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Reduction in the Iodine Content of Shuttle Drinking Water: Lessons Learned

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ABSTRACT

Iodine is the disinfectant used in U.S. spacecraft potable water systems. Recent long-term testing on human subjects has raised concerns about excessive iodine consumption. Efforts to reduce iodine consumption by Shuttle crews were initiated on STS-87, using hardware originally designed to deiodinate Shuttle water prior to transfer to the Mir Space Station. This hardware has several negative aspects when used for Shuttle galley operations, and efforts to develop a practical alternative were initiated under a compressed development schedule. The alternative Low Iodine Residual System (LIRS) was flown as a Detailed Test Objective on STS-95. On-orbit, the LIRS imparted an adverse taste to the water due to the presence of trialkylamines that had not been detected during development and certification testing. A post-flight investigation revealed that the trialkylamines were released during gamma sterilization of the LIRS resin materials. The LIRS effluent water quality was not completely tested after gamma sterilization as previous experience and limited testing suggested that gamma irradiation would not degrade the resins. In addition, concerns about microbial contamination ruled out testing of the flight hardware following sterilization. The lessons learned from the experience were that experiments with the potential to impact the Shuttle life support system should be classified as critical hardware, and that certification testing of all hardware parameters must be carried out in the final flight configuration.

INTRODUCTION

NASA has utilized iodine for disinfection of spacecraft potable water supplies since the Apollo program [1,2]. Potable water on the Shuttle Orbiter consists of fuel cell product water that is iodinated with a Microbial Check Valve (MCV®) [3] to a level of 2-4 mg/L to control bacterial growth in the storage tanks, distribution lines and the Shuttle Orbiter Repackaged Galley (SORG), as shown in Figure 1[4]. Recent long-term testing with human subjects has raised concerns about excessive iodine consumption and the potential for thyroid function changes among the astronaut population. A NASA-convened panel of independent experts has determined that the maximum safe iodine consumption for astronauts who have a history of routine exposure to iodine is on the order of 1 mg of total iodine per day, with no more than 0.5 mg/day from either food or water [5]. Iodine analysis of the food in a typical Shuttle diet revealed that dietary exposure averages 0.26 mg/day [6].

Efforts to limit crew uptake of iodine during Shuttle flights were initiated with STS-87 in November 1997, using existing water treatment equipment originally designed to deiodinate water for transfer to the Mir Space Station [7]. The Galley Iodine Removal Assembly (GIRA) [8] uses either a combination of an Activated Carbon Iodine Removal Assembly (IRA) with a mixed bed ion exchange resin Iodide

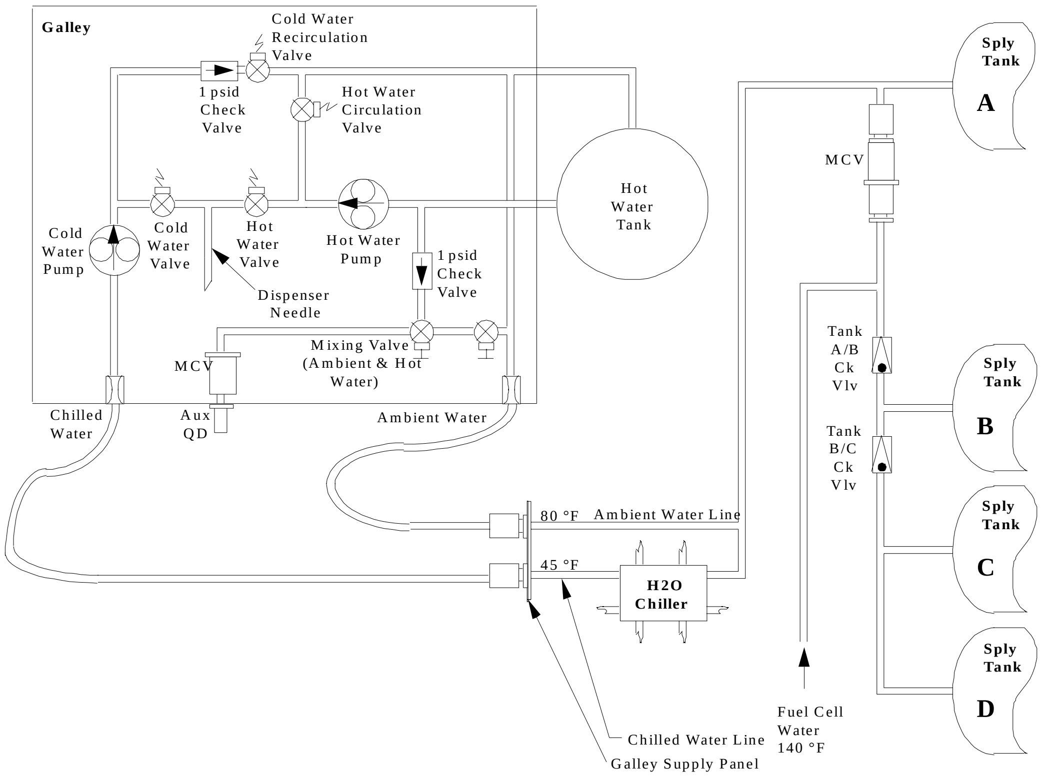

Figure 1. Shuttle/SORG water supply system configuration prior to STS-87

Removal Cartridge (IRC), or an all-in-one Activated Carbon/Ion Exchange (ACTEX) cartridge to completely eliminate all forms of iodine from the chilled water. Because there is no residual disinfectant in the chilled water loop, a 0.2 μm filter is installed to prevent microbial infiltration into the SORG. An MCV® cartridge is installed on the ambient inlet. Because the MCV® functionality is temperature-dependent, this cartridge which is designed to iodinate 130 ºF water to 4 mg/L will actually reduce the level of iodine in the ambient water to about 1.5 mg/L. Because of the 1.5 mg/L iodine still remaining in the hot water, the crew is limited to only 12 ounces of hot water per day, or the equivalent of rehydrating two food items. Any other rehydrated food must utilize the deiodinated cold water, and be heated in the SORG oven. The GIRA installation is shown in Figure 2. To reinstate a measure of bacterial control to the chilled water lines, the deiodination cartridge(s)

