Towards and Effective Method for the Analysis of Meteoritic Amides

José L. Ramírez-Colón[1], José C. Aponte[2,3], Jamie E. Elsila[3], and Jason P. Dworkin[3]

(1) Department of Biology, University of Puerto Rico Río Piedras, Puerto Rico, USA (jose.ramirez34@upr.edu), (2) Department of Chemistry, Catholic University of America, Washington DC, USA, (3) Solar System Exploration Division, NASA Goddard Space Flight Center, Maryland, USA (jose.c.aponte@nasa.gov)

Abstract

The study of meteoritic organics in carbonaceous chondrites has shown how these extraterrestrial materials record valuable information about the formation of the Solar System and their potential as sources of starting materials for prebiotic organic synthesis [1]. In this study, a method for the analysis and quantification of aliphatic amides, a class of compounds that may have been precursors for other meteoritic organics, has been optimized and tested.

1. Introduction

Carbonaceous chondrites are a siliceous class of meteorites that constitute some of the most primitive extraterrestrial materials. As such, they represent a great tool to study the prebiotic chemistry of our Solar System. The chemical composition of some carbonaceous chondrites has revealed a few percents of soluble and insoluble organics including aromatic and aliphatic hydrocarbons, carboxylic acids, and amino acids among other compounds, suggesting that they could have served as vehicles for the delivery of prebiotic molecules to the early Earth [1].

Recent studies have identified aliphatic amides such as formamide as potential precursors of meteoritic and complex organics [2,3,4]. However, to date, the identification of aliphatic amides has not been reported in meteorites. Here, we present the results of our method development for the identification and quantification of meteoritic aliphatic amides.

2. Derivatization Testing

Silylation derivatization of amides increases their thermal stability and facilitates their analysis by gas chromatography-mass spectrometry (GC-QqQMS). We tested the silylation of eleven aliphatic amides and urea (Figure 1) using *N*-methyl-trimethylsilyl trifluoroacetamide (MSTFA). We also tested other three silylation reagents: *N*,*N*-diethyltrimethylsilylamine (TMSDEA), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA + TMCS, 99:1), and *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacet-amide (MTBSTFA), at different temperatures, reaction times, solvents, volume of solvents, and catalytic conditions (using acids or bases; *e.g.*, hydrochloric acid, boron trifluoride, pyridine, triethylamine, trimethylamine, etc.). The derivatization of the aliphatic amides with MSTFA resulted in the highest yields, the shortest derivatization times, and the best derivative stability.

To evaluate the effects of likely meteoritic minerals on extraction and derivatization of the amides, pyrolyzed Allende meteorite powder was impregnated with amide standards and taken through our optimized method. No decomposition of the amides and no significant byproduct formation was observed due to the influence of minerals (Figure 1).

3. Meteorite Results

We extracted 200 mg of the Murchison meteorite in anhydrous dichloromethane/acetonitrile and evaluated for aliphatic amides after MSTFA derivatization. From our analysis (Figure 1), we observed a tentative detection of meteoritic acetamide, however, this detection may be a byproduct of the extraction and silylation derivatization. It is possible that no acetamide is present in Murchison (or present below our detection limits), as we believe that at least a portion of the acetamide we found in our Murchison meteorite sample may have resulted from the partial hydrolysis of the acetonitrile either during meteorite extraction or during extract derivatization.

Additional studies to understand the effects of water during extraction and derivatization of aliphatic amides are needed. Future experiments may involve the use of Allende pyrolyzed powder impregnated with trace amounts of water in the absence and presence of aliphatic amide standards. Additionally, to absorb water in the medium during extraction and derivatization, we may test (*i*) molecular sieves or celite, and (*ii*) drying agents such as anhydrous salts.

4. Conclusions

Based on the possibility that aliphatic amides could serve as possible precursors to the prebiotic chemistry

of early Earth, this study evaluated and developed a derivatization technique for the analysis of this compound class in carbonaceous chondrites. The low levels of organic content and the high molecular complexity of carbonaceous chondrites make method development targeting specific compound classes a challenging and lengthy process [5]. Further optimization of this protocol is needed before applying it to carbonaceous chondrites of different petrological types.

