

Introduction: Development of a new SPME-GCMS Method

In 2008 our group used solid phase microextraction (SPME) methods originally developed by Pawliszyn [1] to determine monocarboxylic acids in meteorite leachates [2].

We have managed to combine sorption of alkyl and aryl amines on an SPME fiber with the direct GC-MS analysis of the unmodified amines on modern columns with high peak-resolving power.

We have used this new technique to identify and quantify polar aromatic species in a water leachate of a chip from the Tagish Lake stone 10a.

Determination of Amines

The Restek corporation has developed base-deactivated columns that give good separations of underivatized aliphatic and aromatic amines [3].

Volatile amines in aqueous media can now be routinely and reproducibly analyzed by the combination of SPME techniques with base-deactivated GC columns that have been specifically engineered to directly separate amines(see for example [4]).

This analytical method sidesteps derivatization, which invariably entails the loss of amines through side reactions and incomplete transfer during isolation and workup.

Results and Discussion

Proof of Concept of the Amine-Ammonium-Amine Cycling Procedure

The MacEwan/UAlberta team succeeded in developing a direct SPME-GC-MS method for amines. The method involved the following steps:

An aqueous test solution containing the in-house collection of amines standards, viz. N-ethylaniline (100 ppm), dipropylamine (100 ppm), methylamine (100 ppm) and piperidine (100 ppm) was prepared in 80 mL of Millipore water.

70 mL was set aside for SPME-GC(CP Volamine)MS analysis while the remaining 10 mL was adjusted to pH = 2 using concentrated HCl(aq) to convert all of the amines into their corresponding, non-volatile ammonium salts.

The water from this acidified mixture was removed, affording a colourless residue. The residue was dissolved in ca. 3 L of Millipore water and the pH was raised 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 (see Figure 2 and Table I).

Thus, the amine to ammonium to amine methodology can be used for the direct determination of volatile amines. The great value of this technique is that it retains volatile amines (as their involatile ammonium salts) that would otherwise be lost along with the water upon concentration or complete evaporation with a rotary evaporator or a vacuum line.

Sampling

A ca. 2 gram subsample of the Tagish Lake specimen 10a was analyzed by our new SPME(PDMS/DVB* or PEG** fibers)-GC(CP-Volamine) method.



Figure 1: Sampling of the Tagish Lake specimen 10a

Use of SPME-GC(CP Volamine)MS Method for the Determination of Amines in the Tagish Lake Sample 10a

Application of our newly proven SPME(PDMS/DVB* or PEG** fibers)-GC(CP-Volamine) method to the aqueous extract of 10a afforded GC traces that contained a collection of four different types of polar aromatic compounds, namely acetophenone, N-ethylaniline, 4-phenylpyridine and 2-phenyl-1,2-propane diol (see Figure 3 and Table II)

No alkyl amines were found in the extract of 10a using the new method. It may simply be that the four aromatic species are present in much higher concentration than the amines and thus the alkyl amine signals do not stand out above the noise. In the absence of any isotope ratio data, we cannot conclude whether these four aromatic species are indigenous or terrestrial contaminants.

Acetophenone, has been liberated from the Tagish Lake meteorite by heating [5], and thus it likely that the acetophenone seen in the trace for 10a likely has an extraterrestrial origin.

(* PDMS/DVB = polydimethylsiloxane/divinylbenzene, ** PEG = polyethylene glycol)

Table I : Amines in the Trial Standards Mixture

Compound Number	Test Amine Standard
-----------------	---------------------

- | | |
|---|----------------|
| 1 | methylamine |
| 2 | dipropylamine |
| 3 | piperidine |
| 4 | N-ethylaniline |

