

MASS SPECTROMETRIC STUDIES OF SEMIFLUORINATED N-ALKANES USED IN SKI WAXES

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Introduction

Highly fluorinated compounds like perfluorinated carboxylates (PFCAs) are studied with major interest due to their ubiquitous distribution in the environment and toxicological effects. This study looked at other fluorinated substances, namely semifluorinated *n*-alkanes (SFAs). These exist as di-block and tri-block SFAs, with the general formulas $\text{CF}_3\text{-(CF}_2\text{)}_n\text{-(CH}_2\text{)}_m\text{-CH}_3$ and $\text{CF}_3\text{-(CF}_2\text{)}_n\text{-(CH}_2\text{)}_m\text{-(CF}_2\text{)}_k\text{-CF}_3$, respectively, with n and $k = 1 - 15$ and $m = 13 - 17$, hereafter abbreviated as F_nH_m and $\text{F}_n\text{H}_m\text{F}_k$. SFAs are produced from perfluoroalkyl iodide and an olefin^{1,2}. Depending on the way of preparation, SFAs contain a lot of by-products and cannot easily be purified¹. SFAs are used in ski waxes due to their water and dirt repellence. Moreover they are also applied in medicine, especially in ophthalmology.

So far nothing is known about the environmental fate and distribution of SFAs after abrasion from ski bases onto the snow surface. It is unknown if they stay in the snow until the last melt, sorb to the soil or even volatilize from the snow surface and are transported via air. Based on their molecular structure, it can be suspected that they might be degraded to PFCAs, in analogy to fluorotelomer alcohols³.

In order to investigate the environmental behavior of SFAs, analytical methods based on gas chromatography coupled to mass spectrometry (GC-MS) have been developed. Only one study exists so far about SFAs and their mass spectral characteristics in electron ionization (EI)-MS⁴. Nothing is known about their behavior in electron capture negative ionization (ECNI) and their retention in GC. In this study, EI and CI mass spectra of SFAs found in four different ski waxes and a standard mixture employed in the production of ski waxes are investigated and fragmentation patterns are discussed.

Materials and Methods

Chemicals:

Four different ski waxes from three brands (Ski-go: Newsnow High Fluor and Ultima Low Fluor; Swix: Cera Nova LF4; Toko: Dibloc Low Fluoro yellow) and a standard of a SFA mixture (kindly provided by the ski wax manufacturer Rex, Finland) were analyzed. Samples were dissolved qualitatively in cyclohexane (Suprasolv, Merck) and methyl-*tert*-butyl-ether (MTBE, for HPLC, Rathburne).

Instrumentation:

A HP5890A gas chromatograph (Agilent Technologies) was coupled to a Finnigan TSQ 7000 triple quadrupole mass spectrometer (Thermo Scientific). A volume of 1 μL of standard solution was injected in splitless mode onto a DB5-MS capillary column (15 m; i.d. 0.25 mm; 0.10 μm film thickness, Agilent JW Scientific). Helium was used as carrier gas (1.4 mL min^{-1}) and ammonia was used as reagent gas (7000 mTorr) for ECNI studies. The injector temperature was set to 200 °C and the column temperature gradient was started at 80 °C (hold time 2 min), ramped with 30 °C min^{-1} up to 315 °C and held at 315 °C for 5 min. The transfer line was set to 300 °C and the ion source temperature was varied from 100 to 200 °C. The electron energy was 70 eV for both ECNI and EI.

Results and Discussion

Solvent tests showed that both the SFA mixture and the ski waxes were soluble in cyclohexane as well as in MTBE, although dissolving the ski waxes in MTBE led to particles in the solution. These might have arisen from the excess of paraffins present in the waxes, exceeding their solubility in MTBE. Solutions of ski waxes were centrifuged and