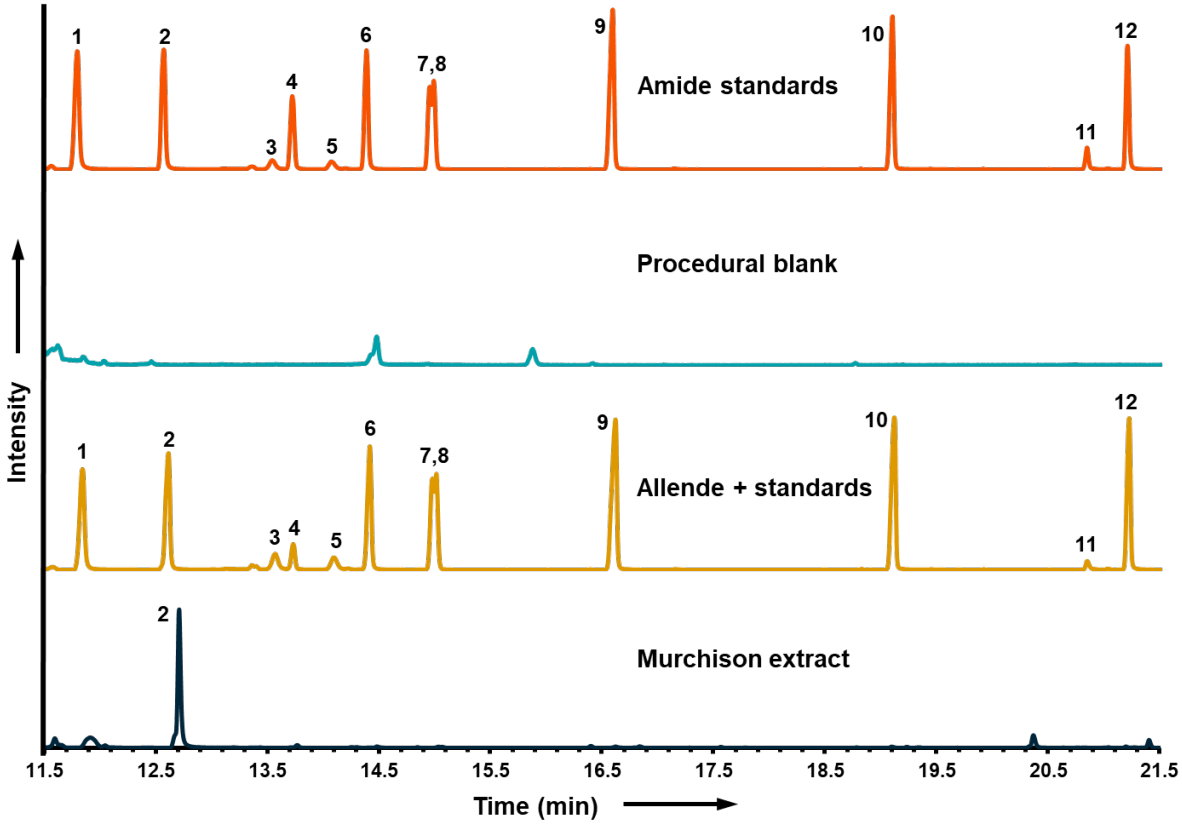

Figure 1. GC-MS chromatograms of MSTFA-amide derivatives in standard mixture, procedural blank, standard mixture + 200mg of pyrolyzed Allende, and 200mg of Murchison extracted in dichloromethane/acetonitrile (7:3). Peak ID: **1**, formamide; **2**, acetamide; **3**, *N*-methylformamide; **4**, *N*-methylacetamide; **5**, *N*-ethylformamide; **6**, propanamide; **7**, isobutyramide; **8**, trimethylacetamide; **9**, butanamide; **10**, pentanamide; **11**, urea; **12**, hexanamide.

Acknowledgements

This research was supported by the Goddard Center for Astrobiology, and a grant from the Simons Foundation (SCOL award 302497 to J.P.D.).

References

[1] Glavin D. P., Alexander C., Aponte J. C., Dworkin J. P., Elsila J. E., and Yabuta H.: The Origin and Evolution of Organic Matter in Carboneceous Chondrites and Links to Their Parent Bodies, *Primitive Meteorites and Asteroids*, Amsterdam, Netherlands: 205-271, **2018**.

[2] Saladino R., Botta G., Pino S., Costanzo G., and Di Mauro, E.: From the one-carbon amide formamide to RNA all the steps are prebiotically possible, *Biochimie*, 94, 1451-1456, **2012**.

[3] Saladino R., Carota E., Botta G., Kapralov M., Timoshensko G., Rozanov A. Y., Krasavin E., and Di Mauro E.: Meteorite-catalyzed syntheses of nucleosides and of other prebiotic compounds from formamide under proton irradiation, *PNAS*, 112, 21: E2746-E2755, **2015**.

[4] Costanzo G., Saladino R., Crestini C., Ciciriello F., and Di Mauro E.: Formamide as the main building block in the origin of nucleic acids, *BMC Evol. Biol.*, 7, S1, **2007**.

[5] Simkus D. N., Aponte J. C., Elsila J. E., Parker E. T., Glavin D. P., and Dworkin J. P.: Methodologies for analyzing soluble organic compounds in extraterrestrial samples: Amino acids, amines, monocarboxylic acids, aldehydes, and ketones, *Life*, 9, 47, **2019**.