Discovery and Identification of Dimethylsilanol as a Contaminant in ISS Potable Water

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Nomenclature

TOC = total organic carbon
WPA = Water Processor Assembly
GC/MS = gas chromatography/mass spectrometry
DMSD = dimethylsilanediol
QqTOF = quadrupole quadrupole time of flight
ICP/MS = inductively coupled plasma/mass spectrometry
PWD = potable water dispenser
SRV-K = system for regeneration of condensate water
DART TOF = direct analysis in real time / time of flight
TOFMS = time-of-flight mass spectrometry
MS/MS = mass spectrometry/mass spectrometry
ISS = International Space Station
SIM = selected ion monitoring
EI = electron ionization
m/z = mass to charge ratio in mass spectrometry
HPLC = high performance liquid chromatography
RI = refractive index
LC/MS/MS = liquid chromatography/mass spectrometry/mass spectrometry
APCI = atmospheric pressure chemical ionization
NMR = nuclear magnetic resonance spectroscopy

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I. Abstract

IN September 2010, analysis of ISS potable water samples was undertaken to determine the contaminant(s) responsible for a rise of total organic carbon (TOC) in the Water Processor Assembly (WPA) product water. As analysis of the routine target list of organic compounds did not reveal the contaminant, efforts to look for unknown compounds were initiated, resulting in discovery of an unknown peak in the gas chromatography/mass spectrometry (GC/MS) analysis for glycols. A mass spectrum of the contaminant was then generated by concentrating one of the samples and analyzing it by GC/MS in full-scan mode. Although a computer match of the compound identity could not be obtained with the instrument database, a search with a more up-to-date mass spectral library yielded a good match with dimethylsilanediol (DMSD). Inductively coupled plasma/mass spectrometry (ICP/MS) analyses showed abnormally high silicon levels in the samples, confirming that the unknown compound(s) contained silicon. DMSD was then synthesized to confirm the identification and provide a standard to develop a calibration curve. Further confirmation was provided by external direct analysis in real time time of flight (DART TOF) mass spectrometry. To routinely test for DMSD in the future, a quantitative method was needed. A preliminary GC/MS method was developed and archived samples from various locations on ISS were analyzed to determine the extent of the contamination and provide data for troubleshooting. This paper describes these events in more detail as well as problems encountered in routine GC/MS analyses and the subsequent development of high performance liquid chromatography and LC/MS/MS methods for measuring DMSD.

II. Introduction

The Water and Food Analytical Laboratory (WAFAL) at the Johnson Space Center analyzes water samples from the space program. Hundreds of analytes are monitored through various laboratory analyses. In testing for organic compounds, the goal is to attain 100% “TOC accountability” through identification of all the specific organic constituents of the TOC. Low TOC accountability means that the organic compounds in the sample are largely unidentified and could include toxic chemicals.

From April through September of 2010, the TOC levels of product water from the International Space Station (ISS) Water Processor Assembly began a dramatic increase, to a range of 1.1 to 2.2 mg/L as carbon. Months earlier the TOC remained in a narrow range from 0.14 to 0.17 mg/L. The water is considered unacceptable if the TOC exceeds 3.0 mg/L[1]. No corresponding increase was observed in the concentration of any organic compounds routinely quantified. TOC Accountability was also dropping and the presence of one or more unknown contaminants was suspected. This paper gives account of the discovery, *c*haracterization, and identification of the contaminant, and the difficulties encountered in the development of quantitative laboratory analysis methods.

III. Discovery of Unknown Compound

On September 29, 2010, ISS water samples, returned on Soyuz 22, were being analyzed for ethylene glycol and propylene glycol, using gas chromatography/mass spectrometry (GC/MS), employing selected ion monitoring (SIM) for increased sensitivity. During this routine glycols analysis an interfering peak was consistently appearing just before the elution of ethylene glycol. Because the interferant contained a trace of the ion used to quantify ethylene glycol, mass 31, it initially appeared to be ethylene glycol. Closer inspection, however, revealed the presence of another ion not normally observed in ethylene glycol. Figure 1 shows a comparison of the GC/MS chromatogram of a water sample, containing the unknown, and one of a standard containing 4 ppm ethylene glycol. The black (middle) trace is mass 31. Figure 1 shows that the instrument has detected some mass 31 at a retention time of 4.50 minutes in the water sample. This is sufficiently close to the retention time of ethylene glycol, 4.601 minutes, that the instrument software might have reported it as a trace of ethylene glycol. Fortunately, however, the unknown contained another ion that this instrument routinely monitors, mass 45. The upper (red) trace in both chromatograms represents mass 45. It is obvious that the unknown contains a substantial fraction of mass 45, whereas ethylene glycol contains virtually none. Because this contaminant was found in WPA product water, further work was immediately begun to identify it.