the supernatant was analyzed. The compounds detected in EI and ECNI spectra of all investigated samples were tentatively identified as di-block SFAs by means of the mass-to-charge ratio (m/z) of the molecular ion, the relative intensity of the $M+1$ isotope signal and comparison with mass spectra from other studies (see below). Signals for F_6H_{16} , $F_{10}H_{16}$, $F_{12}H_{16}$, $F_{14}H_{16}$ and $F_{16}H_{16}$ showed highest abundances in the full scan MS spectra. With much lower intensities F_8H_{16} , $F_{10}H_{14}$ and $F_{12}H_{14}$ and only in the ski wax Newsnow High Fluoro from Ski-go some $F_{10}H_{18}$, $F_{12}H_{18}$ and $F_{14}H_{18}$ could be detected. These latter compounds could be impurities resulting from the production process¹. There might have been even longer chain compounds present, but the scan range of the mass spectrometer did not exceed m/z 1100. The di-block SFAs present in all four tested ski waxes were found in different absolute quantities depending on the wax. However, the relative intensities of signals from different compounds were very similar in all ski waxes and the SFA mixture. In the ski waxes a lot of other signals were detected, most probably corresponding to paraffins of chain lengths between 20 and 34 carbon atoms. F_6H_{16} showed comparable abundance to the other F_nH_{16} compounds (except F_8H_{16}) in EI, but in ECNI its intensity is much lower. The ionization efficiency in ECNI, and thus the response, probably is a function of the number of fluorine atoms in the molecule. F_8H_{16} is barely detectable in EI and cannot be found in ECNI, suggesting that it is an impurity from the production process.

The mass spectra in EI mode showed exactly the same fragmentation pattern as described by Napoli et al. for SFAs with shorter chain lengths⁴. Figure 1 shows EI-MS full scan mass spectra of three different SFAs. In figure 1a) the whole mass-to-charge scale of the spectrum of F_6H_{16} is depicted, showing sequential losses of CH_2 -groups in the high mass range and the fragments of the hydrocarbon part of the molecule in the low mass range. The intensity of the hydrocarbon fragment ions is much higher than for the fragments resulting from the perfluorinated part of the molecules. This might be explained by the stability of the C-F bond, making the fluorinated part stable against fragmentation, and the high electronegativity of fluorine, which rather favors formation of negative than positive ions. Napoli suggested that SFAs form a pseudo-six-membered ring by interaction between fluorine and hydrogen⁴. Therefore the most abundant ions are the ones with the intact perfluorinated chain plus $-(CH_2)_n^+$ with $n = 5 - 7$. Fluorinated fragment ions like $C_2F_5^+$ and $C_3F_7^+$ with m/z values of 119 and 169, respectively, were present in the spectra, but showed very low relative intensities of usually 0.2 to 4%. With decreasing ion source temperature less fragmentation was observed and at 150 °C or below also the molecular ion M^+ was detected.

Tests using positive chemical ionization did not show any ions, which again can be explained by the high electronegativity of fluorine. However, applying ECNI the molecular ion M^+ and fragments resulting from sequential HF losses were observed as illustrated in figure 2. HF elimination was also reported in a metastable ion study using mass-analyzed ion kinetic energy (MIKE) spectroscopy⁴. Relative abundances of the fragment ions observed in the spectra shown in figure 2 are presented in table 1. Depending on the perfluorinated carbon chain length the $[M-6HF]^+$ or $[M-4HF]^+$ fragment ion showed the highest relative abundance next to the molecular ion. Lowering the temperature of the ion source led to an enhancement of the relative intensity of the molecular ion. This effect was more pronounced with increasing perfluorinated chain length. This might be due to higher stability of the compounds with a longer chain length. However, at the same time the relative intensity increased, the absolute intensity decreased with decreasing ion source temperature. In general, the molecular ions of the investigated di-block SFAs were detected with better sensitivity by ECNI-MS compared to EI-MS.

The optimized parameters of the GC-ECNI-MS method will be used to develop analytical methods for investigation of SFAs in environmental samples. A single ion monitoring (SIM) approach will be chosen with typically the molecular ion as quantifier and the most abundant fragment as qualifier ion. ECNI is preferred over EI due to the better sensitivity and selectivity, which could be a great benefit in the presence of environmental matrix compounds.

