water samples, but were present in humidity condensate samples. © 1998 Elsevier Science B.V.

Keywords: Water analysis; Space Shuttle; Mir Space Station; Inorganic cations; Inorganic anions; Carboxylic acids; Amines

# 1. Introduction

Ground-based analyses of water samples obtained from both the US Space Shuttle and the Russian Mir Space Station are currently the principal means of assessing water quality on board the spacecraft as part of an array of environmental monitoring measures NASA has implemented to protect crew health [1]. For Shuttle water samples, the analyses include inorganic anions, cations, transition metals, physicochemical properties, total organic carbon (TOC) and microflora. For Mir water samples, the same inorganic profile plus a full organic compound profile is conducted [2]. Appropriate testing also ensures that adequate biocide is present, since there is currently no on-board means to measure this parameter. Historically, NASA has used iodine as a drinking water bactericide in spacecraft, whereas the Russian Space Agency has used ionic silver.

On the Shuttle, hydrogen and oxygen from cryogenic reserves are electrolytically combined in the fuel cells to produce electricity, with water as a byproduct. The water is used for drinking and food rehydration, and cooling of the vehicle via a flash evaporator system. Any excess water produced during a mission is routinely jettisoned overboard through a heated nozzle. Water destined for drinking or food rehydration passes through an iodinated ionexchange resin bed – the microbial check valve (MCV) – which adds 2 to 3 mg/l of iodine along

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Fig. 1. Simplified diagram of the Shuttle storage and distribution system for water derived from the fuel cells. The microbial check value (MCV) provides iodine for disinfection.

with 0.5 to 1.5 mg/l of iodide, and then flows into bellows tanks for storage (Fig. 1) [3].

The Mir Space Station, over its 11.5-year operation, has had two sources of potable water; water recovered from humidity condensate and water delivered by the Russian Progress resupply spacecraft that is stored and dispensed in the SVO-ZV system (Fig. 2). Catalytic oxidation, carbon adsorption and ion-exchange are employed to remove contaminants from the humidity condensate, and a conditioning bed imparts silver ions for disinfection and minerals for aesthetics. Russian water requirements specify mineral content because of nutritional concerns for long-duration flights. Water also is recovered from urine, but the product is used only for generating oxygen and flushing the waste system.

During the joint NASA–Mir program, a third source of potable water for the Mir Space Station has been the Shuttle. Since 1995, excess Shuttle fuel cell water has been treated and transferred to Mir as an inexpensive alternative to supplying water from Earth. The water is transferred using 44-1 collapsible bags with bladders called contingency water containers (CWCs). Before filling the CWCs, iodinated Shuttle fuel cell water is treated by passing it through an activated carbon bed and an ion-exchange resin bed as shown in Fig. 3. The activated carbon bed is designed to remove the iodine, and the ion-exchange



Fig. 2. Conceptual diagram of Mir water systems. Dashed lines denote manual water transfer routes. The galley provides hot and cold water dispensing of recovered or resupplied water, and the SVO-ZV system dispenses ambient temperature water from the resupply tanks.

resin is designed to remove the iodide in the Shuttle water and avoid formation of silver iodide in the CWCs that is both insoluble and nonbiocidal. Silver, fluoride, calcium and magnesium contained in concentrates are then injected into the stream while the CWC is filling. Highly soluble formate salts are used to prepare the mineral concentrate to minimize the injection volume. After filling, a small sample is collected from representative CWCs [4] for analysis. As of the STS-86 mission in October 1997, about 4500 l have been supplied to Mir in this manner.

Because there is little equipment on board Mir for monitoring water quality, samples of recycled and



Fig. 3. System for batch processing of Shuttle water for transfer to Mir.

297

stored water are collected periodically by the crew and transported to Earth on Shuttle or Russian Soyuz vehicles for analysis as part of joint science experiments with the Russian Space Agency. Humidity condensate samples, which represent the spacecraft atmosphere in terms of compounds present in the air at the time of sample collection, also are being collected and returned for analysis to assess crew exposure to potentially toxic compounds, and to aid in the design of water reclamation systems for future spacecraft. Samples of water loaded in Progress vehicles before launch also are being analyzed. As part of the test battery performed on these samples, ion chromatography (IC) is used to determine anions and cations, while capillary electrophoresis (CE) is used to determine carboxylates and amines. Table 1 lists the target ions for this work along with their

Table 1

Target inorganic anions, cations, carboxylates and amines

Target ions	NASA limit (mg/l), where applicable
Anions	
Bromide	N/A
Chloride	200
Fluoride	N/A
Nitrite	N/A
Nitrate	10
Phosphate	N/A
Sulfate	250
Cations	
Ammonium	0.5
Calcium	30
Lithium	N/A
Magnesium	50
Potassium	340
Sodium	N/A
<i>Carboxylates</i> <sup>a</sup>	
Formate	N/A
Glycolate	N/A
Glyoxylate	N/A
Acetate	N/A
Lactate	N/A
Propionate	N/A
Amines <sup>a</sup>	
Methylammonium	N/A
Trimethylammonium	N/A
Ethylammonium	N/A
Propylammonium	N/A

<sup>a</sup> Used for total organic carbon characterization.

respective limits, where applicable, as specified by NASA [5].

