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Unexpected peaks in mass spectra of trimethylsilyl derivatives resulting from the presence of trace amounts of water and oxygen in GC-QTOF systems

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Silylation is one of the most prevalent derivatization method. Replacement of active hydrogen (in -OH, -SH or =NH groups) by a silyl group reduces the polarity of the compound and hydrogen bonding¹. Electron ionization (EI) mass spectra of trimethylsilyl ethers or esters exhibit a significant $[M - 15]^+$ ion formed by loss of a methyl group bonded to silicon, which is very useful in determining the molecular mass. EI mass spectra of trimethylsilyl (TMS) derivatives may be employed not only for molecular weight determinations, but also for structural deductions.² They are generally stable during GC-MS analyses, although contamination of the mass spectrometer source with organic substances has been reported to cause some decomposition.³ Moreover, it may be noted that if the amount of water is too high

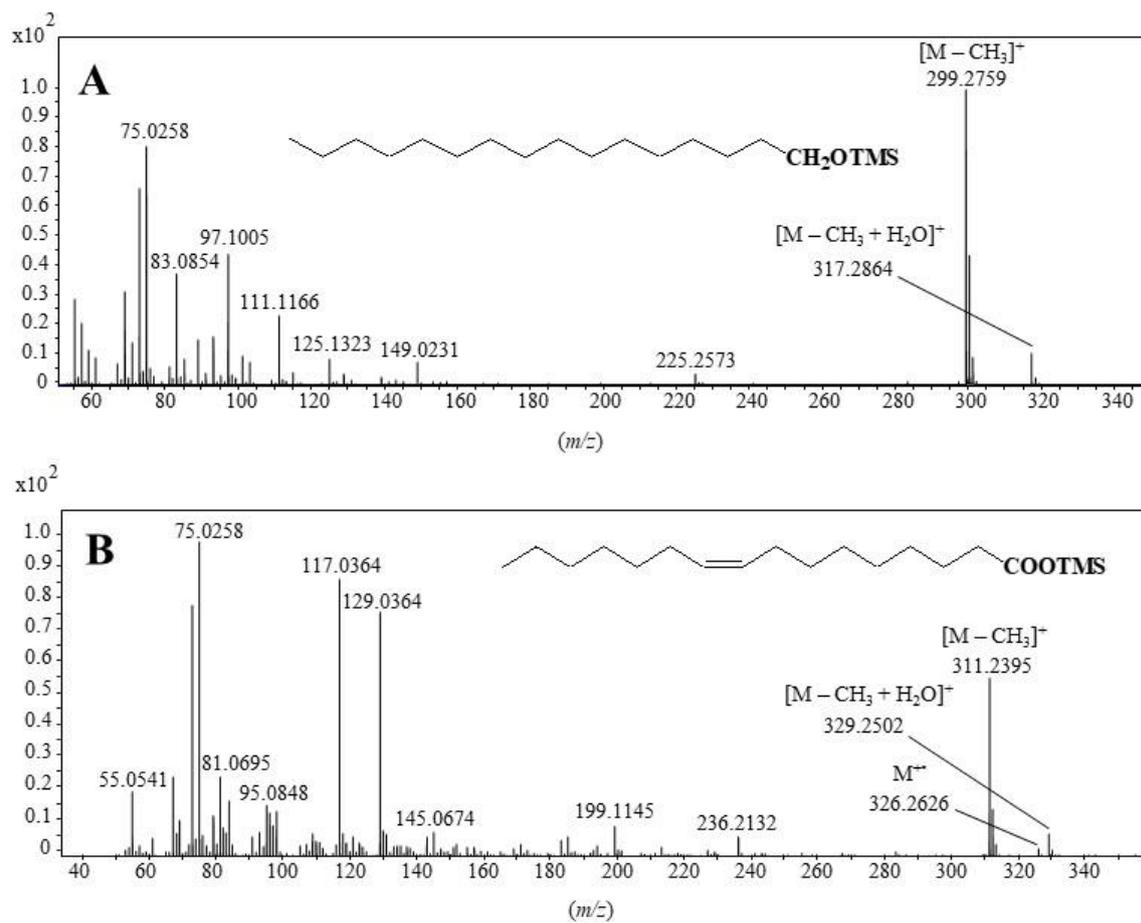


FIGURE 1 TOF mass spectra of TMS derivatives of hexadecan-1-ol (A) and hexadec-9-enoic acid (B) showing the presence of $[M - CH_3 + H_2O]^+$ ions.