References:

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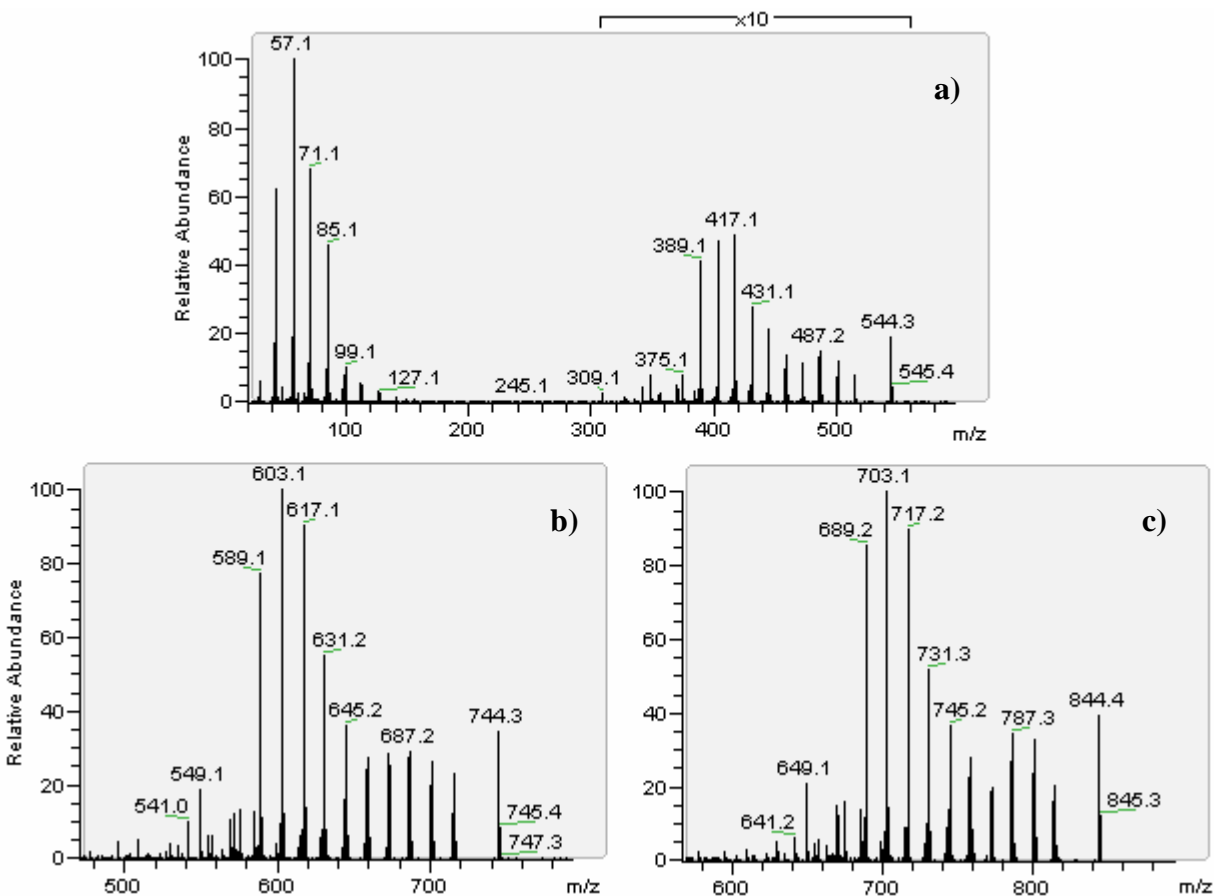


Figure 1: EI full scan mass spectrum of a) F_6H_{16} and details of the EI spectra of b) $F_{10}H_{16}$ and c) $F_{12}H_{16}$ using an ion source temperature of 150 °C.

Table 1: Relative intensities in % of the fragment ions of F₆H₁₆, F₁₀H₁₆ and F₁₂H₁₆ in ECNI full scan spectra applying different ion source temperatures. For spectra see figure 2.