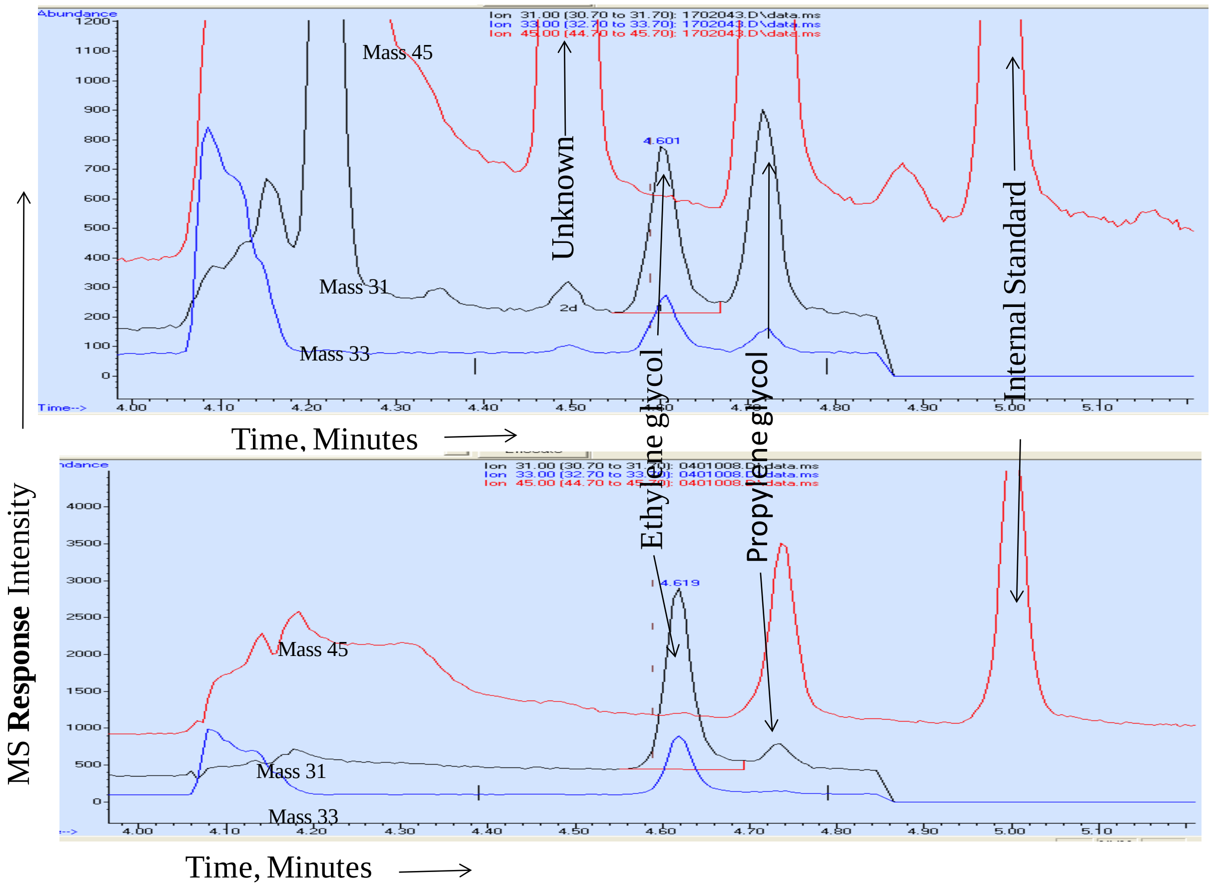


Figure 1. GC/MS of ISS humidity condensate above, glycols standard below

IV. Characterization and Identification

A. Concentration

The first objective was to generate a mass spectrum of the unknown compound in scan mode. Scan mode is much less sensitive than SIM mode, but can give a signal from the unknown at each unit mass over a given range. A full scan allows potential identification by comparison with a mass spectral database. By contrast, only 3 masses had been monitored for the unknown in SIM mode and therefore a complete mass spectrum, or fingerprint was not available. However, analyzing an unknown analyte in scan mode at trace levels often shows no peaks, because of the lack of sensitivity compared to SIM mode; thus, the unknown compound needed to be concentrated.

The unknown compound had been found to elute later than a compound that boils at 85°C (acetonitrile) and almost as late as ethylene glycol, which boils at 197°C. While retention times in a gas chromatograph are more than just a function of boiling point, they can suggest relative boiling points among analytes. There was a good chance that this unknown compound boiled at greater than 100°C, and could therefore be concentrated from water by evaporation. A sample of ISS potable water was heated to 55°C in a heating block while a slow stream of ultrapure helium was blown onto its surface. In 82 minutes, the sample weight reached 1/13 of the original. This 13x concentrate was re-analyzed by GC/MS (again under the same SIM conditions) and gave a peak with approximately 10-fold greater amplitude. This accomplished the goal of yielding a sample from which a scanning mass spectrum could likely be obtained. A secondary benefit from this 10-fold increase in peak amplitude was to confirm that this unknown definitely came from the water sample, and not from a part of the GC/MS instrument or gas supply.

B. Scanning Mass Spectrometry (Electron Ionization or EI Mode)

A GC/MS method was developed with the same temperature program used in the glycols analysis, but now scanning from 29 *m/z* (mass to charge ratio) to 284 *m/z*. This generated the mass spectrum shown in Figure 2, with mass 77 as the base peak.