Results of the Mir water quality monitoring program are being incorporated into the development of a water recycling system for the International Space Station (ISS). The NASA potable water specification for ISS requires that the TOC content be less than 0.5 mg/l and the uncharacterized TOC be less than 0.1 mg/l [6]. The uncharacterized TOC is the TOC of the water minus the sum of the TOC of the organic compounds identified and quantified by specific organic analyses. These requirements represent a significant analytical challenge for both water recycling and water monitoring. A water recycling system must be designed to meet these strict TOC requirements. In addition, monitoring equipment must be provided to ensure that the requirements are met. Although current ISS on-board monitoring requirements call for only TOC to be measured, additional instrumentation to measure specific organics may be required in the future. Because CE generally requires lower sample and eluent volumes than IC, zero-gravity CE technology is currently being developed to meet these possible future requirements.

The purpose of this paper is to present the current IC and CE analytical methods used during the analysis of Shuttle and Mir water samples, along with representative results. Progress on the development of zero-gravity CE technology has been reported elsewhere [7].

#### 2. Experimental

#### 2.1. Ion chromatography system and conditions

Inorganic anions were determined using a Model 4000i IC system with a DS4 conductivity detector (Dionex, Sunnyvale, CA, USA) [8]. The system was configured with an AG14 guard column and an AS14 (250 mm×4 mm) analytical column, and operated with a mobile phase of NaHCO<sub>3</sub> (1.0 m*M*) and Na<sub>2</sub>CO<sub>3</sub> (3.5 m*M*) at a flow-rate of 1.2 ml/min [9]. Background conductivity was reduced using a Dionex Anion Self-Regenerating Suppressor (ASRS-I, 4 mm) in the chemical suppression mode with 25 m*M* H<sub>2</sub>SO<sub>4</sub> at a flow-rate of 3 ml/min. All samples

were introduced directly into the IC by an AS-40 autosampler, using 5-ml sample tubes. PeakNet 4.3 software (Dionex) on a personal computer was used to control the IC systems, collect the data and perform the data analyses.

Inorganic cation analysis was performed on a Dionex DX-120 IC system with a conductivity detector. The system was configured with a CG12A guard column and a CS12A (250 mm×4 mm) analytical column, and operated with a mobile phase of 11 mM H<sub>2</sub>SO<sub>4</sub> at a flow-rate of 1.0 ml/min [10]. The background was reduced using a Cation Self-Regenerating Suppressor-I system (CSRS-I, 4 mm) in the autosuppression recycle mode.

Eluents were prepared from ultrapure-grade sulfuric acid (J.T. Baker, Phillipsburg, NJ, USA), U.S.P. TAC-grade sodium hydrogencarbonate (Malinckrodt, Paris, KY, USA), and ACS-grade sodium carbonate (Aldrich, Milwaukee, WI, USA). The seven common anion and six common cation standards were obtained from SPEX (Metuchen, NJ, USA), and mineral and nutrient check standards from Analytical Products Group (APG, Belpre, OH, USA) were used for quality control (QC). All vials and volumetric flasks used in sample and standard preparation were made of polypropylene and purchased from Dionex or Nalgene (Milwaukee, WI, USA). The instruments were recalibrated whenever either a calibration check standard or external APG check standard fell out of range. The acceptable range for the calibration check was  $\pm 10\%$  of the true value. The acceptable range for the APG QC check was the 95% confidence limits published in the Certificate of Analysis for each lot. Both check standards were analyzed with each batch of samples and the results were used to verify that the methods were under control.

# 2.2. Capillary electrophoresis system and conditions [11–13]

Carboxylates were determined on a 3D CE system (Hewlett-Packard, Wilmington, DE, USA). Bare fused-silica, 50  $\mu$ m I.D.×360  $\mu$ m O.D., extended light path capillary columns from Hewlett-Packard were used. The total length of the capillary was 62.5 cm with an effective length of 56 cm. New capillaries were flushed with 1.0 *M* NaOH for 10 min, 0.1 *M* NaOH for 10 min, followed by a 10-min flush

with running buffer and allowed to equilibrate overnight. To condition the capillary before each run, the capillary was flushed with sample buffer for 5 min followed by 20 s of -20 kV. Sample injections from 1-ml vials were made with a pressure injection of 5 kPa for 20 s (1000 mbar s) followed by a buffer injection of 5 kPa for 3 s (150 mbar s). The run voltage was -30 kV (negative polarity at injection end) for 10 min. Indirect photometric detection was used with the sample wavelength at 350 nm and the reference at 200 nm. Slit widths were 20 nm and 10 nm, respectively. The capillary was automatically maintained at 20°C, and the inlet and outlet vials were replenished before each run.