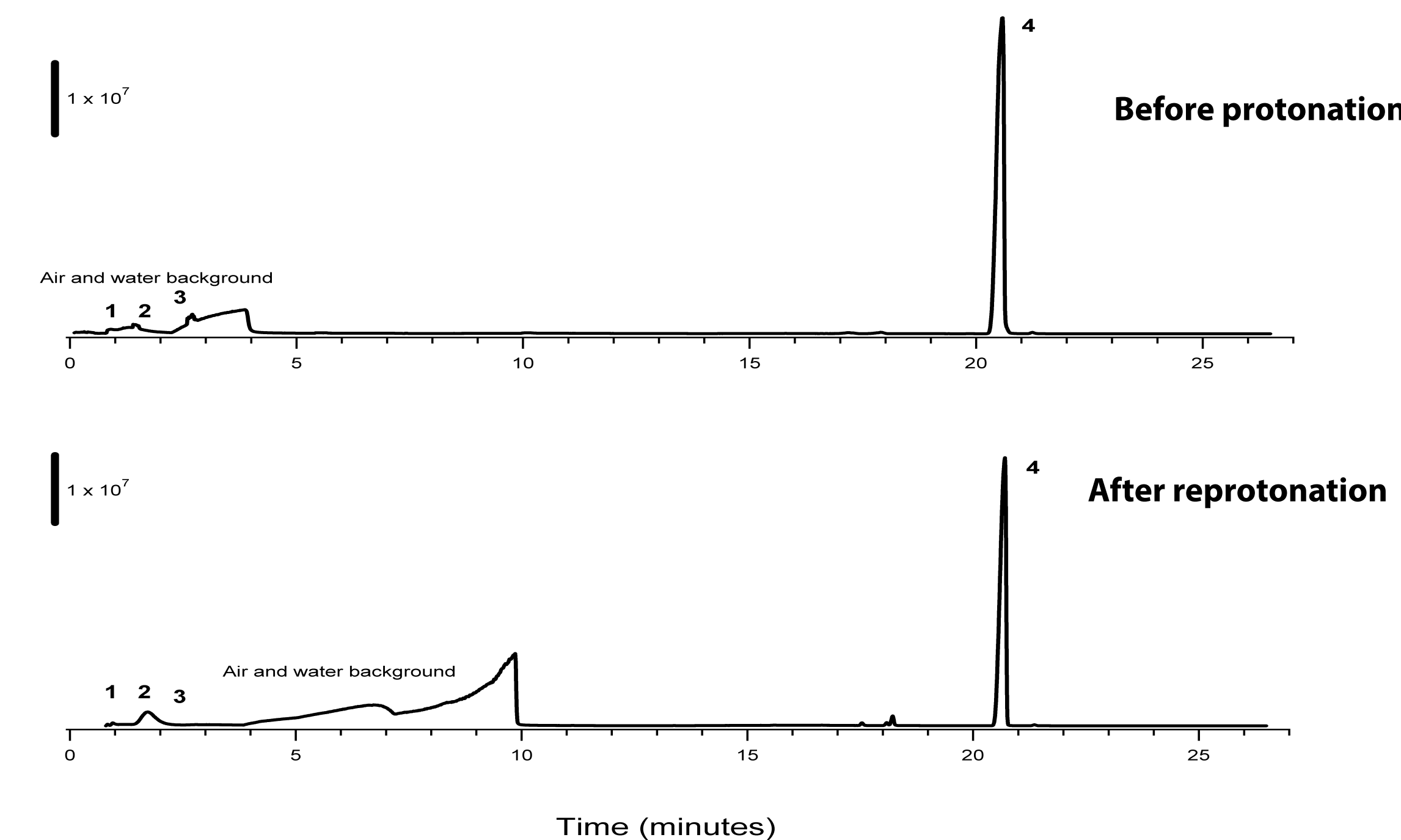


Figure 2: GC traces showing the successful completion of an amine to ammonium to amine cycle performed on an in-house standards mixture.