This mass spectrum was searched against the mass spectral database that was in the instrument software, the Wiley Registry 7N Edition, containing 392000 mass spectra[2]. None of the mass spectra in the database matched this spectrum even remotely.

We still did not know the molecular weight of the unknown compound, or its identity, until collegues at Boeing Analytical Services Laboratory input the EI masses into a newer computer database at that location[3] and found a very close match: dimethylsilanediol. Figure 3 displays the mass spectrum of the unknown next to the mass spectrum of DMSD in a newer database. Their computer listed a 74.5% probability of a match for DMSD with the unknown mass spectrum, with the next closest of the 192108 mass spectra in the database matching the unknown at only 18.1% probability.

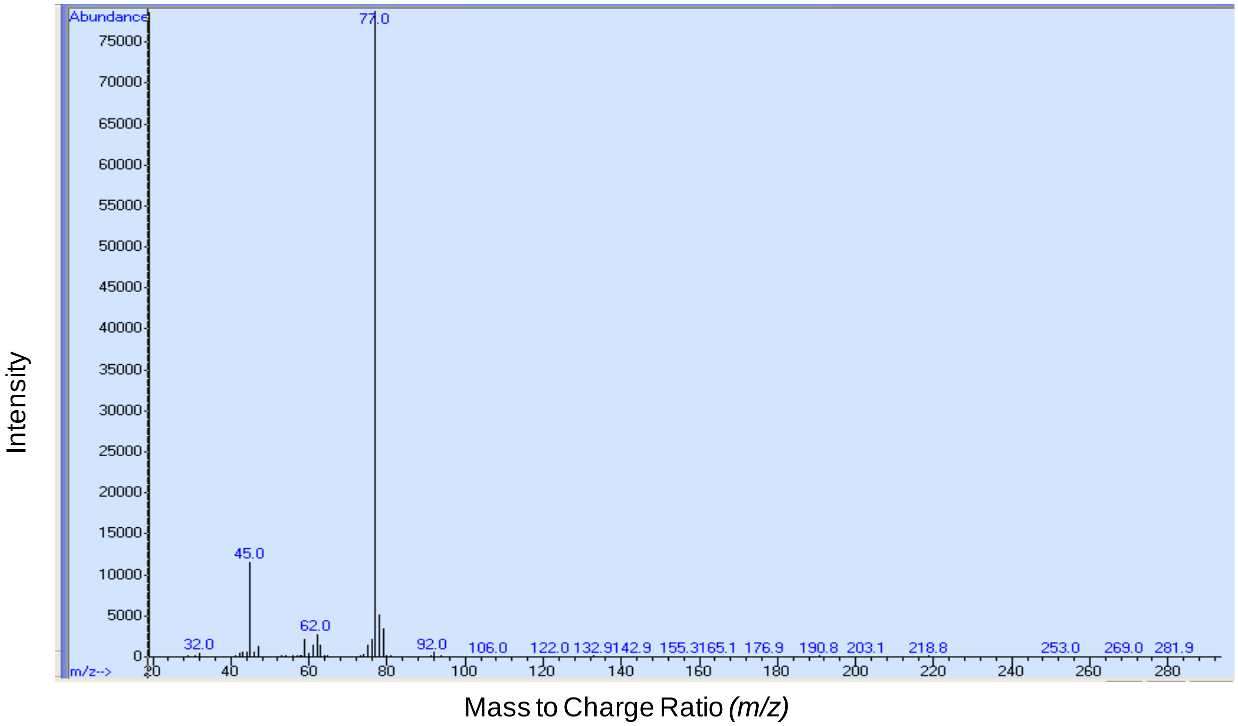
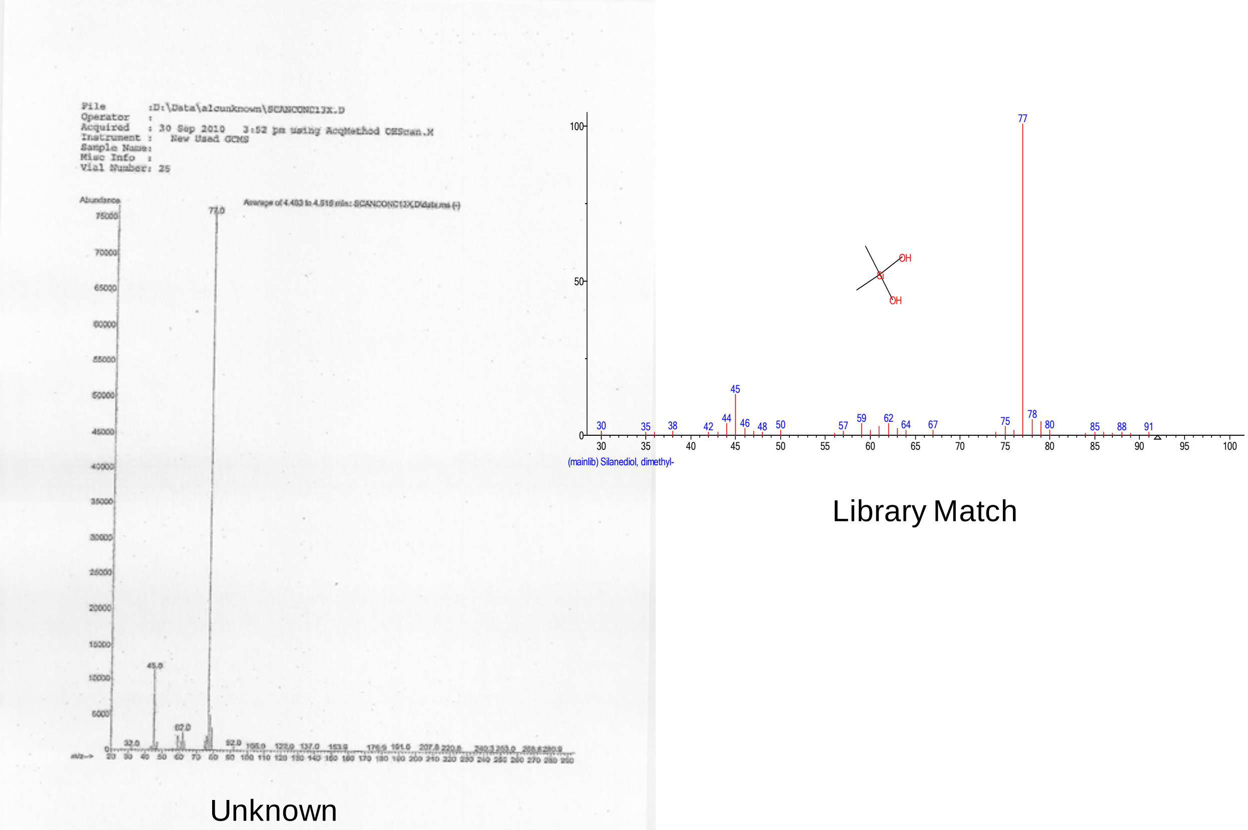