The buffer was a commercial preparation (Organic Acids Buffer Solution, Hewlett-Packard), with a pH of 5.62 and a conductivity of 0.745 mS/cm. On occasion, when the commercial buffer was not available, a buffer was prepared in house. For this, separate 50 mM and 20 mM stock solutions were prepared from potassium hydrogenphthalate (KHP) (Aldrich) and tetradecyltrimethylammonium bromide (TTAB) (Aldrich), respectively. Deionized water of 17.8 M $\Omega$  or greater specific resistance was used to prepare all solutions. The run buffer was made from these stock solutions by making a 1:10 dilution that yielded a 5 mM KHP and 2 mM TTAB solution that was filtered through a 0.45-µm membrane filter. Before completing the dilution, the pH was adjusted to 5.56 using 0.1 M sodium hydroxide. Conductivity was measured to ensure that the conductivity of the buffer was 10- to 15-times greater than that of the samples [14]. Instrument control and data acquisition were performed using ChemStation software (Hewlett-Packard) on a personal computer.

Carboxylates (Table 1) were quantified by an internal standard method using succinic acid (Aldrich) as the internal standard. A five-point calibration curve was established by preparing standards from commercially available acid salts (Aldrich). For each batch of samples and standards, two blanks were run, one with and one without the internal standard. A commercial volatile acid standard mix (Supelco, Bellefonte, PA, USA) was used as an independent calibration check for three compounds. Deviations of 20% or less from the published values were deemed acceptable. Samples exhibiting significant matrix effects (typical for organic carbon-laden condensate samples) were verified with a 1.0-mg/l carboxylate standard spike to confirm retention times.

Amines were determined using a Quanta 4000 CE system (Waters, Milford, MA, USA). Capillaries used were bare fused-silica, 50  $\mu$ m I.D. $\times$ 360  $\mu$ m O.D. (Phenomenex, Torrance, CA, USA). Total length of the capillary was 80 cm with an effective length of 72 cm. Capillaries were cut from a 5-m roll, and the detection window and ends were burned with a flame and cleaned with methanol.

New capillaries were conditioned as in the carboxylates procedure. Between runs, the capillary was flushed with run buffer for 4 min. Sample injections were made by hydrostatic injection for 200 s from 0.5-ml vials. The capillary temperature was not controlled, but the average was 22°C. The run voltage was 20 kV (positive polarity at injection end) for 8 min. A zinc lamp was used with a 214-nm filter. Data acquisition and processing were performed using Millenium data acquisition software (Waters) on a personal computer.

The amines buffer was made using imidazole (Aldrich) as the background electrolyte, and  $\alpha$ -hydroxyisobutyric acid (HIBA) (Aldrich) as a complexing agent. A stock concentrate of 100 m*M* HIBA and 50 m*M* imidazole was prepared. The run buffer was prepared by diluting the stock concentrate 1:10 and filtering it through a 0.45-µm membrane filter. No pH adjustment was necessary.

Amines (Table 1) were quantified by an external standard method. A five-point calibration curve was established by preparing standards from amine salts. A blank and a separately prepared standard were used as a calibration check with each batch of samples and standards. Again deviations of 20% or less from the prepared values were accepted. Samples exhibiting matrix effects were spiked with a 1.0-mg/l mixed amines standard to confirm retention times.

# 2.3. Sample collection and analysis

To minimize sample degradation, all samples are analyzed as soon as possible. Shuttle samples are taken within 24 h of landing and transported on ice to the laboratory. Analyses for anions and cations are normally completed within 28 days. Shuttle water samples are not analyzed for carboxylates and amines since organics usually are not a concern.

Unfortunately, the samples collected periodically on Mir are not refrigerated before transport back due to a lack of refrigerator space. Once the samples arrive, they are transported on ice to the laboratory and kept refrigerated until analyzed. Analyses of Mir samples are performed as soon as possible and normally completed within 28 days.