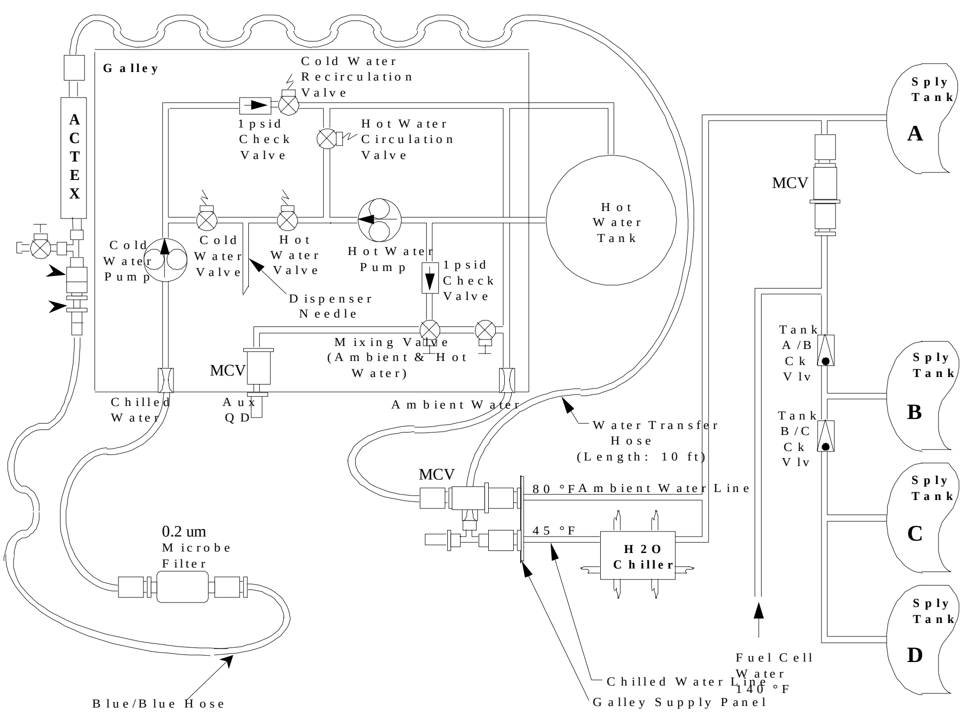

Figure 2. Shuttle/SORG with GIRA (ACTEX configuration)

and filter are disconnected from the system at the end of each day. The MCV® cartridge on the ambient line remains in place, and provides an iodine residual to the SORG while the crew sleeps. The IRA, IRC and filter are then reconnected each morning.

The GIRA, in these forms, has been used on all subsequent flights, awaiting a permanent solution to reduce the iodine concentration to acceptable levels while not eliminating it from the SORG water supply.

Development of the LIRS Assembly was undertaken to meet the following programmatic goals:

- Reduce iodine concentration in all water dispensed by the galley to a medically acceptable level.
- Retain sufficient iodine residual in the water distribution system to prevent violation of the Shuttle water microbial specification or biofilm accumulation over the span of a Shuttle mission.
- Eliminate crew time required to remove and reinstall iodine removal hardware during the sleep periods, as well as time required to oven-heat cold-rehydrated food items.
- Bring SORG water dispense quantities within the allowable specification of ±10% of the requested volume (the microbial filter in the GIRA produces large pressure drops that reduce dispense quantities by up to 20%).
- Develop the technology required to permanently modify the galley to eliminate crew time requirements (and lead to technologies to limit iodine on the U.S. water supply system on the International Space Station.)

The LIRS hardware was initially flight tested as a Johnson Space Center (JSC) Detailed Test Objective (DTO) on STS-95, while the GIRA was retained as the primary iodine reduction system. This paper presents an overview of the hardware, the results of the DTO, and the results of a subsequent postflight investigation to determine why the hardware imparted an adverse taste to the water.

LIRS HARDWARE DESIGN AND DEVELOPMENT

The primary requirement of the LIRS Assembly is to reduce aqueous iodine to a medically acceptable level. Based on historical average crew water consumption of 2 L/day per crewmember, a 0.25 mg/L iodine concentration meets the 0.5 mg/day limit on consumption from water. The design and placement of the LIRS were selected to minimize costs while demonstrating effectiveness in a timely manner. Modifications to the SORG were considered infeasible for the demonstration experiment, due to cost considerations. Instead, several options for installing the LIRS in the influent water lines to the SORG were explored.

