



# Contamination Knowledge Report, Part 1

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## Summary

- Witness foils that were taken out at different times from a curation cabinet were received at NASA GSFC. Samples were labeled:
  - Day 1
  - Day 2
  - Day 5
  - Day 14

This report will be updated as more time points are examined and results of different techniques are compiled

- Glycine was the only amino acid that was detected using LC-FD/ToF-MS and the AccQ•Tag derivatization method. The concentration of glycine on the witness plates are well below the saturation point of 180 ng/cm<sup>2</sup>.
- Low-molecular weight organics were monitored via DART-high resolution mass spectrometry.
- Pyrolysis GCMS is planned
- Solvent extraction GCMS is planned

## Introduction

Samples from the materials archive curation cabinet are collected on Reynolds wrap aluminum foil (standard duty). The ~10 cm<sup>2</sup> foil sheets were baked at 500 °C overnight in air, and then placed in the bottom dessicator cabinet in a 3 x 8 array. Samples are collected for analyses over a period of one year. Samples are collected in triplicate. One sample for aqueous extraction, one for organic, and one held for the option of simultaneous analysis of all time points at the end of the study. Samples were then shipped from NASA-JSC to NASA-GSFC with three tubes from each time point sampling inserted into a "BEL-ART" screw cap container padded with bubble wrap.

## Procedure

For each time point one of the three tubes was selected for aqueous extraction. 1 mL ultrapure water was added to each glass centrifuge tube (previously cleaned via 500 °C bake out overnight in air) containing ~10 cm<sup>2</sup> of aluminum foil. The centrifuge tube was flame-sealed and placed into an oven at 100 °C for 24 h. The sample extract was split.

One 500  $\mu\text{L}$  portion was dried down in a vacuum centrifuge. The other 500  $\mu\text{L}$  portion was dried down in a vacuum centrifuge and then subjected to an acid hydrolysis step. Acid hydrolysis was accomplished using 6 M HCl vapor in sealed glass tubes at 150  $^{\circ}\text{C}$  for 3 h. The acid hydrolyzed residue was dried down in a vacuum centrifuge. Both unhydrolyzed (free amino acids) and acid-hydrolyzed (total amino acids) extracts were taken up in 100  $\mu\text{L}$  ultrapure water.

### LC-FD/ToF-MS Analysis

30  $\mu\text{L}$  out of 100  $\mu\text{L}$  was dried in a total recovery vial and reconstituted in 10  $\mu\text{L}$  of water, 20  $\mu\text{L}$  of Waters AccQ•Tag derivatizing agent, and 70  $\mu\text{L}$  of borate. Both samples and standards were heated for 10 minutes at 55  $^{\circ}\text{C}$  immediately following the addition of the derivatizing agent. The sample was then analyzed via the commercial Waters AccQ•Tag protocol on a Waters LCT Premier time-of-flight mass spectrometer equipped with an electrospray ionization source (positive ion mode), mass resolution setting of 5,000  $\text{m}/\Delta\text{m}$  but without external mass accuracy calibration. Sample was introduced via a Waters Acquity UPLC with fluorescence detector. For UPLC analysis a 250  $\mu\text{L}$  syringe, 50  $\mu\text{L}$  loop, and 30  $\mu\text{L}$  needle were used. The total injection volume was 1  $\mu\text{L}$ . A set of 9 proteinogenic amino acids (0.25 to 250  $\mu\text{M}$ ) was prepared in water and analyzed, which was used for amino acid identification and quantitation. A linear least-square model was fit to each analyte. Mass traces only were used for quantitation.

### DART-MS Analysis

Sample extracts were spotted (5  $\mu\text{L}$ ) on a steel mesh sampling unit at the inlet of the DART SVP (Direct Analysis in Real Time) source. The DART source (He gas, 350  $^{\circ}\text{C}$ , positive ion mode) was coupled to a LTQ-Orbitrap XL hybrid mass spectrometer with a mass resolution setting 60,000 and a lock mass enabled (on a polysiloxane compound found in air background) for high resolution, accurate mass measurements of low-molecular weight organics. Before sample analysis, the mass accuracy of the Orbitrap was checked using a standard solution of quinine in methanol. Mass error was typically <1 ppm for quinine.