Figure 2. Electron ionization mass spectrum of unknown

ICP/MS analysis of all of the water samples containing the unknown compound seemed to show correlation between unknown GC/MS peak area and total silicon.

C. APCI, Electrospray, and DART Time-of-Flight Mass Spectrometry

Before the unknown had been identified with the newer database, the concentrated potable water sample was analyzed by direct infusion into APCI (atmospheric pressure chemical ionization) and electrospray sources of a quadrupole time-of-flight mass spectrometer (QqTOF, a “QStar Elite” from AB Sciex). The objective was to attempt to determine the molecular weight of the unknown. A second objective was to attempt identification by determining accurate masses of the unknown and its fragments. Scientists from the University of the Pacific were also requested to conduct TOFMS (time-of-flight mass spectrometry) analysis of the potable water concentrate using a different ionization technique-direct analysis in real time, or DART.



Unknown

Library Match

Figure 3. Mass spectrum library match for DMSD

Table 1 lists the major QStar peaks observed in the September 2010 ISS potable water that were low or absent in the April 2010 sample. Expecting to find one major peak in TOFMS mode, representing the molecular ion of the unknown, we found many peaks, and after fragmenting some of these ions in mass spectrometry/mass spectrometry (MS/MS) mode, it was determined that some ions in the same mass spectrum were fragments of others.

Once the unknown mass spectrum had matched up with that of DMSD, we immediately began researching this compound and found that it is unstable and interconverts among several oligomeric forms of silanols. This explains the multiple peaks observed in the QStar data and also explains why we could not find a source to purchase the compound. No custom synthesis service would agree to synthesize DMSD because a mixture of oligomers would likely result.

E. DART TOF Results

At this point, a report was received from University of the Pacific on results of their qualitative analyses[4]. Initially, Dr. Sparkman's group had searched the spectrum of the unknown compound against the newer NIST08 database of mass spectra and gotten a match for DMSD. From there, Pacific had introduced a concentrate of ISS potable water into the DART source of a time-of-flight mass spectrometer. The instrument detected 7 of the ions previously detected on the QStar instrument (which could be from separate compounds or fragments of one another) and 13 new ones. The instrument software proposed tentative formulas and many of them contained silicon. Of special interest were peaks in the negative mode at 91.0211, 165.0395, and 239.0591. These masses are consistent with those of the anions of the monomer, dimer, and trimer of DMSD.

Table1. QqTOF mass spectrometer peaks observed in September samples not in April samples

Ionization Mode	Mass/Charge	Corrected Instrument Response Counts	Fragments
Electrospray-Negative	74.9907	22500	93.0012, 75.9642,59.9713,42.0037
	93.0003	21750	76.9719,75.9643,74.9946,59.9709
	91.0209	21250	93.0009,75.9643,74.9942,59.9711
	165.0393	10000	149.0040,137.0217,120.9963, 91.0233,76.9721, 74.9923
	167.0186	10000	
	149.009	5000	132.9788,121.0226,74.9925,59.9711
	124.0217	2500	91.0234,74.8829,59.9708,31.9957
Electrospray - Positive	158.0305	16745	167.0360,130.0255,121.0213
	130.0274	7500	187.0028,168.9951,150.9745,132.9770,114.9599, 93.0387,75.0280
	115.0231	10500	75.0288
	189.039	9000	243.0241,206.9528,170.9698,188.9821,152.9641,128.9633,75.0297
	75.0269	8750	102.0267,93.0365,56.9660,46.9954,44.9779
APCI Negative	89.0283	986	
APCI Positive	93.1103	24000	