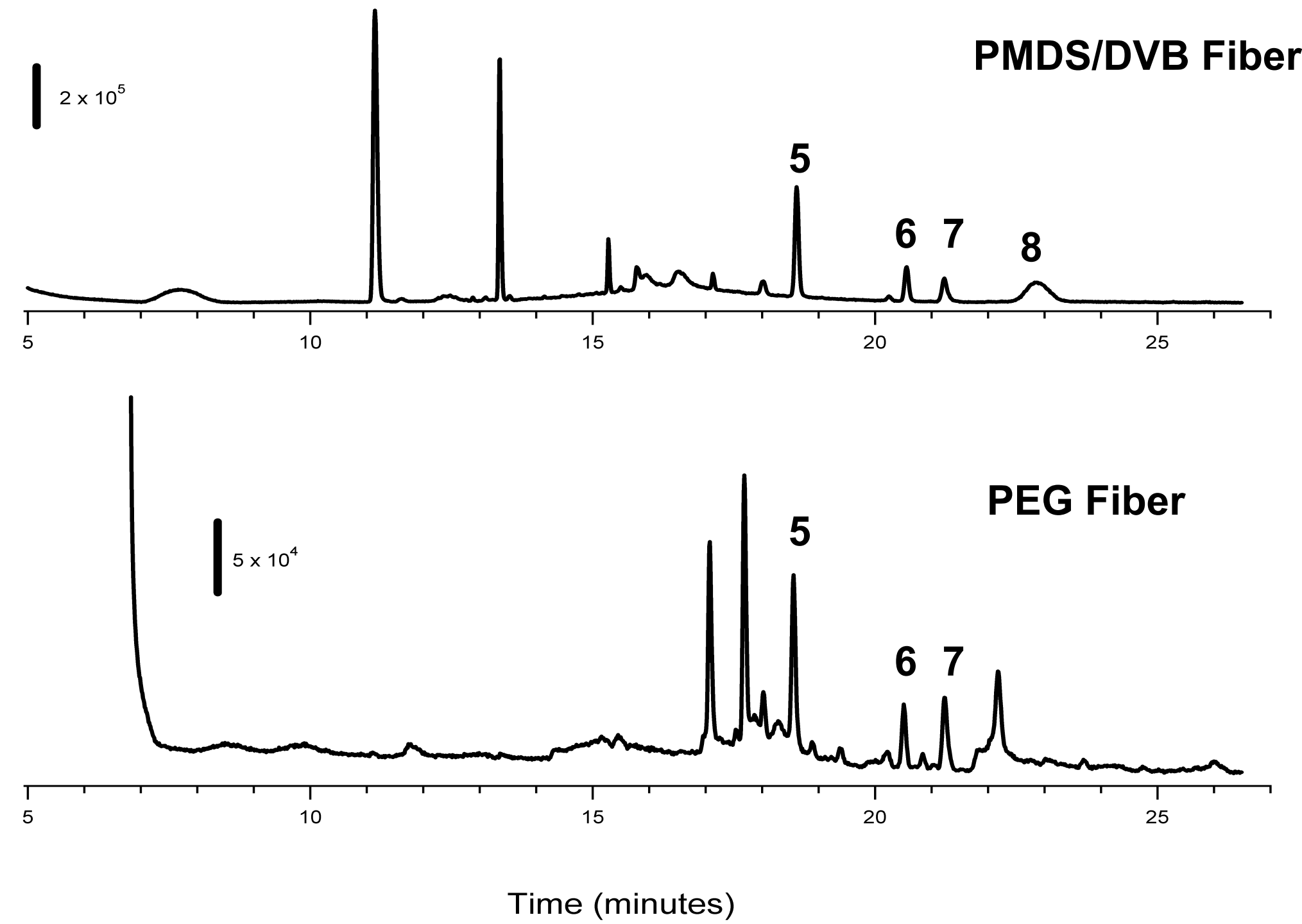


Figure 3: SPME-GC(CP Volamine)MS analyses of the water extract of 10a

Table II: Compounds detected in the aqueous extract of 10a using the SPME –GC(CP Volamines)MS Procedure

Compound	Compound Number
acetophenone	5
N-ethylaniline	6
2-phenyl-1,2-propanediol	7
4-phenyl pyridine	8

Future Work

New subsamples of 10a will be analyzed by our new SPME(PDMS/DVB* or PEG** fibers) -GC(CP-Volamine) method to assess the reproducibility of the method. If it proves to be reproducible, we will apply the method to other stones in the Tagish lake collection.

Acknowledgements

We thank McEwan University for the internal dissemination grant (RH) and the Natural Sciences and Engineering Research Council of Canada for the Discovery Grant 261740-08 (CDK).

References

- [1] “Handbook of Solid Phase Microextraction”, J. Pawliszyn, Elsevier (2011).
- [2] R.W. Hilts et al, LPSC, XL (2009)
- [3] Jaap de Zeeuw et al, Resteck Corp., Bellefonte, USA.
- [4] L. Muller et al, Journal of Chromatography A, 791 (1997), 221-230
- [5] H. Yabuta, G.D. Cody and C.M.O.D. Alexander, LPSC, XXXVIII (2007).