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ANALYSIS OF PHYTOL, ALCOHOLS, CUTIN ACIDS AND STEROLS IN MARINE AND LAKE SEDIMENTS BY ON-LINE TMAH/THERMOCHEMOLYSIS GC-MS

Shuichi YAMAMOTO[1] and Ryoshi ISHIWATARI[2]

1. Faculty of Engineering, Soka University, Tangicho 1-236, Hachioji, Tokyo 192-8577, Japan;
2. Geotec Inc., Takaido-nishi 3-16-11, Suginami, Tokyo 168-0071, Japan.

On-line TMAH/thermochemolysis GC-MS analysis (TMAH method) consists of thermally-assisted hydrolysis and *in situ* methylation with tetramethyl ammonium hydroxide (TMAH) reagent. We have previously reported a rapid analytical method of lignin phenols and alkanoic acids for small amount of sediment sample (Yamamoto and Ishiwatari, 2005). We report here the result of examining an optimum condition for analyzing compounds with hydroxyl group (e.g. alcohols, sterols etc.) in a sediment sample using TMAH reagent.

A Curie point pyrolyzer (used as a TMAH reaction chamber) directly connected to GC-MS instrument was used in this study. We examined an influence of TMAH reaction temperatures on the yield of derivatization of compounds with hydroxyl group. We used marine (offshore California) and lake (Lake Baikal) sediments for this study. Typically, 5-7mg of dry fine powdered sediment sample is placed in a pyrofoil (ferromagnetic plate) and 20μl of a 25% TMAH methanol solution and internal standard (e.g. *n*-C_{19} fatty acid) was added. After methanol was evaporated to dryness, the pyrofoil was set into the pyrolyzer and heated at various temperatures (315, 358, 445, 500, 590, 670°C) for 20 seconds. The TMAH products were analyzed by GC-MS.

Major TMAH reaction products from the sediment are phytol methyl ether (plus its underivative), cutin acid derivatives, *n*-alcohol methyl ethers (plus their underivatives), sterol methyl ethers and *n*-$C_{22:1}$ amide (plus *N*-methyl and *N*,*N*-dimethyl derivatives), other than *n*-C_{18}-C_{30} fatty acids methyl esters (Fig. 1). A possible source of 11,18-diOH C_{18} acid is marine organisms (Yamamoto et al., 1992). The other compounds are typical biomarkers, e.g., phytol from chlorophyll from phytoplankton, *n*-$C_{22:1}$ and *n*-$C_{24:1}$ alcohols and *n*-$C_{22:1}$ fatty acid from zooplankton or shrimp (e.g., Yunker, et al. 1995). 9, 16- or 10, 16-diOH C_{16} acid from cuticle of leaves (e.g., Gôni and Hedges 1990), cholesterol from zooplankton or algae, brassicasterol from diatoms, and dinosterol from dinoflagellate (e.g., Volkman 1986).

The yields of all compounds are apparently high at TMAH reaction temperatures of 315-445 °C as compared with higher temperatures (>500 °C) (Fig. 2). At higher reaction temperatures, the amounts of underivatized compounds for phytol and *n*-$C_{22:1}$ alcohol are high. Therefore, the optimum TMAH reaction temperature is concluded to be 315-445 °C for phytol, fatty alcohols, sterols and cutin acids, in so far as the present reaction system is concerned. The maximum amounts of sterols obtained by this TMAH method at 358 ℃ are considerably higher than those obtained by a solvent extraction method (2.0-7.3μg/g-ds vs. 1.7 -3.8μg/g-ds for offshore California sediments).