F. Synthesis of DMSD

In order to verify the presence of DMSD and quantitate the levels, a standard of DMSD was needed. Unfortunately, a search of available suppliers indicated this compound is not commercially available. A reference had been found[5] describing the synthesis of ^{14}C – labeled DMSD using isotopically-labeled dimethoxydimethylsilane precursor. In the synthesis, a small quantity of the precursor was stirred in 100 mL of water, in a Teflon bottle, to yield a 100 mg/L solution. Non-isotopically labeled dimethoxydimethylsilane (Sigma-Aldrich) was procured and synthesis was attempted using the published procedure. This hydrolysis reaction mixture was stirred for one hour as prescribed, but seems to take place in minutes. The hydrolysis reaction was reported to go to completion in the paper and it was confirmed that our reaction yielded nearly 100% of theoretical via analysis of the product mixture for methanol, the other product of the reaction. Methanol production, however, only confirms complete hydrolysis of the precursor. Formation of oligomers of DMSD during the synthesis cannot be ruled out (this would also produce methanol) and would lower the concentration of DMSD synthesized. Without a way of quantifying oligomers, 100% yield of DMSD, a 100 mg/L solution in water, was assumed.

G. Confirmation of Identity

The 100 mg/L synthesized DMSD was diluted to 10 mg/L and analyzed using the GC/MS laboratory method for glycols analysis whereby the unknown had been initially observed. A similarly sharp peak with the same retention time was observed. The standard solution was then analyzed in scan mode, generating a mass spectrum with a very good match for DMSD in the NIST08 database. This was repeated on GC/MS instruments with two different GC column stationary phases in order to best rule out the existence of any synthesis byproducts that may have been detected as GC/MS peaks. Although no stray peaks were noted, it is possible that the dimer of DMSD was breaking down in the inlet of the gas chromatograph, so the dimer could have still been present as a byproduct, converting to more DMSD and eluting in a single peak. It is also possible, as reported in the literature[6], that using a GC column that was not conditioned with a silanizing agent made chromatography of the synthesis byproducts impossible.

Table 2. Survey of ISS water samples

Sample Description	TOC (mg/L)	DMSD (mg/L)	Silicon (mg/L)
PWD Ambient – 11/10/09	0.14	<0.4	0.04
PWD Ambient – 1/6/10	0.16	<0.4	0.02
PWD Ambient – 3/3/10	0.17	<0.4	0.14
PWD Hot – 3/3/10	0.16	<0.4	0.18
PWD Ambient - 7/14/10	1.51	6.1	1.53
PWD Hot - 8/25/10	2.19	8.2	2.13
PWD Ambient - 9/15/10	1.11	4.7	1.21
WPA RIP - 7/29/10	2.18	7.3	1.77
WPA MFU Bed #2 Effl - 7/29/10	27.9	37.1	9.67
Waste Water Tank – 2/11/10	125	37.1	22.4
WRS Rack 2 Line B – 3/31/10	29.4	29.9	8.14
WRS Rack 2 Line B - 9/16/10	41.7	22.8	7.98
US Condensate – 3/11/09	61	30.5	18.2
US Condensate – 7/16/09	119	19	23.8
US Condensate - 8/30/09	97.6	16.8	15.3
US Condensate – 11/17/09	105	42.2	14.5
US Condensate – 1/31/10	83.1	45.4	19.1
US Condensate - 4/6/10	335	107	48.6
UPA Distillate – 4/10/10	21.8	5.6	1.25
SRV-K – 5/18/10	0.27	<0.4	0.07
ULF3 - Potable CWC #1	23.1		0.09
ULF3 - Technical CWC #2	2.46		0.08
ULF3 - Technical CWC #6	1.37		0.05

V. Initial Analytical Method and Results

At this point, it was thought that an ideal analytical method for DMSD was the glycols method in which it had initially appeared, with slight modifications. The DMSD peak was sharp and symmetrical in this method, and a large base peak of mass 77 ensured that the method would be sensitive using mass 77 as the quantitation ion. A rapid accurate quantitative analysis of all of the water samples previously screened (as described in Part D above) for DMSD concentration was needed to identify the source of DMSD in the ISS water system. This modified GC/MS method was used to add to data from the previously-completed silicon survey of a number of archived water samples– humidity condensate, wastewater, ISS potable water from the Lab module, and ISS potable water from the service module. A well-defined correlation was observed among a sample's TOC level, silicon level, and DMSD concentration. Table 2 summarizes the results of the survey. The DMSD concentration correlates well with both carbon and silicon levels, especially in the potable water samples, where DMSD is the only significant contaminant present. The humidity condensate and wastewater samples contain other compounds of carbon and silicon besides DMSD, weakening the correlation. The potable water samples are labeled PWD (potable water dispenser) and SRV-K (system for regeneration of condensate water-this is potable water from the Russian water system). DMSD was not detected in ISS potable water until July of 2010, but it was already at high levels in ISS humidity condensate samples collected by the crew as early as March of 2009.

