DETECTION OF VOLATILE ORGANIC COMPOUNDS IN SPACECRAFT ENVIRONMENTS USING GAS CHROMATOGRAPHY-ION MOBILITY SPECTROMETRY

Thomas Limero and Eric Reese
Wyle Laboratories

EXTENDED ABSTRACT

Archival sampling followed by ground-based analysis has been the primary method in the past for assessing volatile organic compound (VOC) concentrations aboard U.S. spacecraft. This data helps the NASA toxicologist determine if the air quality was acceptable during the mission. It was recognized early in the International Space Station (ISS) development that onboard monitoring would be a necessity due to the continuous human presence and limited return options.

This approach was validated by the contingency events that occurred on MIR Station during the NASA/MIR program. The need for near real-time data to direct crew actions was apparent following the major combustion event (2/97) and chemical leaks (5/97-onward) on MIR. Beyond these spectacular events, it was obvious that periodic, near real-time monitoring of airborne contaminants was essential to identify minor annoyances before they become major problems.

The Toxicology Laboratory at Johnson Space Center (JSC) has been involved in instrumentation development for the past ten years. Initially, gas chromatography-mass spectrometry (GC-MS) was selected to measure trace VOCs on ISS; however, resources limitations, reliability concerns, and cost ultimately led to the decision to use gas chromatography-ion mobility spectrometry (GC-IMS) technology for the ISS volatile organic analyzer (VOA). The purpose of the VOA is to measure target trace VOC contaminants in the ISS atmosphere daily and be ready to assess cleanup efforts following an incident.

The VOA is equipped with a sample preconcentrator to provide low compound detection limits, GC columns to separate the components of the complex spacecraft atmosphere, the IMS to detect the compounds, and an integrated computer for data processing and instrument control. The VOA target compounds encompass a wide range of chemical classes from very volatile Freons to xylenes; therefore, 60 meter GC columns are used for separation. Compound identification starts with the determination of the compound’s GC retention time. This is accomplished by monitoring the reactant ion peak (RIP), an ever present reservoir of charged ions, for any decrease in area which would signal the presence of an analyte ion. This parameter is combined with a measure of the time it takes the ion to traverse the IMS drift tube (ion mobility) creating a two-dimensional plot. The addition of standard deviations for each parameter results in elliptical windows. When the GC retention time and ion mobility measurements for an analyte correspond to one of the elliptical windows, the analyte is identified as the compound associated with that window. Quantitation of analytes is performed by integrating the area of the product ion peak (PIP) in the mobility spectra. Quantitation is more accurate using this method as opposed to integrating the GC peaks, since overlapping peaks are less of a problem.

Wyle Laboratories and Graseby Dynamics teamed to build a VOA flight prototype for NASA to fly as an experiment onboard the Shuttle. The critical questions about the VOA’s ability to operate in a spacecraft environment were answered by this experiment on the STS-89 Shuttle mission.

The most pressing issues were related to heating and cooling processes that are unique in space due to the lack of convection. Accurate compound identification relies on acquiring reproducible GC retention times and ion mobilities, which in turn depends upon reproducible GC temperature programming and stable IMS detector temperatures. Other concerns included operational issues such as sample size and sampling methods. The experimental results indicated that heating and cooling processes were well-managed, producing accurate compound identifications. Another important finding was that calibrations completed on the ground maintained their integrity in orbit. Figure 1 shows the results from one of the analytical runs during STS-89 with compounds identified by the database, with exception of the siloxanes which were unexpected. Finally, it was clear from this flight experiment that the sample volume was too large, given the concentration of components in the Shuttle atmosphere and the sensitivity of the instrument.

Lessons learned from the flight of the VOA experiment were incorporated into two VOA flight units for ISS. Following fabrication, one of these units was calibrated and then challenged with a test mixture of 19 compounds. The results from this initial calibration and challenge follow:

- Greater than 90% of the compounds were correctly identified;
- Quantitative precision of ±20% for all but three compounds (benzene-29%, hexane-21%, ethanal-ND); and
Quantitative accuracy was ±35% for 14 compounds with higher values for dichloromethane-60%, ethanal-qualitative, and 2-propanol, F22, and F113-greater than ±100%.

The poor detection of dichloromethane, F22, and F113 were attributed to errors in database entry or creation of the calibration curve, which were easily corrected. However, 2-propanol and ethanal are GC column issues. A higher than desired initial GC column program temperature was required because of elevated ambient temperatures in the Shuttle. This created chromatographic problems for 2-propanol (overlaps with acetone) and ethanal. Losses of ethanal in the preconcentrator may also have contributed to the quantitative difficulties with this compound.

The preliminary results from the initial VOA testing indicate that the unit will perform well during operations on ISS. The problems encountered with 2-propanol and ethanal may be partially solved by adjusting GC and preconcentrator parameters; however the best solution, reserved for the next generation unit, would be to remove the preconcentrator and replace it with a sample loop. The sensitivity of the IMS detector is such that preconcentration is not required for the compounds of interest and the sample loop would greatly improve the chromatography as a narrow slug of sample can be put on the head of the column.