Fragment ion	F ₆ H ₁₆				F ₁₀ H ₁₆				F ₁₂ H ₁₆			
	m/z	Ion source temperature			m/z	Ion source temperature			m/z	Ion source temperature		
		200°C	150°C	100°C		200°C	150°C	100°C		200°C	150°C	100°C
M ⁻	544	-	-	12	744	0.3	76	100	844	4	100	100
[M-HF] ⁻	524	-	-	-	724	-	2	6	824	1	4	4
[M-2HF] ⁻	504	-	-	-	704	12	27	27	804	13	20	8
[M-3HF] ⁻	484	4	6.1	26	684	37	67	31	784	29	49	11
[M-4HF] ⁻	464	12	71	100	664	100	100	42	764	100	66	13
[M-5HF] ⁻	444	17	66	15	644	60	75	38	744	47	22	7
[M-6HF] ⁻	424	100	100	9	624	36	36	12	724	25	14	3
[M-7HF] ⁻	404	19	4	-	604	18	10	1	704	12	3	0.2

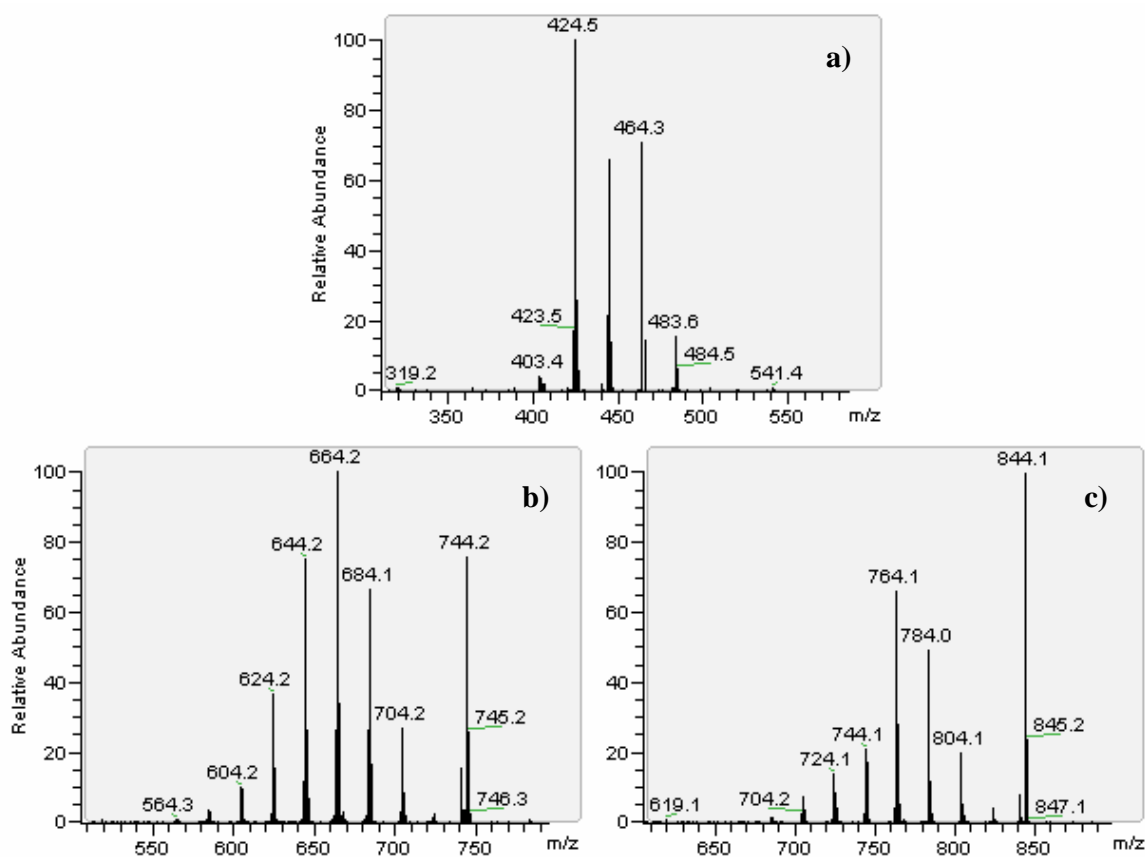


Figure 2: Details of the ECNI full scan mass spectra of a) F₆H₁₆, b) F₁₀H₁₆ and c) F₁₂H₁₆ using an ion source temperature of 150 °C. See table 1 for relative intensities of fragment ions.