VI. Improved Analytical Methods

During the DMSD survey described in Section V., a problem with the method had quickly become evident. "Carryover" was causing DMSD to appear at high levels in relatively clean samples, including "water blanks" consisting of ultrapure water and internal standard only. Trial and error, involving instrument maintenance, indicated that DMSD had contaminated multiple parts of the inlet of the gas chromatograph as well as a substaintial portion of the column of the gas chromatograph. Whereas normal maintenance of a gas chromatograph involves trimming 6" of column material from the head of the column, it was found that trimming 1 meter did not completely eliminate DMSD contamination. The DMSD also appeared to cause carryover of propylene glycol in the routine glycols analysis. Days before the discovery of DMSD, it had already ruined one GC column, which was thought to have failed due to age. After the discovery of DMSD, it ruined two other GC columns before the incompatibility with gas chromatographs became known. DMSD is believed to be highly soluble in the polysiloxane stationary phases that coat the wall of the capillary column of a gas chromatograph. In addition, the column wall, the septum, the liner, and the o-ring of a gas chromatograph all contain silica which may adsorb DMSD.

Two high performance liquid chromatography (HPLC) – based methods were developed for DMSD-one employing refractive index detection (RI) and one employing MS/MS detection. The LC/MS/MS method involves the introduction of the constituents of an HPLC peak into the atmospheric pressure chemical ionization (APCI) source of the QStar instrument. A negative charge in the source removes a proton from most analytes, thus converting DMSD, molecular weight 92, into the mass 91 anion. The quadrupole of the mass spectrometer is set to block all ions except for those of *m/z*=91, which pass through. This removes essentially all analytes differing in molecular weight from DMSD. These mass 91 ions are then fragmented. A major fragment of DMSD under these conditions is the ion of *m/z*=75, believed to be CH3-(Si=O)-O-. This ion is monitored and used to calculate DMSD concentration. This method is highly selective by virtue of three “filtration” processes. An interfering compound must first elute from the HPLC column at the same time as DMSD, or 4.8 minutes. It must then form an anion of *m/z*=91. Its fragments must then include an abundant fragment of *m/z*=75. No known interferents meet all of these criteria. An early – eluting peak is sometimes observed with mass 75, but is screened out by its retention time of 3 minutes. Glycerol forms an anion of mass 91 and can be seen getting past the quadrupole, but it does not yield any fragments of mass 75 and elutes later than DMSD from the HPLC column, failing two of the three criteria. This LC/MS/MS method produces a visible peak for concentrations of DMSD as low as 0.1 mg/L, but our laboratory defines the reporting limit as 0.4 mg/L. Figure 4 is an example of the mass 75 extracted ion chromatogram, used to quantitate DMSD, showing a 1.23ppm DMSD peak in a product water sample returned on STS-133.

The HPLC/RI method produces a sharper HPLC peak than the LC/MS/MS method. It employs a different type of octadecylsilane HPLC column (polar endcapped), and chromatographs DMSD under acidic conditions. Detection is by refractive index. This method has an official reporting limit of 2 mg/L, but a peak is observable at 1 mg/L. Figure 5 is an example of a chromatogram from this method, showing an 8ppm DMSD peak (retention time 5.033) in another product water sample returned on STS-133.