The SORG itself contains only the apparatus for heating and storage of the ambient water. Chilled water must be supplied by the Orbiter. When the temperature of the chilled water within the SORG exceeds 55 ºF, a pump activates, recirculating water in reverse through the ambient supply line, into the floor of the Orbiter and through the chiller to reduce the temperature to 45 ºF, and back into the SORG (see Figure 1). Early in the design phase of the LIRS Assembly, it was determined that a single water treatment device, configured as shown in Figure 3, could provide a decreased iodine

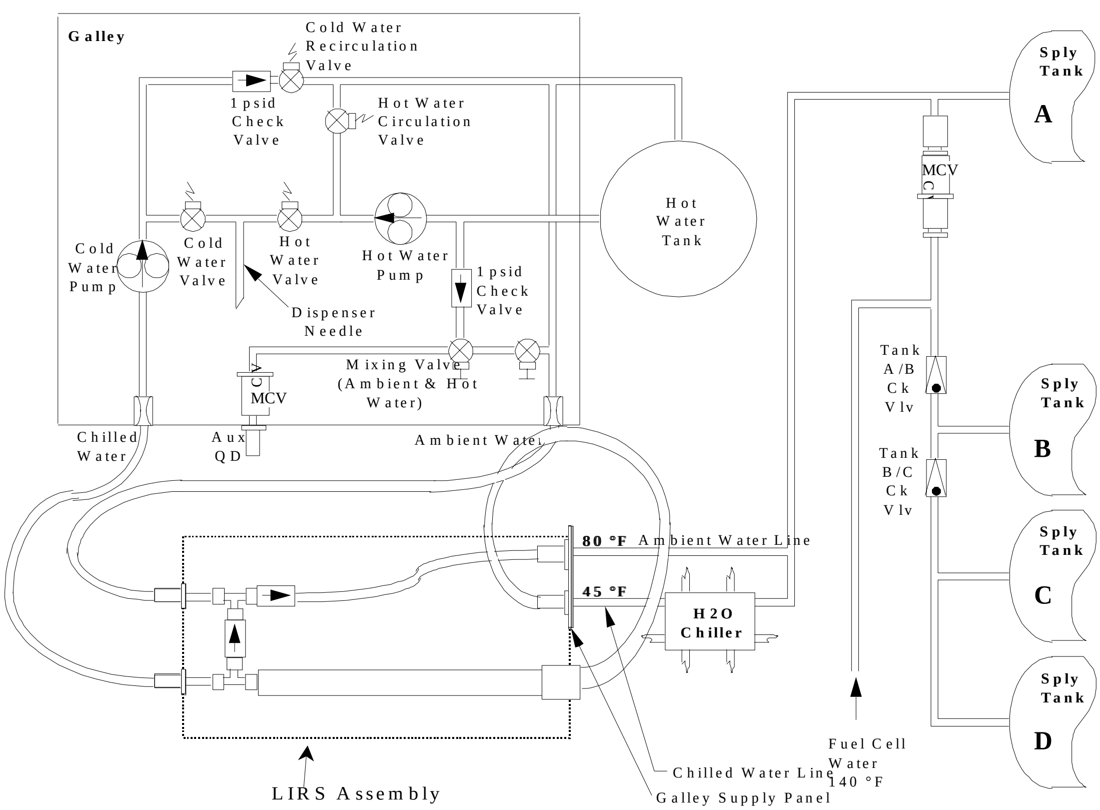

Figure 3. Shuttle/SORG with LIRS

concentration to both the chilled and ambient water supplies. This configuration contains crossover plumbing that diverts chilled LIRS product water to either the chilled or ambient SORG inlet line on demand, and a pair of mechanical check valves that permit the chilled water recirculation loop to function properly. This arrangement results in a small but acceptable energy penalty for heating water from chilled, rather than ambient, temperatures, but has no impact on either the time required to heat water or the total volume of hot water available to the crew.

In this configuration, the LIRS cartridge was required to reduce the total iodine concentration in the water entering the SORG from approximately 4 mg/L (3 mg/L I_2 and 1 mg/L I^-) to less than 0.25 mg/L total iodine, with the majority in the I_2 form. Iodide has no bactericidal effect, but contributes to total iodine intake. The first option was to look at the use of a modified MCV® resin as an iodine scavenger. MCV® resin will scavenge iodine from solution if the iodine concentration is higher than that which the resin was prepared to impart (i.e., the effluent iodine concentration from 3 mg/L resin will be 3 mg/L if fed either influent at 5 mg/L, or de-ionized water influent). The chemical equilibrium at the resin bead surfaces either drives iodine into solution or scavenges iodine from solution to achieve the target concentrations. However, in addition to the target iodine (I_2) concentration, current MCV® resin imparts approximately 0.2 mg/L of iodide (I-) to the effluent at room temperature, a level which was unacceptable for this application. This is true whether the resin is imparting iodine or acting as a scavenger.

Schedule constraints mandated that methods of most probable success be investigated first, and optimization was to be conducted only if time allowed after a system meeting the primary goals was developed. It was relatively certain that a modified MCV® resin could be developed that imparted iodine (I_2) in the target concentration range of 0.25 mg/L, with very little iodide (I^-) release. It was less certain that iodide, at the 1.0 mg/L level, could be stripped from incoming solutions by the MCV® resin. The removal of iodide required special consideration as the LIRS was required to operate with the SORG in recirculation mode for approximately 50% of the total treatment volume. In this mode, iodide concentrations could build up with time. Thus, a decision was made to develop a module that would strip all iodine species from solution at the front end, and then impart the desired level of iodine with a special formulation of MCV® resin at the exit end of the module.

Iodosorb II® resin was selected to remove the influent iodine species as it has a high affinity for both iodide and iodine. It is a patented resin that has been used in commercial water purification devices for the removal of iodine and iodide [9]. A bed volume of 200 cc was deemed well in excess of that required in this application, and efficiency studies would follow.

A new formulation of MCV® resin was required to impart the very low total iodine target concentration of 0.25 mg/L. The basic principle of iodinated resin preparation is to first load an anion exchange resin with iodide, and then to load iodine (I_2) on to the bound iodide (I^-). To minimize iodide release, the anion base resin was not loaded to capacity with iodide. This left exchange sites open for sorption of iodide anions as they are released from other sites. The sites that are loaded with iodide are then iodinated with sufficient I_2 to achieve the desired 0.25 mg/L level of iodine in the effluent. Preliminary estimates showed that a resin bed volume of 300 mL would meet the mission requirements.