Water transfer samples were collected immediately after filling the CWCs, and Mir samples were collected in flight from the galley hot and cold ports and from the potable water storage-tank dispenser (SVO-ZV). Mir humidity condensate samples were collected using in-line Russian-built titanium samplers. The Mir samples were returned on the Shuttle and split between US and Russian laboratories. Because of small sample volumes of some Mir samples, not all analyses could be performed on every sample. The US portion of the condensate samples (typically 35 to 50 ml volume) were aliquoted primarily for organic analyses. Consequently, IC analyses of the condensate samples were not performed. All other samples received with adequate sample volumes (>250 ml) were analyzed for anions and cations by IC.

IC samples were analyzed in triplicate on undiluted sample aliquots. If sample quantities fell outside the calibration curve range, appropriate dilutions were made and ran in triplicate as well. For the Shuttle–Mir water transfer samples, only IC cation results are reported herein. Carboxylate and amine analyses were performed only on Mir samples. Dilutions were necessary prior to CE analyses of samples because matrix interferences were encountered.

# 2.4. Method detection limits

Method detection limits (MDLs) for the IC results were calculated by running seven standards and obtaining the averages and standard deviations (S.D.s). The S.D. was multiplied by the corresponding Student-t value to obtain the MDL [15]. The IC methods had no significant interferences that would compromise the MDL.

For CE results, the lowest point in the calibration curve was used since this method was susceptible to matrix interferences. CE is very sensitive to samples that alter the ionic strength or pH of the buffer system. Many condensate samples, laden with organic compounds, cause baseline disturbances of CE samples that can only be remedied with dilutions thus raising the respective MDL.

# 3. Results and discussion

Since a large number of samples have been collected during the past 16 years of Shuttle missions and 2.5 years of the Shuttle-Mir program, only the results of select groups of the samples are reported in the Tables that follow. In each table, minimum, maximum and average values are provided where meaningful. IC results for Shuttle water samples representing 11 missions in 1996 and 1997 are shown in Table 2. Sulfate was present in seven of the samples and ranged in concentration from 0.02 to 0.73 mg/l. No bromide, nitrite, nitrate or phosphate was detected (detection limit: 10  $\mu$ g/l), and fluoride and chloride were detected infrequently. Of the cations, ammonium and potassium were most prevalent, although the concentrations were only 2 to 33 µg/l. Small levels of potassium are expected in the Shuttle water because the Shuttle fuel cells contain potassium hydroxide as an electrolyte. The source of ammonium is not certain, but could stem from the iodinated resin used in the MCV. Sodium, magnesium and calcium concentrations, when detected, also were quite low (2 to 17  $\mu$ g/l). No lithium was detected.

IC cation results for the CWCs sampled during STS-81 (January 1997) and STS-84 (May 1997) Shuttle-Mir missions are presented in Table 3. Of particular interest are the concentrations of calcium and magnesium, since they were added purposefully. Magnesium concentrations were found to be 4.2 to 5.5 mg/l, with an average of 4.9 mg/l, and calcium levels were between 24.5 to 30.2 mg/l, with an average of 28.0 mg/l. The expected (design) concentrations were 5 and 30 mg/l, respectively. Sodium and potassium also were detected between 0.1 and 1.3 mg/l. Sodium was expected because the silver concentrate (the biocide solution added to each CWC) is formulated from silver fluoride and sodium fluoride. No lithium or ammonium was detected in the CWC samples.

Table 4 contains results of IC analysis of water loaded into the Russian resupply vehicle Progress before launch. The source is municipal tap water that is processed by adding minerals and silver. Upon delivery to Mir, the water is dispensed to the crew via the SVO-ZV system. Of the anions, nitrate exhibited the most variance, with concentrations ranging from 0.2 to 2.5 mg/l as nitrogen. No nitrite, bromide or phosphate was detected, and ammonium

Table 2

IC data for Shuttle galley water samples collected post-flight (units: mg/l)