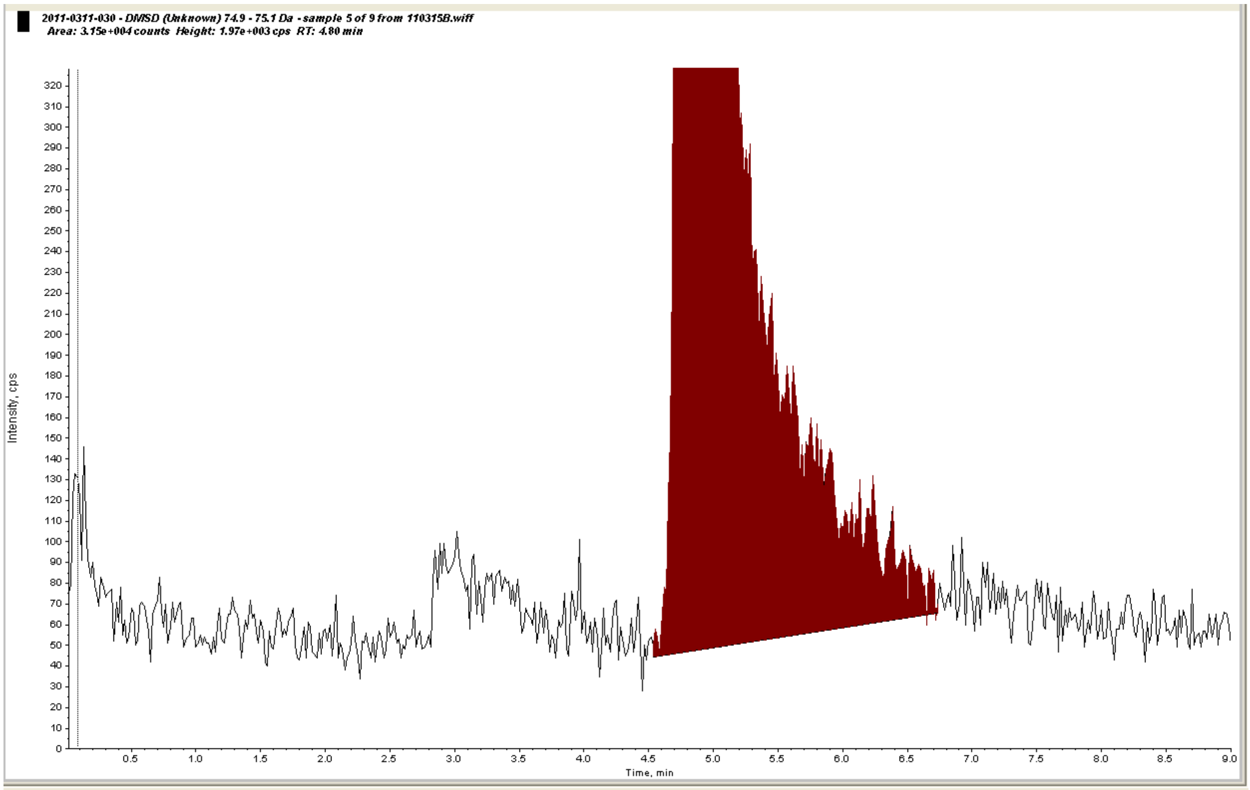


Figure 4: LC/MS/MS extracted ion chromatogram for DMSD in ISS potable water

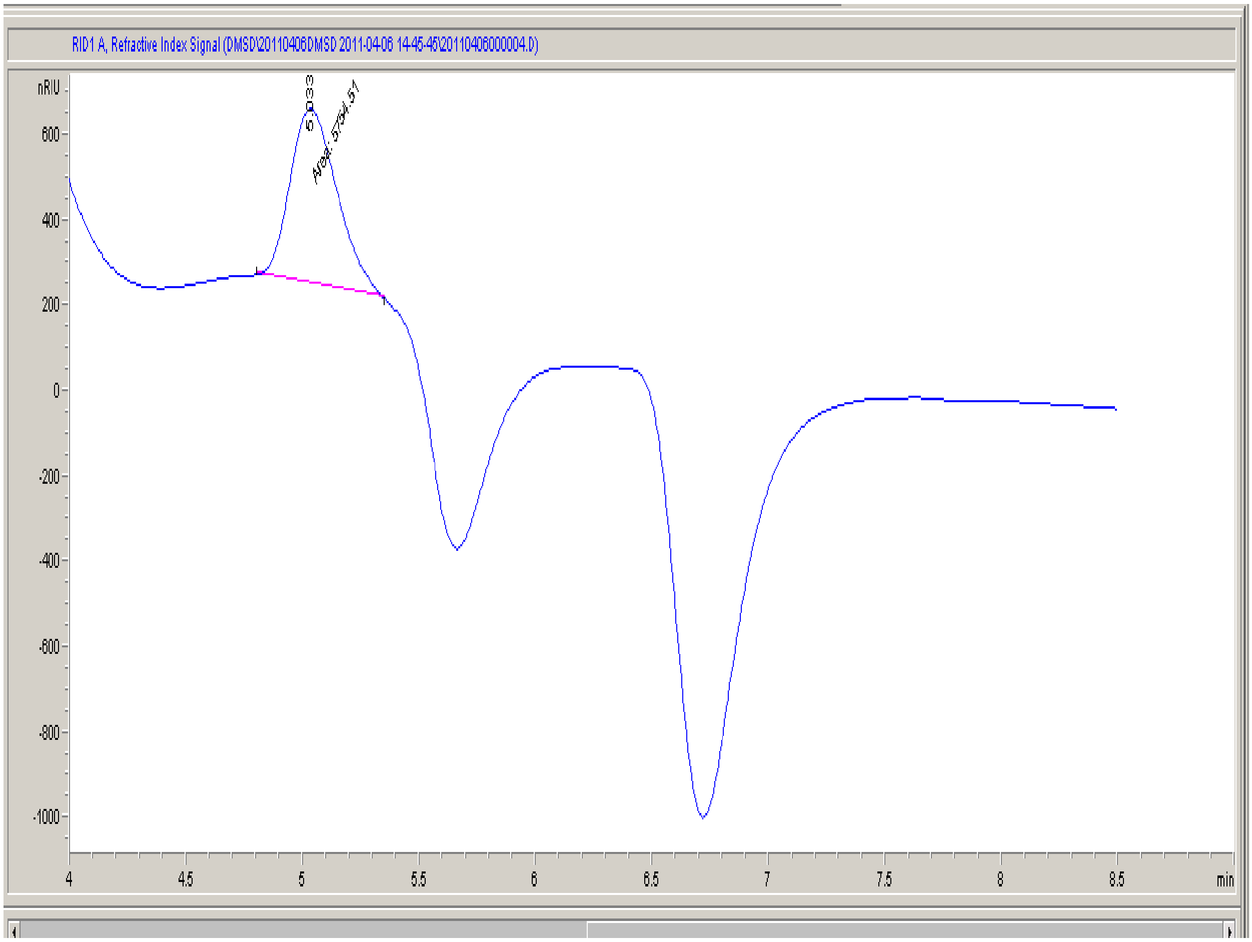


Figure 5. HPLC/Refractive Index chromatogram for DMSD in ISS potable water

VII. Experimental

The GC-MS instrument on which DMSD was discovered was an Agilent 6890GC with a Model 5973 mass selective detector and a Model 7683B Autosampler. The GC capillary column used stationary phase DB-VRX (JW Scientific). Column dimensions were 60M x 0.25mm x 1.4µM. Sample injections were 0.5µL split injections, of split ratio 30, with inlet temperature 225°C, column temperature 210°C isothermal, and helium column flow of 0.8 mL/min. The mass spectrometer source temperature was 230°C, quadrupole temperature was 150°C, and electron multiplier voltage was 1400V. SIM masses were 31, 33, and 45 with a dwell time of 120 msec for each.

The water sample shown in Figure 1 was effluent from a multifiltration bed in the water processor assembly collected onboard ISS on 7/29/10. Potable water samples had the impurity peak also, but the mass 31 component was not always detected by the instrument. The water sample from which DMSD was concentrated was collected onboard ISS on 8/25/10, from the potable water dispensor's hot side. It was selected for concentration because potable water would have lower percentages of other organic compounds present , and this particular sample had the biggest unknown peak of the four potable water samples returned on Soyuz 22.

Total silicon analyses were done on an ICP/MS instrument. The model is the PE Sciex Elan 6000 with a Model AS-90 autosampler.

DART TOF mass spectrometry was done using a JEOL (Peabody, MA) mass spectrometer-the DART AccuTOF model.

The observation of the synthesis of DMSD, from the precursor, being complete in minutes is based on having prepared calibration standards by serially diluting the reaction product solution after two minutes of shaking the mixture and observing no difference in LC/MS/MS peak intensities from those obtained after one hour of stirring.

The LC/MS/MS method employs a Restek Allure HPLC column, 150mm x 3.2mm x 5µM. Mobil phase, 25% methanol w/w, flows at 0.27 mL/min. 30µL of sample is injected onto the column. The ABSciex mass spectrometer heated nebulizer (APCI) is held at 325°C. The QStar Elite is operated in product ion mode with the precursor ion selected as 91+/- 0.5 *m/z*. Collision energy is set at 18. Calibration is by six external standards ranging in concentration from 0.3 mg/L to 5.0 mg/L. Quantitation is by peak area on extracted ion chromatograms of *m/z* = 74.9-75.1.

The LC/RI method for quantitating DMSD employs a Phenomonex Synergi Hydro-RP, 150mm x 3.0mm x 4µM), and a 20mM phosphate buffer mobil phase, pH2.9, at 0.65mL/minute. 100µL sample is injected. Four external standards are employed ranging from 2 ppm to 50 ppm DMSD. Detection is by refractive index. The instrument is Agilent's Model 1200.