Prototype testing confirmed that this two step design, a cartridge containing 200 mL of Iodosorb II® followed by 300 mL of the new formulation of MCV® resin, effectively reduced the total iodine concentration from 4 mg/L to approximately 0.25 mg/L, while keeping iodide levels below 0.05 mg/L throughout the specified throughput life of 2000 liters. In order to meet the required schedule for STS-95, fabrication of flight hardware was initiated, and proceeded in parallel with certification testing.

ACCEPTANCE AND CERTIFICATION TESTING

Acceptance and certification testing included verification of the cartridge's iodine reduction life cycle under Quality Control (QC) inspection, and testing of flight cartridges to verify that the product water quality met the parameters outlined in JSC-SE-S-0073[10]. Additional hardware safety and reliability testing were also required.

During development of the LIRS cartridge, it was observed that Iodosorb II® did not appear to support microbial growth. However, at the outset of certification testing, it was discovered that the Iodosorb II® was experiencing significant growth, and that sterilization would be required. Previous experience with autoclaving resins has indicated that this process can degrade the resin's functionality. The only method identified as feasible for sterilization of the LIRS was gamma irradiation at a level of 25-40 kGy. This technique has been used extensively in the past on similar resins with no apparent deleterious effects, but the requirement to test the irradiated Iodosorb II® resin was identified.

Because halting the life cycle certification to send that cartridge for sterilization would have caused the required delivery date for STS-95 to be missed, and because no flight cartridges were yet fabricated, a sample of Iodosorb II® was sent for irradiation and testing in parallel with the life cycle qualification unit. This approach was deemed acceptable for a non-critical experiment by JSC Safety & Mission Assurance.

The irradiated Iodosorb II® resin was tested to verify that its ability to remove iodine and iodide was not adversely impacted. However, , and no testing for organic compounds, taste or odor was performed on the product water.

Based upon the finding of no change in the resins due to gamma irradiation, LIRS development continued, with gamma irradiation identified as the last step in the processing of LIRS hardware. During safety reviews, concern from the JSC Safety Review Panel was the risk of bacterial growth due to the low level of iodine in the water. It was decided that, once irradiated, the sterile seals of the LIRS Assembly were not to be violated until installation on-orbit, for fear of microbial contamination of the water. Therefore, no water samples were drawn from the irradiated STS-95 LIRS Assembly, and the LIRS Assembly was certified for flight use.

Prior to irradiation, water processed through the LIRS cartridge built for STS-95 met all Shuttle water quality specifications per JSC-SE-S-0073, as shown in Table 1. The LIRS certification was closed based on these results. The hardware was then irradiated, and shipped directly to KSC for flight.

Table 1. Analytical results of LIRS product water, prior to irradiation of hardware

Parameter	Measurement	Limit
Conductivity	2.6 μmho/cm	Reference only
pH	5.2	Reference only
Total Solids	<3 mg/L	10 mg/L
Total Organic Carbon	0.6 mg/L	Reference only
Turbidity	<1 NTU	11 NTU
Color, true	<5 units	15 units
Cadmium	<0.001 mg/L	0.01 mg/L
Chromium, total	<0.02 mg/L	0.05 mg/L
Copper	0.02 mg/L	1.0 mg/L
Iron	<0.02 mg/L	0.3 mg/L
Lead	<0.002 mg/L	0.05 mg/L
Manganese	<0.01 mg/L	0.05 mg/L
Mercury	<0.001 mg/L	0.005 mg/L
Nickel	<0.01 mg/L	Reference only
Potassium	<0.01 mg/L	1.0 mg/L
Selenium	<0.003 mg/L	0.01 mg/L
Silver	<0.01 mg/L	0.1 mg/L
Zinc	<0.02 mg/L	5.0 mg/L
Dissolved Gas	Not Detected	No visible free gas
Iodine	0.28 mg/L	Reference only
Taste	None*	Reference only
Odor	None*	Reference only

(* conducted informally, not by a convened panel)

ANALYTICAL METHODS

Total Organic Carbon (TOC) levels were determined with a Sievers' Model 800 Total Organic Carbon analyzer. Iodine and iodide concentrations were determined by the Leuco Crystal Violet method, according to Standard Methods [11]. Semivolatile Organics and trialkylamines were determined by methylene chloride extractions for semivolatile organics using a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard 5971 Mass selective detector. Volatile organics were determined by headspace/gas chromatography/mass spectroscopy (HS/GC/MS) using a system consisting of a Hewlett Packard 7694 headspace sampler, a Hewlett Packard 6890 gas chromatograph and a Hewlett Packard 5973 mass selective detector.

Smaller anions (methylamine, ethylamine, propylamine and trimethylamine) were determined by indirect UV detection capillary electrophoresis using a Hewlett Packard 3D diode array capillary electrophoresis system.

Cations were determined by ion chromatography using a Dionex DX-120 ion chromatograph equipped with a CS-12A guard and separator (4 x 250 mm) columns. Anions were determined by ion chromatography using a Dionex DX-500 ion chromatograph with an AS-14 guard and separator (2 x 250 mm) columns. Metals were determined by Inductively Coupled Plasma Mass Spectrometry.

RESULTS

STS-95 OPERATIONAL RESULTS. The LIRS Assembly launched on STS-95 was initially installed on Flight Day (FD) 1, but a leaking hose mandated removal while an In-Flight Maintenance (IFM) procedure was developed. The hose was repaired, and the LIRS Assembly was re-installed on FD 2. Approximately six hours later, during pre-sleep activities, a report of unusual-tasting water was called down to Mission Control. The crew reported an "old canteen" or rubbery taste in the LIRS-produced water. Ground-based taste testing on water from a second gamma-irradiated flight unit, intended for use on STS-88 the following month, confirmed an adverse taste to the first-flush water drawn from the LIRS. A second sample was drawn, but it did not demonstrate an adverse taste. Chemical analysis of this product water was immediately initiated. Although it appeared that the contaminants were flushing out of the hardware, it was decided to remove the LIRS from the Galley and to use the GIRA for the remainder of the flight. These operations were performed promptly when the crew awakened the following morning.