Mission	Collection date <sup>a</sup>	$F^{-}$	$\mathrm{Cl}^-$	$NO_2^ N$	$\mathrm{Br}^{-}$	$NO_3^ N$	$HPO_4^{2-}-P$	$\mathrm{SO}_4^{2-}$	Li <sup>+</sup>	Na <sup>+</sup>	NH4 <sup>+</sup> -N	$\mathbf{K}^+$	${\rm Mg}^{2+}$	Ca <sup>2+</sup>
	(month/day/year)													
STS-72	1/20/96	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.030	0.032	0.016	0.002	0.010
STS-75	3/10/96	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.002	0.143	0.007	0.006	0.003
STS-76	4/1/96	< 0.01	0.16	< 0.01	< 0.01	< 0.01	< 0.01	0.73	< 0.002	0.002	0.071	0.020	< 0.002	< 0.002
STS-77	5/30/96	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.73	< 0.002	< 0.002	0.052	0.018	< 0.002	0.016
STS-78	7/8/96	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.73	< 0.002	< 0.002	0.128	0.019	< 0.002	0.008
STS-79	9/27/96	< 0.01	0.06	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.002	0.018	0.104	0.033	< 0.002	< 0.002
STS-80	12/8/96	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.002	0.002	0.089	0.007	0.008	< 0.002
STS-81	1/23/97	0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.07	< 0.002	< 0.002	0.090	0.003	0.003	< 0.002
STS-82	2/21/97	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.07	< 0.002	< 0.002	0.120	0.002	< 0.002	0.003
STS-83	4/9/97	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.014	0.073	0.025	< 0.002	0.004
STS-84	5/25/97	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.008	0.089	0.007	< 0.002	0.017
	Average	0.03	0.11	< 0.01	< 0.01	< 0.01	< 0.01	0.34	< 0.002	0.011	0.090	0.014	0.005	0.009
	Minimum	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	< 0.002	0.032	0.002	< 0.002	< 0.002
	Maximum	0.03	0.16	< 0.01	< 0.01	< 0.01	< 0.01	0.73	< 0.002	0.030	0.143	0.033	0.008	0.017

Description	Collection date (month/day/year)	Li <sup>+</sup>	Na <sup>+</sup>	$NH_4^+ - N$	$K^+$	Mg <sup>2+</sup>	Ca <sup>2+</sup>
STS-81 CWC #1	1/12/97	< 0.002	0.567	< 0.002	1.28	4.73	27.7
STS-81 CWC #3	1/13/97	< 0.002	0.563	< 0.002	0.510	4.69	27.7
STS-81 CWC #9a	1/16/97	< 0.002	1.12	< 0.002	0.463	4.78	28.0
STS-81 CWC #9b	1/16/97	< 0.002	0.573	< 0.002	0.093	4.84	28.4
STS-81 CWC #15	1/19/97	< 0.002	0.747	< 0.002	0.240	4.17	24.5
STS-84 CWC #1	5/16/97	< 0.002	0.753	< 0.002	0.928	5.16	29.2
STS-84 CWC #11	5/21/97	< 0.002	1.39	< 0.002	0.290	4.72	26.4
STS-84 CWC #3	5/17/97	< 0.002	0.813	< 0.002	0.244	5.47	30.2
STS-84 CWC #9	5/20/97	< 0.002	0.643	< 0.002	0.103	5.54	30.0
	Average	< 0.002	0.797	< 0.002	0.461	4.90	28.0
	Minimum	< 0.002	0.563	< 0.002	0.093	4.17	24.5
	Maximum	< 0.002	1.39	< 0.002	1.28	5.54	30.2

Table 3 IC data for Shuttle mineralized water transferred to Mir (units: mg/l)

was detected in only one of the five samples. Lithium was detected at 2  $\mu$ g/l in three of the samples. The mineral content was similar to US tap water, with mg/l concentrations of chloride, sulfate, potassium, magnesium and calcium.

Results of IC and CE analyses of samples from the Mir water storage and dispensing system (SVO-ZV) are given in Tables 5 and 6, respectively. As expected, IC results for two of the three samples were similar to results for the ground-supplied water (Table 4). The sample collected on 6 November 1996, however, is clearly distinct, with no chloride, nitrate or sulfate detected, and significantly lower levels of sodium and potassium. The distinction is further exhibited in the CE results. Formate was detected in the 6 November and 5 September 1996 samples at 40.5 and 73.0 mg/l, respectively. In fact,

formate was the only target ion among the carboxylates and amines detected in this group of samples. The source of formate is the highly soluble calcium and magnesium formate salts used in the concentrate formulation for mineralizing Shuttle water for Mir use. It appears that the CWC water was plumbed into the Mir system, diluted slightly, and dispensed. Russian Space Agency water experts have confirmed this conclusion [16].

Tables 7 and 8 contain the results of IC and CE analyses of samples of Mir potable water recovered from condensate, with hot and cold samples grouped. Again, nitrite, bromide and lithium were not detected. Nitrate, phosphate and ammonium were detected in only a few samples and at insignificant concentrations. The calcium concentrations varied over an order of magnitude. Three of the samples

Table 4							
IC results for Mir	ground-supply wate	r. before	loading int	o Progress	vehicles	(units:	mg/l