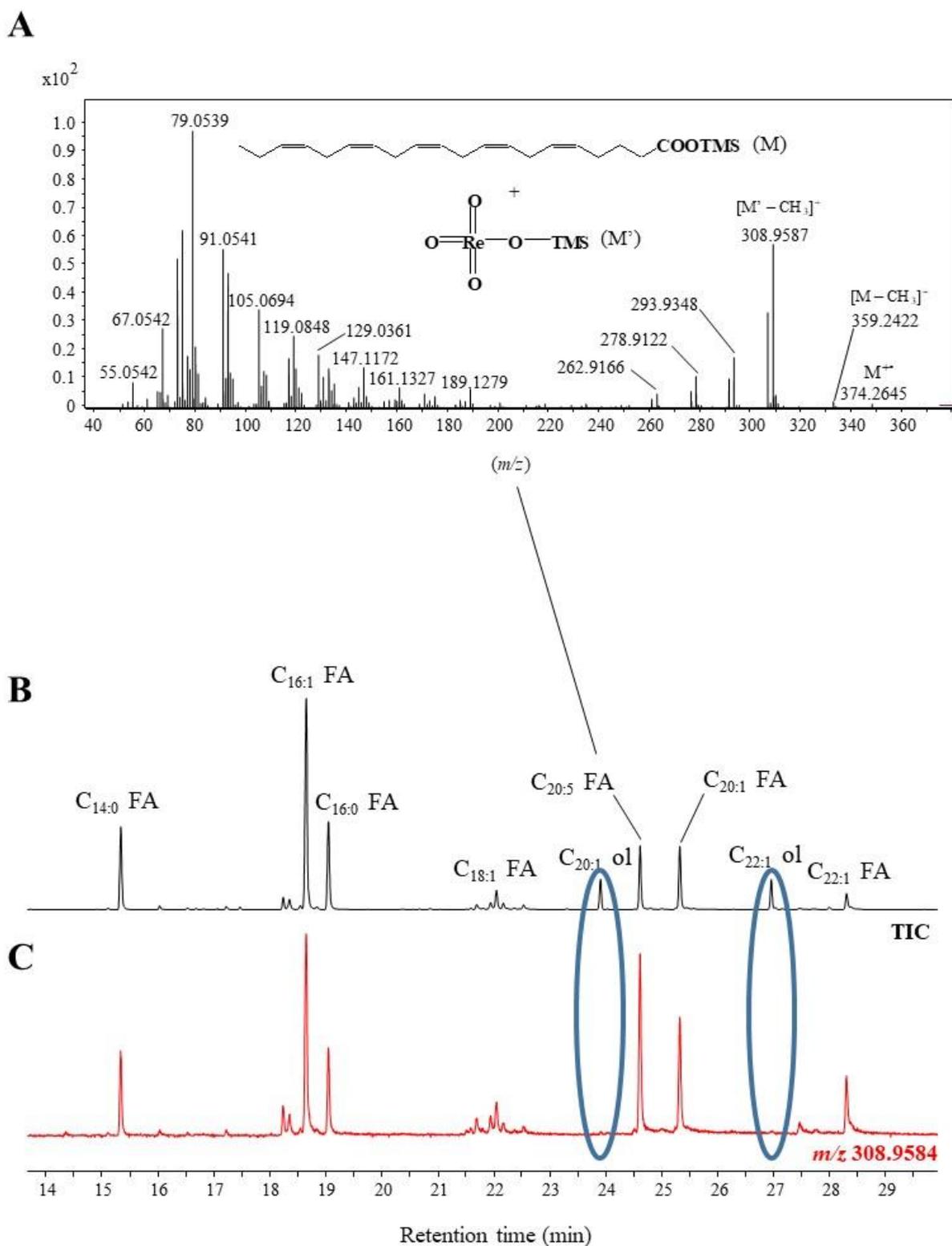
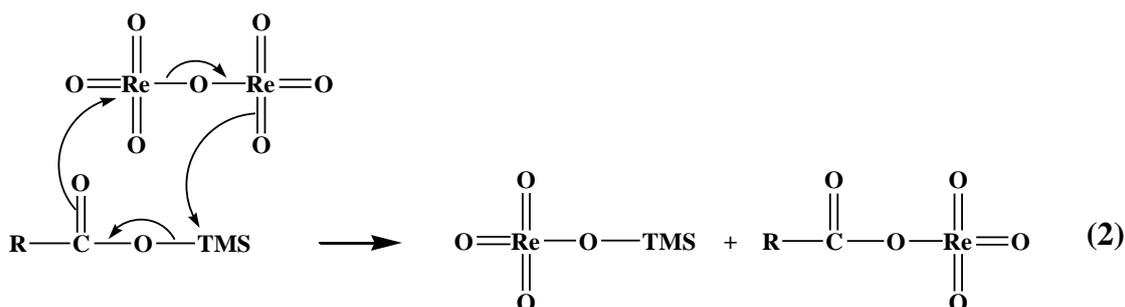


FIGURE 2 TIC chromatogram (B) and mass chromatogram of m/z 308.9584 (C) of silylated total lipid extract obtained from sea ice (0-3 cm) collected in Baffin Sea (Canadian Arctic) during summer 2016. The TOF mass spectrum of the $C_{20:5}$ fatty acid TMS derivative obtained after subtraction of background and exhibiting intense trimethylsilyl perrhenate fragment ions is also shown (A).

