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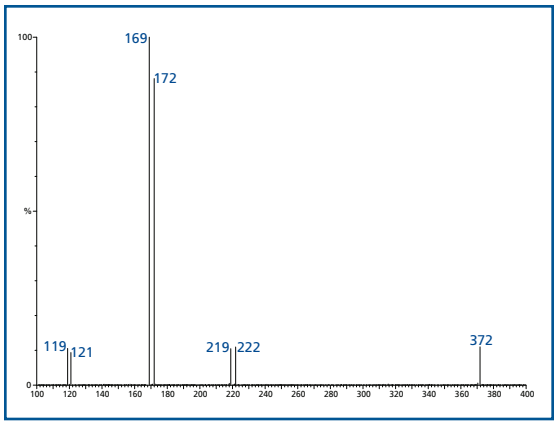
Perfluoroalkyl Anion Fragmentation Pathways



It is well known that, under LC/ESI-MS/MS conditions, the primary fragmentation of perfluorocarboxylates ($[R_fCO_2]^-$) is loss of CO_2 to give a perfluoroalkyl anion (R_f^-). It has also been generally accepted that subsequent fragmentation (secondary, tertiary, etc.) of R_f^- involves cleavage of the C_nF_{2n} segments through loss of carbene ($:CF_2$) or tetrafluoroethylene (C_2F_4) units. However, our observation of *double signals* resulting from secondary fragmentation of the perfluoroalkyl anion of $^{13}C_4$-PFOA resulted in a re-evaluation of the accepted fragmentation pathways.

In an attempt to explain these *double signals*, a mechanism involving rapid fluorine migration along the perfluoroalkyl chain prior to fragmentation was proposed.