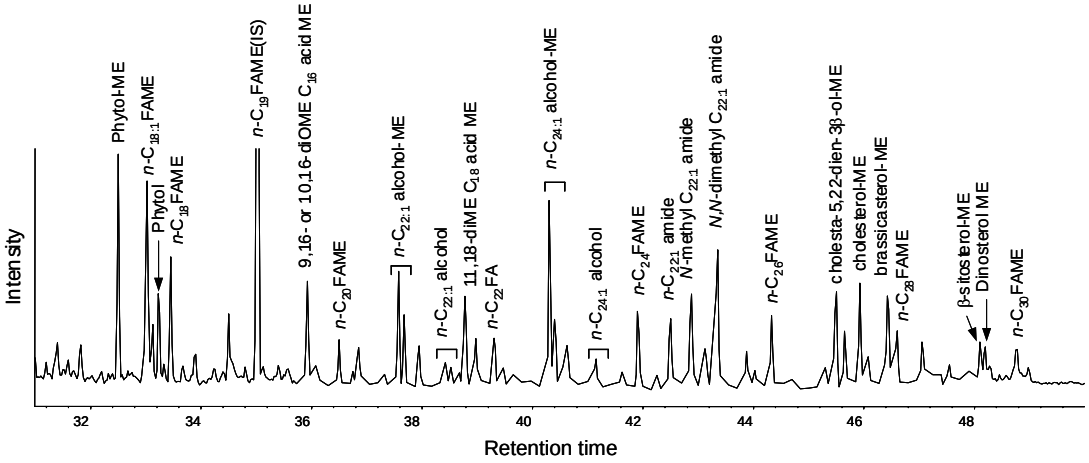

Figure 1. Total ion chromatograms (TIC) and the major organic compounds produced by the on-line TMAH/thermochemolysis from the California offshore sediment. Abbreviation: FAME: fatty acid methyl ester, n:carbon number, IS:internal standard, ME: methyl ether and methyl ester derivatives.

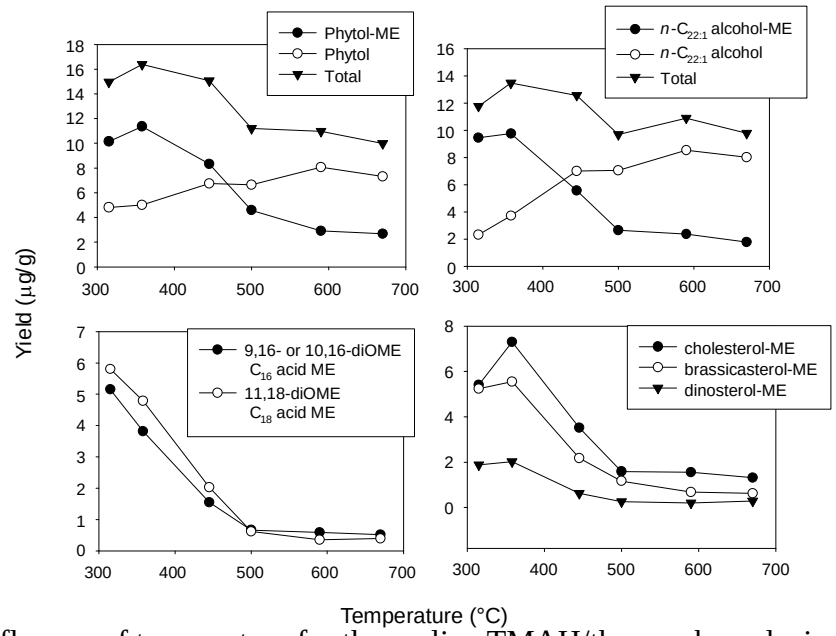

Figure 2. Influence of temperature for the on-line TMAH/thermochemolysis on the yields of phytol, *n*-$C_{22:1}$ alcohol, cutin acids and sterols from the marine sediment. ME indicates methyl ether and methyl ester derivatives.

REFERENCES

Gôni M.A. and Hedges J.I. (1990) *Geochimica et Cosmochimica Acta,* **54**, 3065-3072.
Volkman J.K. (1986) *Organic Geochemistry,* **9**, 83-99.
Yamamoto S. and Isihwatari R.(2005). *IMOG 2005 Abstract*, **2**, 953-954.
Yamamoto S. et al. (1992) *Umino-Kenkyu*, **1** , 329-342 (in Japanese).
Yunker M.B. et al. (1995) *Marine Chemsitry*, **49**, 1-50.