EPSC
European Planetary Science Congress

Identification of volatile organic compounds coming from the heating of cometary ice analogs- VAHIIA Project

N. Abou Mrad, F. Duvernay, P. Theulé, T. Chiavassa and G. Danger
Aix-Marseille Université, CNRS, PIIM, UMR 7345, 13013 Marseille, France (gregoire.danger@univ-amu.fr).

Abstract

Studying organic volatile compounds (VOC) coming from the heating of cometary ice analogs through laboratory simulations is of great interest in understanding the reactivity that leads to the formation of the organic refractory residues available in interplanetary objects. They will enlighten us on conditions prevailing on the primitive nebula and during the formation of the Solar system and will support understanding and interpreting space mission data for comet surveys such as the ongoing Rosetta mission. In this contribution, we present an analytical system developed in our laboratory for cometary VOC analyses which is conducted by gas chromatography - mass spectrometry (GC-MS) coupled to a cryogenic chamber through a specific interface. This interface is constituted by a preconcentration unit allowing VOC enrichment and transfer to the GC-MS, and of an injection unit allowing online gaseous sample introduction into the GC injector.

1. Introduction

To understand the origin and evolution of the solar nebula, studying organics in comets is of a prime interest because these latter have undergone the least alteration during this evolution. Cometary ice analogs can be recreated during laboratory experiments during which analogs can be subjected to physical processes simulating what a cometary material would undergo when a comet evolves around the Sun. Analogs of cometary ice are formed inside an ultra-vacuum chamber (generally 10^{-9} mbar) by depositing a gas mixture relevant of a cometary ice composition, and are subsequently irradiated and/or warmed. This warming allows the sublimation of volatile organic compounds (VOC) resulting in a complex residual organic residue, representing organic matter in planetary objects. Even though the VOC play an important role in the residue formation, their characterization has been limited. Furthermore,

current space missions such as the Rosetta mission will analyze VOC sublimating from cometary grains and will need information of the various VOC that can come from such grains for enhancing their data interpretation. These reasons justify the need for VOC analysis. However, to our knowledge, experiments dedicated to the characterization of VOC from experimental simulations have not been developed yet. Hence we were interested in developing an experimental set-up for a non-specific and an online analysis of these VOC. In this context, three main problems needed to be addressed: the low pressure under which VOC are formed in the vacuum chamber since their analysis by gas chromatography coupled to mass spectrometry (GC-MS) is conducted at atmospheric pressure; the low sensitivies due to slow desorption kinetics while a narrow injection is needed to ensure the best GC efficiency; and the presence of water, the main constituent of cometary ice analogs. This contribution presents the development, calibration and optimization of an analytical system to transfer the VOC sublimating from cometary ice analogs from the vacuum chamber where they are formed to the GC-MS where they are analyzed.

2. Experimental set-up of the VAHIIA project

Cometary ice analogs are formed in a high vacuum chamber presenting a pressure of 5.10^{-9} mbar at 295 K and 10^{-9} mbar at 20 K. The ice formed is monitored using infrared spectroscopy. When warmed-up, sublimating species are pumped to a **preconcentration unit** directly connected to the chamber. This developed unit has two main objectives: firstly, preconcentrate analytes prior to the GC analysis since they desorb with large time scales in the vacuum chamber; secondly, reaching a pressure sufficient to provide a GC analysis. This unit is constituted of a preconcentration loop and 6 valves: V1 is connected to a helium gas via a thermal mass flow meter/controller, V2 is connected

to the vacuum chamber, V3 and V4 are connected to a preconcentration loop, V5 is connected to the injection unit of the GC, and V6 is connected to the turbomolecular pump of the vacuum chamber (figure 1). Sublimating VOC are recovered through opening valves 2, 3, 4 and 6 allowing a differential pumping of VOC through the preconcentration loop submerged in liquid nitrogen. After preconcentration, the loop is then rapidly warmed-up to 70°C for obtaining a flash sublimation of stacked compounds. Helium is then introduced in the loop by opening valves 1 and 3 to increase sample pressure and facilitate analyte transfer to the injection unit through the opening of valves 4 and 5. The **injection unit** developed in collaboration with Interscience Belgium allows the introduction of the gaseous sample coming from the preconcentration unit into the GC injector classically conceived for liquid sample injections. It is mainly constituted by rheodine 6 port valves before each GC injector (E1 before the front GC inlet and E2 before the back GC inlet). On each valve is branched a sample loop of a determined volume that receives the gaseous sample from the preconcentration loop. Depending on its position, the valve E2 either allows the loading of the sample loop or the injection of its content into the GC-injector which has also been modified for gaseous injections.
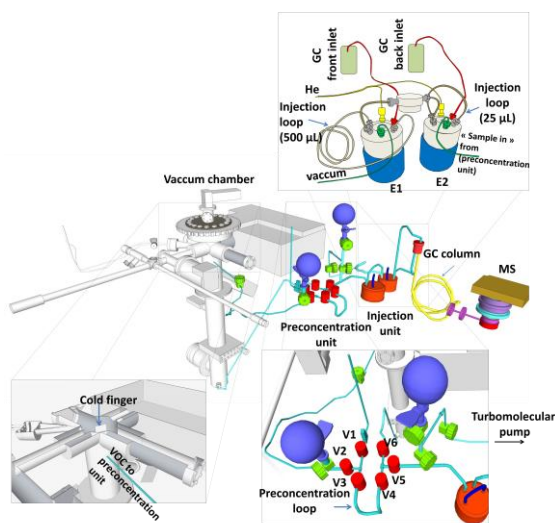

Figure 1: The VAHIIA system for VOC analysis.

3. Summary and Conclusions

Different parameters in both the preconcentration and injection units have been optimized to ensure the best analytical sensitivity. Various preconcentration loop volumes and helium pressures added in the loop for transferring its content to the GC have been tested. The 2.5 mL loop and 100 mbar pressure have been selected. Various injection loop volumes have also been experimented and the best sensitivity is obtained with the 1000 µL loop while maintaining good separation efficiency and chromatographic resolution. Transfer of VOC mixtures from the vacuum chamber to the GC-MS under the selected conditions were successful highlighting the utility and performance of the original developed interface. The GC-MS allowed the detection of trace level compounds in the order of nanomol injected quantity, the separation of compounds present in a mixture (figure 2) and their unambiguous identification, encouraging the use of the system for complex cometary ice analog characterization.
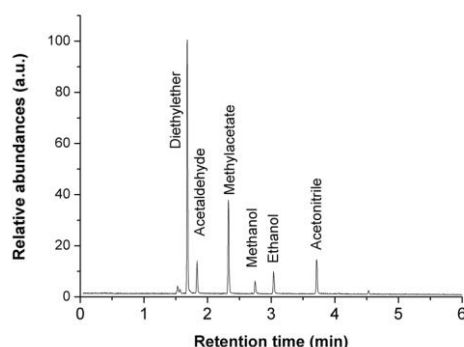

Figure 2: GC-MS chromatogram of a mixture of 6 compounds deposited in the chamber with 4.1 µmol each.

Acknowledgments

References

Abou Mrad et al., 2014 under submission.