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Collection date (month/day/year)	$F^{-}$	Cl	NO <sub>2</sub> <sup>-</sup> -N	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup> -N	HPO <sub>4</sub> <sup>2-</sup> -P	$\mathrm{SO}_4^{2-}$	Li <sup>+</sup>	Na <sup>+</sup>	$NH_4^+ - N$	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2</sup>
1/19/95	0.11	11.7	< 0.01	< 0.01	0.60	< 0.01	13.7	0.002	19.3	< 0.002	12.4	10.3	25.0
3/6/95	0.08	14.2	< 0.01	< 0.01	0.89	< 0.01	15.5	0.002	9.87	< 0.002	4.23	8.57	17.0
6/3/96	0.09	13.5	< 0.01	< 0.01	2.53	< 0.01	14.2	0.002	8.30	0.017	2.26	9.23	34.7
8/13/97	0.14	12.1	< 0.01	< 0.01	0.18	< 0.01	13.2	< 0.002	4.31	< 0.002	1.63	6.89	29.7
8/13/97	0.14	12.0	< 0.01	< 0.01	0.19	< 0.01	13.4	< 0.002	4.09	< 0.002	1.65	7.00	29.8
Average	0.11	12.7	< 0.01	< 0.01	0.88	< 0.01	14.0	0.002	9.17	0.017	4.43	8.40	27.2
Minimum	0.08	11.7	< 0.01	< 0.01	0.18	< 0.01	13.2	< 0.002	4.09	< 0.002	1.63	6.89	17.0
Maximum	0.14	14.2	< 0.01	< 0.01	2.53	< 0.01	15.5	0.002	19.3	0.017	12.4	10.3	34.7

Table 5								
IC results for	r Mir stored	l water	samples	from	SVO-ZV	system	(units:	mg/1)

Collection date (month/day/year)	$F^{-}$	$Cl^{-}$	$NO_2^ N$	$\mathrm{Br}^-$	$NO_3^ N$	HPO <sub>4</sub> <sup>2-</sup> -P	$\mathrm{SO}_4^{2-}$	Li <sup>+</sup>	Na <sup>+</sup>	$\mathrm{NH}_4^+\mathrm{-N}$	$K^+$	${\rm Mg}^{2+}$	Ca <sup>2+</sup>
9/5/96	а	а	a	а	a	а	а	а	а	a	а	а	а
11/6/96	0.45	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.56	< 0.002	0.04	4.20	23.3
1/18/97	0.15	13.3	< 0.01	< 0.01	0.17	< 0.01	14.7	0.002	6.35	< 0.002	2.13	7.62	29.9
5/19/97	0.19	12.2	< 0.01	< 0.01	0.44	0.11	16.4	< 0.002	7.53	< 0.002	1.93	9.76	38.5
Average	0.26	12.6	< 0.01	< 0.01	0.31	0.11	15.6	0.002	4.81	< 0.002	1.37	7.19	30.6
Minimum	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.56	< 0.002	0.04	4.20	23.3
Maximum	0.45	13.3	< 0.01	< 0.01	0.44	0.11	16.4	0.002	7.53	< 0.002	2.13	9.76	38.5

<sup>a</sup> Insufficient sample volume for IC analysis.

CE results for Mir stored water samples from the SVO-ZV system (units: mg/l)

Collection date (month/day/year)	Oxalate	Formate	Glycolate	Glyoxylate	Acetate	Lactate	Propionate	Butyrate	Methylamine	Trimethylamine	Ethylamine	Propylamine
9/5/96	<1.0	73.0	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
11/6/96	а	40.53	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<1.25	<2.5	<1.25	<1.25
1/18/97	а	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
5/19/97	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	a	<1.25	<2.5	<1.25	<1.25
Minimum	< 0.25	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.25	< 0.25	< 0.25	< 0.25
Maximum	<1.0	73.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<1.25	<2.5	<1.25	<1.25

<sup>a</sup> Unresolved.

Table 6

had no detectable sulfate, and two of the samples contained little chloride. Absence of chloride and sulfate could not be correlated with the presence of formate, as with the SVO-ZV samples. As with the SVO-ZV water, formate was the only target ion among the carboxylates and amines detected among the Mir regenerated samples. However, it appeared in only 2 of 14 samples analyzed by CE, with one of the two occurrences at high concentration (86.8 mg/ 1). This result is consistent with the undiluted CWC water. No significant differences were noted between the hot and cold samples.

Table 9 contains CE results for a set of Mir condensate samples collected during 1996 and 1997.