STS-88 HARDWARE FLUSH RESULTS. The two "taste-test" samples from the STS-88 cartridge and one additional water flush sample were analyzed for TOC. The results showed TOC levels of 1,270 mg/L, 7.3 mg/L and 1.6 mg/L respectively. In an attempt to identify the compounds causing the taste, samples from the STS-88 cartridge were analyzed by three different GC/MS methods. The first was a headspace GC/MS method developed for volatile organics, the second was a liquid-liquid extraction (LLE) GC/MS method developed for semivolatile organics, and the third was a direct aqueous injection (DAI) GC/MS method developed for alcohols.

The analyses from both the LLE and DAI GC/MS methods showed two significant peaks that were tentatively identified as tripropylamine and tributylamine by both methods. A comparison of the mass spectra of tripropylamine and tributylamine in the Wiley mass spectral library with those of the unknown peaks is shown in Figure 4. These identifications were then confirmed by injecting samples of the pure compounds into the GC/MS and comparing retention times and mass spectra, as also shown in Figure 4.

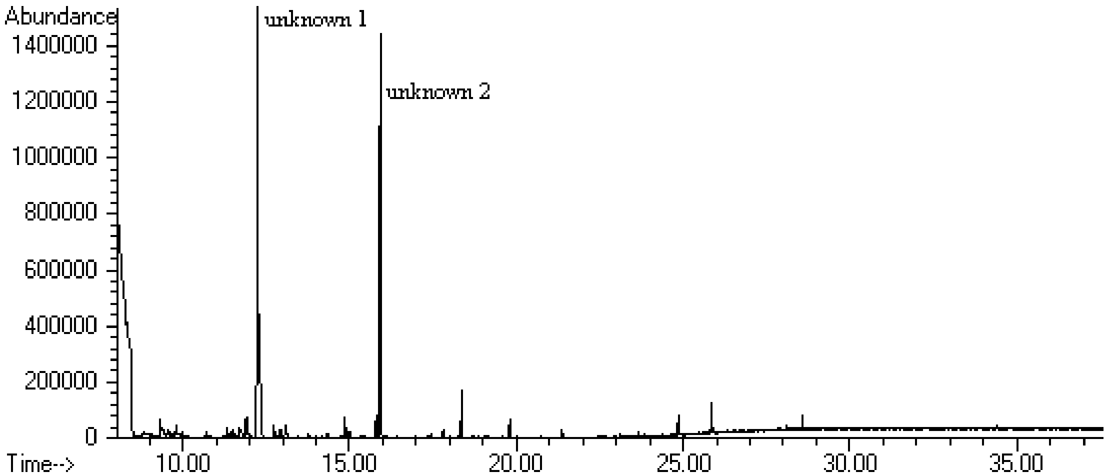

Figure 4(a). Chromatogram of sample showing two unknown peaks

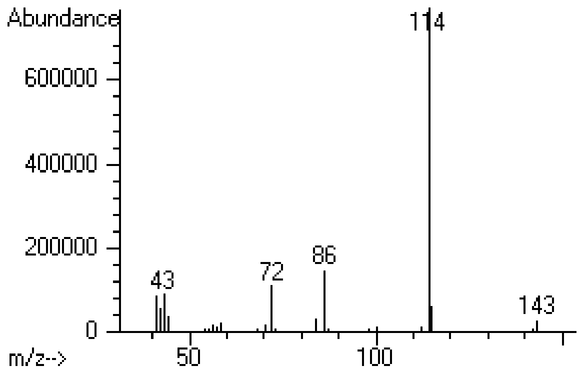

Figure 4(b). Mass spectrum of first unknown peak at 12.23 sec. Retention time

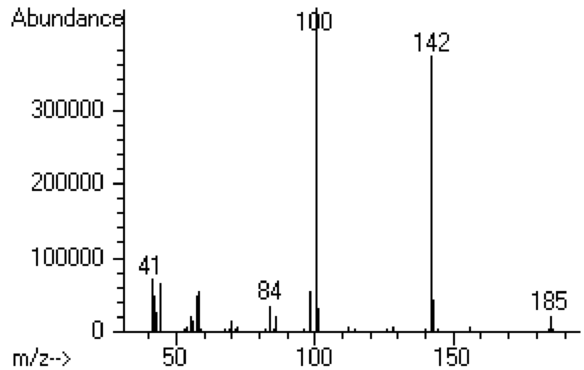

Figure 4(c). Mass spectrum of second unknown peak at 15.92 sec. Retention time

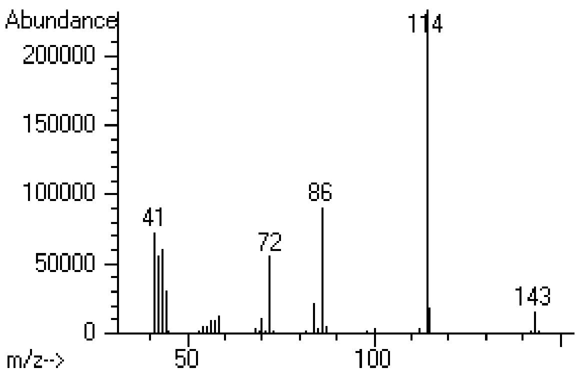

Figure 4(d). Mass spectrum of tripropylamine at 12.22 sec.

