

n-ALKANES ISOLATION FOR COMPOUND SPECIFIC $\delta^{13}\text{C}$ DETERMINATION IN SEDIMENTS AND LEAVES SAMPLES

Milena Ceccopieri^{1,*} (PG), Arthur de Lemos Scofield¹ (PQ), Angela de Luca Rebello Wagener¹ (PQ)

¹Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio)

*E-mail address: milena.ceccopieri@gmail.com

Keywords: n-alkanes, isotopic ratio, UCM, molecular sieves, urea adduction

Introduction

During the last decade, the carbon isotopic analysis of some specific biomarkers have been widely used as a valuable tool for inferring input sources of organic matter. Moreover, they provide important information on the relationship between plant species and the environment in which they developed, supporting the investigation of paleoenvironmental studies.

To achieve more accurate measurements of compound specific $\delta^{13}\text{C}$ by GC-C-IRMS, a good performance during the separation of the chromatographic peaks is essential. In order to determine the specific $\delta^{13}\text{C}$ of n-alkanes from marine sediment samples with a high concentration of UCM and from leaf samples presenting olefinic compounds coeluting with the peaks of interest, methods from the literature were tested to isolate the class of n-alkanes without any losses in the analytical quality of minor compounds or isotopic fractionation during the separation process.

The tested methods include urea adduction^{1,2,3,4} and 5A molecular sieves^{5,6} (without using HF) to remove cyclic and branched compounds; and silica impregnated with AgNO_3 column for removal of n-alkenes. To evaluate quantitatively the possible losses that could occur from the various steps of each procedure, several tests were conducted with a standard mixture of n-alkanes $\text{C}_{12}\text{-C}_{40}$. Quantification was performed by GC-FID before and after the respective tests based on the previous addition of internal standard dC_{24} and a calibration curve.

Results and Discussion

In the 5A molecular sieves method, the highest recovery was achieved by repeating the process three times, increasing the extraction temperature (68 °C, 80 °C and 85 °C, 8 hours each). Combining the three fractions, the recovery was >80% for $\text{C}_{20}\text{-C}_{25}$, but <60% for $\text{C}_{12}\text{-C}_{16}$ and <30% for $\text{C}_{32}\text{-C}_{40}$. In the urea adduction method, the best recovery was obtained when applying a stirring period followed by a cooling period (-4 °C). In this case, recovery was >69% for $\text{C}_{12}\text{-C}_{18}$, >80% for $\text{C}_{19}\text{-C}_{20}$ and >90% for

$\text{C}_{21}\text{-C}_{40}$. Furthermore, the urea adduction method showed no isotopic fractionation when analyzed by GC-C-IRMS, except for n- C_{40} . The silica impregnated with AgNO_3 (10 wt%) column had a recovery >90% for all compounds.

The isolation procedures that showed best results (silica impregnated with AgNO_3 + urea adduction) were applied to the aliphatic hydrocarbon fractions of the sediment samples and the samples were then re-injected into the GC-FID for quantification and verification of possible losses that may have been caused by each method. The same was done for the mangrove leaves, but applying only the AgNO_3 cleanup.

The UCM removal was >90% for all sediment samples. The peaks of n-alkanes that showed coelution in the leaves aliphatic extract were properly isolated, except for the C_{30} for some samples. Significant losses of the compounds of interest were not observed in any of the analyzed samples.

Conclusions

The tests with the n-alkanes standard mixture showed good results for the silica impregnated with AgNO_3 and urea adduction methods. Also, when applied to sediment and leaves samples, no significant losses of the compounds of interest were observed, which makes them ready for further analysis by GC-C-IRMS.

Acknowledgement

CNPq and LABMAM.

¹ Nwadinigwe, C. A.; Nwobodo, I. O. *Fuel*. **1994**, *73*, 779-782.

² Lappas, A. A.; Patiaka, D.; Ikononou, D.; Vasalos, I. A. *Ind. Eng. Chem. Res.* **1997**, *36*, 3110-3115.

³ Ellis, L.; Fincannon, A. L. *Organic Geochemistry*. **1998**, *29*, 1101-1117.

⁴ Yamamoto, S.; Kawamura, K. *Intern. J. Environ. Anal. Chem.* **2012**, *92*, 302-312.

⁵ Tolosa, I.; Ogrinc, N. *Journal of Chromatography A*. **2007**, *1165*, 172-181.

⁶ Grice, K.; Mesmay, R.; Glucina, A.; Wang, S. *Organic Geochemistry*. **2008**, *39*, 284-288.