Table 7 IC results for samples of Mir cold and hot water (units: mg/l)

						0 /								
Description	Collection date (month/day/year)	$F^{-}$	Cl	$NO_2^ N$	Br <sup>-</sup>	$NO_3^ N$	HPO <sub>4</sub> <sup>2-</sup> -P	$SO_4^{2-}$	Li <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup> -N	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
Regenerated cold	11/6/96	0.03	0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.004	0.024	< 0.002	0.068	2.54
Regenerated cold	12/14/96	0.03	2.70	< 0.01	< 0.01	< 0.01	< 0.01	1.98	< 0.002	0.686	< 0.002	0.241	1.61	12.8
Regenerated hot	1/18/97	0.02	1.52	< 0.01	< 0.01	0.02	< 0.01	1.45	< 0.002	0.477	< 0.002	0.163	0.94	8.30
Regenerated hot	11/6/96	0.05	0.19	< 0.01	< 0.01	< 0.01	0.97	< 0.01	< 0.002	0.175	< 0.002	1.49	0.07	2.42
Regenerated hot	12/14/96	0.03	2.40	< 0.01	< 0.01	0.02	< 0.01	1.70	< 0.002	0.537	< 0.002	0.193	1.49	12.5
Regenerated hot	12/4/96	0.13	11.7	< 0.01	< 0.01	0.15	< 0.01	< 0.01	< 0.002	5.97	0.010	2.77	6.35	25.0
	Average	0.05	3.09	< 0.01	< 0.01	0.06	0.97	1.71	< 0.002	1.31	0.017	0.971	1.76	10.6
	Minimum	0.02	0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	0.004	< 0.002	< 0.002	0.068	2.42
	Maximum	0.13	11.7	< 0.01	< 0.01	0.15	0.97	1.98	< 0.002	5.97	0.024	2.77	6.35	25.0

Table 8	
CE results for samples of Mir cold and hot water (units: mg/l)	

Description	Collection date (month/day/year)	Oxalate	Formate	Glycolate	Glyoxylate	Acetate	Lactate	Propionate	Butyrate	Methylamine	Trimethylamine	Ethylamine	Propylamine
Regenerated cold	9/5/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated cold	9/23/96	<1.0	86.8	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	a	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated cold	11/6/96	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.25
Regenerated cold	12/14/96	a	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
Regenerated cold	5/19/97	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	a	0.79	< 0.62	< 0.62	< 0.62
Regenerated hot	7/15/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated hot	8/15/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated hot	9/5/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	a	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated hot	11/6/96	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	0.29
Regenerated hot	12/4/96	a	0.74	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
Regenerated hot	12/14/96	a	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
Regenerated hot	1/18/97	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
Regenerated hot	5/8/97	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	a	< 0.25	< 0.25	< 0.25	< 0.25
Regenerated hot	5/19/97	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	а	< 0.12	< 0.12	< 0.12	< 0.12
	Minimum	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12
	Maximum	<1.0	86.8	< 0.4	< 0.4	0.31	< 0.4	< 0.3	< 0.4	0.79	<2.5	<1.25	<1.25

<sup>a</sup> Unresolved.

Formate was detected in one sample, and acetate in two of the 14 samples. The presence of glycolate in the two samples collected on 19 May 1997 coincides with an ethylene glycol leak from the thermal control system. Glycolate is one of the oxidation products of ethylene glycol. No oxalate, glyoxylate, lactate, propionate or butyrate was detected in any of the samples. Except for 0.25 mg/l of methylamine found in one sample (15 October 1996), no amines were detected. For many of the samples however, dilution was necessary thus having the effect of increasing the detection limits. It is probable that many of these

Table 9

CE results for Mir humidity condensate samples (units: mg/l)

Collection date (month/day/year)	Oxalate	Formate	Glycolate	Glyoxylate	Acetate	Lactate	Propionate	Butyrate	Methylamine	Trimethylamine	Ethylamine	Propylamine
6/22/96	а	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	<1.25	<2.5	<1.25	<1.25
7/26/96	< 0.25	0.45	< 0.25	< 0.25	0.31	< 0.25	< 0.25	а	<1.25	<2.5	<1.25	<1.25
9/12/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
9/18/96	<1.0	< 0.3	< 0.4	< 0.4	< 0.3	< 0.4	< 0.3	< 0.4	< 0.25	< 0.25	< 0.25	< 0.25
10/15/96	a	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	0.25	0.25	< 0.25	< 0.25
12/4/96	а	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.25	< 0.25	< 0.25	< 0.25
12/4/96	a	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.25
3/1/97	<1.25	<1.25	<2.5	<2.5	<1.25	<1.25	<1.25	а	< 0.25	< 0.25	< 0.25	< 0.25
3/1/97	a	< 0.62	< 0.62	< 0.62	0.73	< 0.62	< 0.62	< 0.62	< 0.25	< 0.25	< 0.25	< 0.25
5/19/97	<1.25	<1.25	2.39	<2.5	<1.25	<1.25	<1.25	а	< 6.25	<12.5	< 6.25	< 6.25
5/19/97	<1.25	<1.25	4.18	<2.5	<1.25	<1.25	<1.25	а	<6.25	<12.5	<6.25	< 6.25
5/21/97	<2.5	<2.5	<2.5	<5.0	<2.5	<2.5	<2.5	a	<1.25	<1.25	<1.25	<1.25
5/21/97	<2.5	<2.5	<2.5	<5.0	<2.5	<2.5	<2.5	a	<1.25	<1.25	<1.25	<1.25
8/4/97	< 6.25	< 6.25	<6.25	<6.25	<6.25	< 6.25	<6.25	a	< 0.25	<0.25	< 0.25	< 0.25
Minimum	< 0.25	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12	< 0.12
Maximum	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	< 6.25	< 0.625	<6.25	<12.5	< 6.25	< 6.25

<sup>a</sup> Unresolved.

acids and amines are present, but can not be detected due to matrix effects and other limitations of the methods employed.