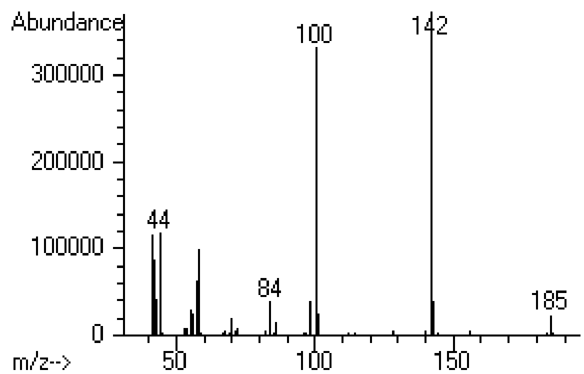

Figure 4(e). Mass spectrum of tributylamine at 15.91 sec.

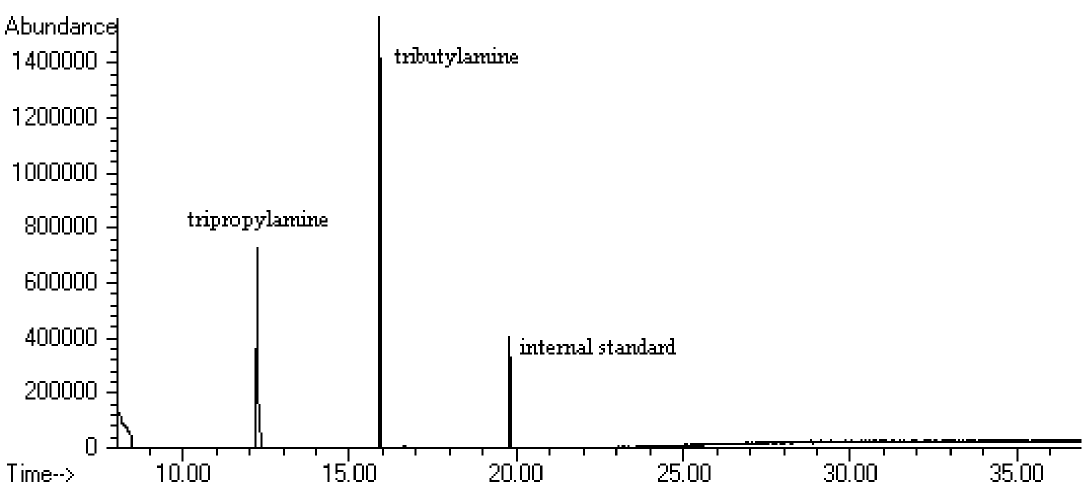

Figure 4(f). Chromatogram of tripropylamine and tributylamine standards

Table 2. Major organic constituents of samples drawn from STS-88 cartridge

Sample Number	Description	TOC, ug/L	Trimethylamine, ug/L	Tripropylamine, ug/L	Tributylamine, ug/L	Dibutylamine, ug/L	Methylamine, ug/L	Propylamine, ug/L	Ethanol, ug/L	Caprolactam, ug/L	Formaldehyde, ug/L	TOC recovered
1	Initial flush	1,270,000	59,600	794,000	176,000	85,400	<1250	20,700	21,700	ND	11,400	68.0%
2	Second capture, after diverting ~1 L to drain.	7,390	<125	4,300	1,340	193	<125	<125	466	ND	NA	63.2%
3	First full sample	1,660	<125	194	112	86	<125	<125	241	ND	34	26.3%
4	Archive sample, drawn 2 hours later	4,830	<125	1,460	1,230	246	<125	<125	392	ND	356	53.6%

(NA = Not Analyzed, ND=Not Detected)

A full organic characterization of the samples was then conducted to determine if there were other components contributing to the TOC. After all analyses were complete, the main constituents of the TOC from the STS-88 cartridge were: tripropylamine, tributylamine, dibutylamine, propylamine, trimethylamine, ethanol and formaldehyde. These constituents accounted for 50-68% of the TOC in the samples. Table 2 summarizes these results.

Additional compounds found in the samples, at levels below 1% of the TOC for each constituent, included lactate, formate, chloromethane, chloroform, chloromethane, iodomethane, dimethylcarbamyl chloride, benzene and toluene.

STS-95 INFLIGHT SAMPLE RESULTS. Samples of the LIRS and GIRA product water were also taken during STS-95, and returned for postflight analysis. Table 3 is a summary of the water samples returned on STS-95.

Table 3. Major organic constituents of samples taken on STS-95

Sample Number	Description	TOC, ug/L	Trimethylamine, ug/L	Tripropylamine, ug/L	Tributylamine, ug/L	Dibutylamine, ug/L	Methylamine, ug/L	Propylamine, ug/L	Ethanol, ug/L	Caprolactam, ug/L	Formaldehyde, ug/L	TOC recovered
5	ACTEX chilled, drawn FD1. Clear drink bag	16,200	<125	ND	ND	ND	<125	<125	25,800	1,584	ND	89.3%
6	ACTEX chilled, FD1. Clear drink bag	20,100	<125	ND	ND	ND	<125	<125	33,000	1,470	ND	90.3%
7	LIRS hot, drawn FD2. Clear drink bag	38,600	8,970	10,068	2,542	1,490	<125	290	31,700	1,309	263	87.5%
8	LIRS chilled, drawn FD2. Clear drink bag	20,500	2,900	3,508	847	418	<125	<125	21,000	1,374	189	84.3%
9	Post LIRS removal Galley Flush. Foil drink bag. Unknown whether hot or chilled	5,720	<125	ND	ND	ND	<1250	<1250	110	ND	6	1.0%
10	Post LIRS removal Galley Flush. Foil drink bag. Unknown whether hot or chilled	5,720	<125	ND	ND	ND	<1250	<1250	145	ND	6	1.4%
11	Foil drink bag, label BJD554 (FD 3). Recovered from wet trash. Unknown whether hot or chilled.	11,000	<125	ND	ND	ND	<125	<125	18,600	ND	2	88.2%
12	Foil drink bag, label BJD511 (FD 7?). Recovered from wet trash. Unknown whether hot or chilled.	5,620	<125	ND	ND	ND	<125	<125	9,980	ND	ND	92.6%
13	ACTEX chilled, drawn FD9. Teflon bag	4,780	<125	ND	ND	ND	<125	<125	7,620	ND	ND	83.1%
14	ACTEX hot, drawn FD9. Teflon bag	5,270	<125	ND	ND	ND	<125	<125	8,760	ND	3	86.7%

