

Development of a GC-MS-SPME Method for the Determination of Amines in Meteorites,

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Introduction: Amines are polar, water-soluble organics found in all meteorites that contain amino acids. It has been proposed that meteoritic amines are produced by the thermal decarboxylation of amino acids [1]. The analysis of amines using GC-MS techniques has proven to be problematical owing to the high water solubility and high volatility of these compounds. In addition, the strong interactions of polar amine molecules with the stationary phase of a typical polysiloxane column lead to extensive tailing, poor resolution of peaks and low detector response [2]. To circumvent these disadvantages the highly polar amines have been converted to less polar derivatives that are more amenable to GC analysis by substitution of amine N-H hydrogens with weakly polar moieties such as acyl, silyl, dinitrophenyl and methyl groups [2]. The derivatives of amines generally have much weaker interactions with stationary phases and thus are more volatile in terms of their chromatographic behavior, which leads to better separation on the column. In the last decade base-deactivated columns that give good separations of underivatized aliphatic and aromatic amines have been successfully developed [3]. Consequently, volatile amines in aqueous media can now be routinely and reproducibly analyzed by the combination of SPME (solid-phase microextraction) techniques with base-deactivated GC columns that have been specifically engineered to directly separate amines (see for example [4]). The great advantage of this analytical method is that it sidesteps derivatization, which invariably entails the loss of amines, especially those that are more volatile, through side reactions and incomplete transfer during isolation and workup.

Results and Discussion: An aqueous test solution containing an in-house collection of amine standards, viz. *N*-ethylaniline (100 ppm), dipropylamine (100 ppm), methylamine (100 ppm) and piperidine (100 ppm) was prepared in 80 mL of Millipore water. The majority of this solution (70 mL) was set aside for SPME-GC (CP Volamine) MS analysis while the remaining 10 mL was adjusted to ca. pH = 2 using concentrated HCl to convert all of the amines into their corresponding, non-volatile ammonium salts. The water from this acidified mixture was removed on a rotary evaporator, affording a colourless residue. The solid was dissolved in ca. 3 mL of Millipore water and the pH was brought up to 8 by adding ca. 1 mL of 8 M NaOH(aq). The SPME-GC (CP-Volamine) trace of the reconstituted amine mixture was found to contain the same four amine standards as were seen in solution prior to the protonation step. Thus, this result proves that our amine to ammonium to amine methodology can be used for the direct determination of volatile alkyl amines and aromatic amines. Application of our new SPME-GC (CP-Volamine) MS method to an aqueous extract of a 2-gram sample of the Tagish Lake stone 10a afforded a GC trace that contained three different polar aromatic compounds, namely acetophenone, 4-phenylpyridine and 2-phenyl-1,2-propane diol. In the absence of any isotope ratio data, we cannot conclude whether these three aromatic species are indigenous or terrestrial contaminants. It should be pointed out, however, that acetophenone has been liberated from the Tagish Lake meteorite by the application of heat [5], and thus it does not seem unreasonable to conclude that the acetophenone seen in the trace for 10a likely has an extraterrestrial origin.

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