### Results

Assuming that the witness plates were one square centimeter on each side and both sides were being used (for a total of 2  $\text{cm}^2$ ), the following concentrations of glycine were detected by LC-FD/ToF-MS and shown in Table 1. None of the other amino acid targets were measured above their detection limits in these samples.

Table 1: Amount of glycine in each sample

	Free ( $\text{ng}/\text{cm}^2$ )	Total ( $\text{ng}/\text{cm}^2$ )	% Free
Day 1	0.10 $\pm$ 0.101	0.18 $\pm$ 0.14	0.54
Day 2	0.22 $\pm$ 0.065	0.60 $\pm$ 0.12	0.37
Day 5	0.33 $\pm$ 0.077	0.65 $\pm$ 0.21	0.51
Day 14	0.15 $\pm$ 0.019	0.59 $\pm$ 0.04	0.25

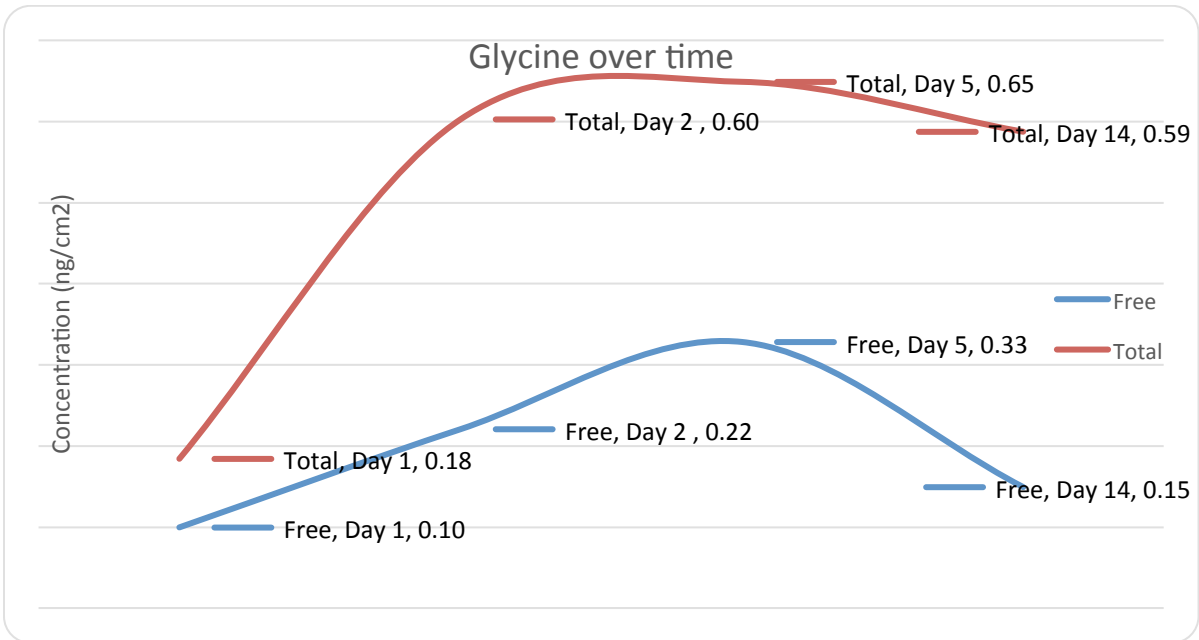


Figure 2. Plot of total and free amino acids over time.

For DART-MS analyses, the measured mass spectra of unhydrolyzed and acid hydrolyzed extracts were complex and strongly resembled the mass spectrum of the stainless steel sampling mesh.