# 4. Conclusions

Results of IC analysis of iodinated fuel cell water samples from Shuttle show that the water is of distilled quality, with a few anions and cations at µg/l concentrations. Mineralized water delivered to Mir by Shuttle and Progress vehicles is distinguishable, based on its chloride, sulfate and formate content. Mineral content of water supplied to Mir from the ground is similar to US tap water. Results of the potable water samples show that none of the concentrations fell outside of the NASA or US Environmental Protection Agency (EPA) limits. Carboxylates were occasionally detected in the Mir condensate samples - an expected result since humidity condensate contains moisture from crew perspiration and respiration. Compared to previous analyses of humidity condensate collected on Shuttle [17] however, the Mir condensate appeared relatively free of carboxylates and amines.

IC and CE methods currently play complementary roles in NASA's water quality monitoring programs. IC methods for anions and cations are mature and routinely able to detect  $\mu$ g/l concentrations. Other than the need to dilute mineralized samples, no problems were encountered with the IC analyses. The AS14 IC column is able to prevent organic acid interference with fluoride. The commercial buffer used for CE is designed for small carboxylates, and is not ideally suited for butyrate and longer-chain carboxylates. Further refinement of the CE methods is required to eliminate matrix effects, improve reproducibility and decrease the detectable concentrations.

### References

 NASA Shuttle Medical Operations Requirements Document, JSC 13956, Rev F, October 1997; International Space Station Medical Operations Requirements Document, SSP-502060.

- [2] L.M. Pierre et al., Collection and Chemical Analysis of Reclaimed Water and Condensate from the Mir Space Station, SAE Technical Paper Series No. 961569, 26th International Conference on Environmental Systems, Monterey, CA, July 1996.
- [3] R.E. Gibbons et al., Recent Experiences with Iodine Water Disinfection in Shuttle, SAE Technical Paper Series No. 901356, 20th Intersociety Conference on Environmental Systems, Williamsburg, VA, July 1990.
- [4] P.D. Mudgett et al., Potable Water Treatment and Transfer from Shuttle to Mir, SAE Technical Paper Series No. 972461, 27th International Conference on Environmental Systems, Lake Tahoe, NV, July 1997.
- [5] NASA Man-Systems Integration Standards, NASA-STD-3000, Vol. 3, Rev. B, 1995.
- [6] NASA System Specification for International Space Station, SSP 41000, Rev. D, Nov 1995.
- [7] D.R. Orta et al., Capillary Electrophoresis for Spacecraft Drinking Water Analysis: Methods and Breadboard Development, SAE Technical Paper Series No. 97ES-226, 27th International Conference on Environmental Systems, Lake Tahoe, NV, July 1997.
- [8] United States Environmental Protection Agency, Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1, August 1993.
- [9] Dionex, System 4000i Operation and Maintenance Manual, Document 031199, Dionex, Sunnyvale, CA, 1996.
- [10] Dionex, System 120 Operation and Maintenance Manual, Document 031132, Dionex, Sunnyvale, CA, 1995.
- [11] P. Jandik, and G. Bonn, Capillary Electrophoresis of Small Molecules and Ions, VCH, New York, 1993.
- [12] J.P. Landers (Editor), Handbook of Capillary Electrophoresis, CRC Press, Boca Raton, FL, 1993, Ch. 9.
- [13] S.Y.F. Li, Capillary Electrophoresis: Principles, Practice and Applications, (Journal of Chromatography Library), Vol. 52, Elsevier, Amsterdam, 1993, pp. 462–477.
- [14] R. Weinberger, Practical Capillary Electrophoresis, Academic Press, Boston, MA, 1993.
- [15] EPA-60014-82-057, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Appendix A, 1992.
- [16] N. Protasov (RSC-Energia) and L. Bobe, NIICHIMMASH, personal communication.
- [17] S.V. Muckle et al., Characterization of Spacecraft Humidity Condensate, SAE Technical Paper Series No. 932176, 23rd International Conference on Environmental Systems, Colorado Springs, CO, July 1993.