VIII. Discussion

In the DART TOF mass spectrometer and the QqTOF instrument, ions corresponding to the dimer and trimer of DMSD and other compounds related to DMSD were observed. Nevertheless their presence in the ion source of the mass spectrometer does not prove that they exist in a water sample as they could have formed during the ionization process. Journal articles report that the dimer of DMSD had been synthesized[6] and that DMSD formed through the degradation of oligomeric siloxanes containing as many as 5 silicons. This suggests that several compounds related to DMSD could also be present in ISS water samples. It also suggests that related compounds could be present in our synthesized "100 mg/L DMSD standard" resulting in an actual concentration of less than 100. The dimer or trimer have yet to be detected, so further chromatographic work is necessary in both GC and HPLC.

Even HPLC analysis of the solution, for oligomers, once a method is developed, will not reveal the concentration of DMSD, as pure forms of the oligomers will also not be commercially available to use as calibrants. A better assay by HPLC would have to be done by employing ratios based on the relative responses of any silanols detected in the standard solution. Silicon nuclear magnetic resonance spectroscopy (NMR)[6] was reported successful in assessing purity in the solid state at 1000 ppm DMSD or lower. It may be possible to assess purity of DMSD calibration standards in the liquid state with silicon NMR, increasing confidence in the accuracy of our DMSD methods by assaying each silanol species in the standard solution.

IX. Conclusions

The unknown peak seen during the routine analysis of glycols was identified as DMSD. This allowed two quantitative methods to be developed for DMSD, substantially increasing the TOC accountability of JSC's Water and Food Laboratory for ISS water samples. The fact that only one silanol peak has been observed by GC/MS does not prove that the water samples do not contain other silanols. Further GC and HPLC work is needed seeking peaks for oligomers of DMSD and other silanols in water samples from ISS and in the calibration standards prepared in the lab.

Currently, the accuracy of the quantitative analysis for DMSD cannot be confirmed, since it is assumed that synthesis of the calibration standard yields 100% of theoretical. Fractions of this synthetic product solution could contain related silanols, resulting in a lower DMSD concentration than assumed. It may be possible to assess purity of much lower concentrations in solution using silicon NMR spectroscopy.

X. References

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