Due to the unexpected results from LIRS, there was an inadequate supply of Teflon sampling bags for all samples collected, so some of these samples were collected in metallized polyethylene drink bags. The first two samples (# 5 and 6) were drawn from the GIRA following the leakage of LIRS on Flight Day 1. Samples 7 and 8 were drawn from LIRS just prior to disconnecting it and flushing the system on Flight Day 2. Samples 9 and 10 show that post-LIRS removal flushing was effective in removing contaminants from the water system. Samples 11 and 12 were taken from drink bags recovered from the wet trash with enough water remaining to perform analyses. Putting these bags in the timeline is tentative, as the date and time of consumption is not recorded on the bags. The results, however, confirm that the flushing was adequate. Samples 13 and 14 were drawn from the GIRA at the end of the mission.

For all samples that were drawn into drink bags, caprolactam was found in the water samples. This is an artifact of the bag, and not caused by LIRS contamination (as demonstrated by the early GIRA samples that have caprolactam before any water was processed through LIRS). In addition, ethanol was found in all water samples, including those drawn prior to installation of LIRS. This is a residual of the tincture of iodine used for pre-launch servicing of the water distribution system. The LIRS contribution to ethanol cannot be distinguished from the Orbiter-supplied ethanol in the STS-95 results.

POSTFLIGHT ANALYSIS AND RESULTS

GAMMA IRRADIATION RESULTS. As soon as the ground-based water analysis tentatively identified tripropylamine and tributylamine as the primary constituents of the TOC, an investigation of potential sources of these compounds was initiated. Tripropylamine was identified as the functional group on the Iodosorb II® resin, and trimethylamine was identified as the functional group on the MCV® resin. The only other components of the LIRS Assembly that come in contact with water are Teflon®, Viton® and stainless steel, and these were eliminated as potential candidates for contamination.

Fresh batches of both the Iodosorb II® and modified MCV® resin were then obtained for experimentation. Water samples were drawn from these resins in their off-the-shelf configurations, after installing the resins into packed coluns and rinsing as would be done during cartridge assembly, and again after irradiation. This testing confirmed that while some small quantity of trialkylamines can be found in fresh batches of resin, these contaminants are washed out during normal processing, and that gamma irradiation was the cause of the large release of trialkylamines.

Table 4 is an attempt to quantify and separate the effects of the two separate resins used in the LIRS cartridge.

Table 4. Major organic constituents of samples taken from resin study

Sample Number	Description	TOC, ug/L	Trimethylamine, ug/L	Tripropylamine, ug/L	Tributylamine, ug/L	Dibutylamine, ug/L	Methylamine, ug/L	Propylamine, ug/L	Ethanol, ug/L	Caprolactam, ug/L	Formaldehyde, ug/L	TOC recovered
15	Void space water drawn from 500 mL of off-the-shelf iodosorb resin	8,640	<125	4,950	204	286	<125	<125	ND	ND	3	47.5%
16	Void space water drawn from 500 mL of off-the-shelf 0.25 ppm MCV resin	9,540	1,530	ND	ND	ND	4,720	<125	NA	ND	948	32.9%
17	effluent from Iodosorb 100 mL packed column AFTER washing to meet conductivity <2 uS/cm	69	<125	ND	ND	ND	<125	<125	NA	ND	2	1.2%
18	effluent from 0.25 ppm MCV 100 mL packed column AFTER washing to meet cond. <5 uS/cm	59	<125	ND	ND	ND	<125	<125	NA	ND	4	2.7%
19	Void space water from non-irradiated Iodosorb after 56 days shelf time	6,040	<125	4,960	260	ND	<125	<125	NA	ND	NA	65.3%
20	Void space water from non-irradiated 0.25 ppm MCV w/56 days shelf time	7,820	173	ND	ND	ND	797	<125	NA	ND	NA	5.3%
21	Void space water from **irradiated** Iodosorb resin (~30 kGy) + 56 days	1,710,000	<1,250	1,650,000	251,000	86,400	<1250	4,320	NA	ND	NA	88.1%
22	Void space water from **irradiated** 0.25 ppm MCV resin (~30 kGy) + 56 days	103,000	24,800	25	ND	ND	1,030	<250	NA	ND	NA	15.1%
23	Void space water from non-irradiated MCV resin after ~6 years shelf time	6,890	<125	421	54	ND	557	<125	NA	328	NA	11.4%

When irradiated, the Iodosorb II® resin exhibits a massive release of tripropylamine, a somewhat lesser release of tributylamine, and propylamine at a reduced but significant level. The MCV®-derived iodine release resin is the source of trimethylamine and methylamine, which are not considered harmful, but the presence of which should be minimized in potable water systems. Of note is the fact that a jar of spent MCV® resin, after sitting on the shelf for six years, exhibited similar levels of organic contaminants as the fresh resin, sitting for 56 days.