The presence of traces of oxygen in the carrier and collision gas or a leak at the junction of the capillary column and the mass spectrometer may induce the attack of filaments and result to the formation of the well-known Rhenium oxide Re_2O_7 .⁶ This oxide is converted to TMS perrhenate ($\text{ReO}_4\text{Si}(\text{CH}_3)_3$) ($M = 323.9823$ and 321.9794 for ^{187}Re and ^{185}Re , respectively) by reaction with silylating reagents.⁷ Its fragmentation affords fragment ions at m/z 308.9584 and 306.9551 $[\text{M} - \text{CH}_3]^+$, 293.9343 and 291.9321 $[\text{M} - 2\text{CH}_3]^+$ and 278.9111 and 276.9088 $[\text{M} - 3\text{CH}_3]^+$. The presence of such fragment ions in the baseline of mass chromatograms is thus indicative of the presence of oxygen in the system and an alteration of filaments.

During GC-QTOF analyses of silylated natural lipid extracts, we could observe that the abundance of fragment ions of TMS perrhenate increased strongly under the peaks of silylated fatty acids (TMS esters) (Figure 2C). This increase was attributed to a reaction of Re_2O_7 in the source not only with the silylating reagent but also with TMS esters (Equation 2). The lack of reaction observed in the case of TMS ethers (Figure 2C) well supports the involvement of the proposed concerted mechanism (Equation 2).



The detection of such fragment ions in TOF mass spectra of TMS esters, which is indicative of the presence of oxygen in the system, should be considered as alarming. Indeed, it indicates a deterioration of filaments, a possible accumulation of Re_2O_7 in the source (mainly at the level of the entrance lens) and a non-negligible desilylation of fatty acid TMS derivatives. It could also result to misinterpreting of mass spectra particularly in the case of polyunsaturated TMS esters exhibiting very weak molecular and $[\text{M} - \text{CH}_3]^+$ peaks (Figure 2A).

In conclusion, we showed that the presence of traces of water in the collision gas may induce the appearance of unexpected peaks corresponding to $[\text{M} - \text{CH}_3 + \text{H}_2\text{O}]^+$ in mass spectra of TMS derivatives. The reaction with water can change the relative abundances of $[\text{M} - \text{CH}_3]^+$ fragment ions and lead to formation of product ions which cannot be formed directly from the original compound. The presence of traces of oxygen results to an alteration of filaments affording Re_2O_7 , which can react with TMS esters in the ion source producing hindering TMS

perrhenate. These observations should be useful for researchers who deal with GC-QTOF analysis of TMS derivatives.

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REFERENCES

1. Pierce AE. *Silylation of Organic Compounds*; Pierce Chemical Co.: Rockford, IL; 1982.
2. Goad LJ, Akihisa T. *Analysis of Sterols*; Blackie Academic and Professional: London; 1997.
3. Sobolevsky TG, Chernetsova ES, Revelsky AI, Revelsky IA, Starostin AB, Miller B, Oriedo V. Electron ionization mass spectra and their reproducibility for trialkylsilylated derivatives of organic acids, sugars and alcohols. *Eur J Mass Spectrom* 2003; 9: 487-495.
4. Neta P, Farahani M, Simon-Manso Y, Liang Y, Yang X, Stein SE. Unexpected peaks in tandem mass spectra due to reaction of product ions with residual water in mass spectrometer collision cells. *Rapid Commun Mass Spectrom* 2014; 28: 2645-2660.
5. Tuytten R, Lemière F, Van Dongen W, Esmans EL, Witters E, Herrebout W, Van Der Veken B, Dudley E, Newton RP. Intriguing mass spectrometric behavior of guanosine under low energy collision-induced dissociation: H₂O adduct formation and gas-phase reactions in the collision cell. *J Am Soc Mass Spectrom* 2005; 16: 1291-1304.
6. Kaoumi D. Investigations of the chemical compatibility of rhenium with uranium dioxide at elevated temperatures. PhD Thesis, University of Florida; 2001.
7. Schmidbaur H. Trimethylsilyl perrhenate - A nonionic reagent soluble in organic solvents for the preparation of perrhenates, In: *Efficient methods for preparing silicon compounds*, Academic Press, 2016; 21-25.