CARTRIDGE LEACHING AND WASHOUT STUDY. Further samples were also taken from the STS-88 cartridge to determine if trialkylamines could be washed from the irradiated cartridge. When the fourth sample, which was drawn only a few hours after the initial three, demonstrated a rise in TOC from 1.6 to 4.8 mg/L, a study was initiated to investigate whether contaminants continued to leach out of the resin with time. This study consisted of taking five more flush samples on a weekly basis, with a two-week gap before the final test. The results in Table 5 show that contaminants continued to appear in the water long after the original apparent washout. Sample 4 shown in this table is the same sample as #4 in Table 2, and the subsequent five samples (#'s 24-18) are the results of this weekly sampling schedule. Of note is the large jump in TOC between sample #4 and 24, and then a slow decrease over the course of the study. Samples 28-30 show a second washout curve, demonstrating that short-duration flushing can appear to alleviate the problem.

DISCUSSION

The resins used in the LIRS Assembly have been used in several potable water systems, both on the ground and in space, with no ill effects. Gamma sterilization was a new variable introduced when these resins were packaged as the LIRS assembly, and it was this factor which led to the unforeseen effect. It was not recognized that irradiation could physically damage the resin without changing functionality. In the case of the LIRS Assembly, the consequences of using offline analysis of the effects of radiation were serious. The project team allowed the compressed schedule for development of the hardware to mandate a less-than-complete analysis of the actual flight hardware.

Because heat-based sterilization (autoclaving) potentially breaks down ion exchange resin functionality, the accepted method for sterilization of resins is Gamma irradiation. This process kills all bacteria and deactivates virii without heating the materials. NASA and NASA vendors have used gamma irradiation on other resins with no unusual effects observed. Due to the compressed delivery schedule for the LIRS cartridge, full water quality analysis was performed only on the non-sterilized cartridge that was used to verify the life cycle, or total water treatment capacity of the cartridge. A small sample of the LIRS component resins were sent for irradiation and no change in resin functionality was found post-irradiation. What escaped notice at the time was the fact that the irradiation caused a large bulk release of trialkylamines from the Iodosorb resin, and a smaller release of trimethylamine from the MCV® resin. Thus, the LIRS was

Table 5. Major organic constituents of samples taken from cartridge washout study

Sample Number	Description	TOC, ug/L	Trimethylamine, ug/L	Tripropylamine, ug/L	Tributylamine, ug/L	Dibutylamine, ug/L	Methylamine, ug/L	Propylamine, ug/L	Ethanol, ug/L	Caprolactam, ug/L	Formaldehyde, ug/L	TOC recovered
4	Archive sample (same as sample 4 at end of STS-88 Study)	4,830	<125	1,460	1,230	246	<125	<125	392	ND	356	53.6%
24	LIRS sample after water residence time of 6 days, 6.5 hours	25,700	20,800	4,320	3,540	747	610	220	875	ND	3,870	84.1%
25	LIRS sample after water residence time of 7 days, 6.5 hours	13,700	8,050	1,760	1,110	459	380	<125	487	ND	2,350	64.1%
26	LIRS sample after water residence time of 7 days, 2 hours	8,670	4,510	ND	ND	165	280	<125	NA	ND	2,120	44.1%
27	LIRS sample after water residence time of 7 days, 35 minutes	6,480	3,220	450	186	61	200	<125	NA	ND	1,948	51.7%
28	LIRS sample (5 L Flush) after water residence time of 13 days, 21 hours	9,810	4,330	1,070	275	86	300	<125	NA	ND	3,500	53.4%
29	LIRS sample (5.5 L Flush) water residence time: none	352	< 125	31	6	ND	<125	<125	NA	ND	100	19.3%
30	LIRS sample (6 L Flush) water residence time: none	250	< 125	32	6	ND	<125	<125	NA	ND	42	18.2%

certifiied for use as Shuttle flight hardware based on incomplete testing..

The LIRS Assembly is currently undergoing a redesign in which the Iodosorb II® resin has been removed from future consideration as a flight-grade resin material. It is currently believed that a biostatic assembly can be fabricated that does not require post-assembly sterilization. An internal NASA investigation of the water contamination concluded that for future flights, LIRS will be classified as Critical hardware (failure poses a threat to mission success). For certification of Critical hardware, a dedicated flight hardware qualification unit will be subjected to all processing steps, with water quality analyses to be performed at any event that has the potential to cause chemical changes in the product water. This qualification unit will then be subjected to a simulated flight profile, with additional water quality testing at several points in the life cycle. Following completion full life cycle test, a final water quality profile will be performed to verify that there is no hazard caused by spent resin materials.

SUMMARY AND CONCLUSIONS

Efforts to reduce iodine consumption by Shuttle crews while minimizing crew time requirements led to development of the Low Iodine Residual System (LIRS) as a Detailed Test Objective on STS-95. The hardware imparted an adverse taste to the water due to the presence of trialkylamines that were not detected during the development and certification testing. The trialkylamines were formed due to degradation of the LIRS resin materials during gamma sterilization. Several conclusions were drawn from the experience, including:

- Assumptions based on previous experience and limited testing of the resin materials led to an inadequate certification testing program
- A compressed schedule and concerns about microbial contamination of the hardware prevented the testing which would have revealed the problem
- LIRS must be reclassified as Critical hardware, and redesigned prior to reflight.
- Current redesign efforts are centered on elimination of the Iodosorb II®, and use of an MCV®-derived biostatic assembly that will not require sterilization.
- The level of iodine imparted by LIRS has not yet been demonstrated as either effective or ineffective at preventing microbial regrowth in the SORG, and a future iteration of the DTO is planned that will include on-orbit microbial testing of the LIRS-treated water.

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