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On-line measurements of multiple alkanes by chemical ionization mass spectrometry using NO^+ as the reagent ion

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Proton transfer reaction mass spectrometry (PTR-MS) is a technique that allows for fast and sensitive measurement of volatile organic compounds (VOCs) at trace levels in air. Proton transfer is an example of chemical ionization: it enables soft ionization of chemical species that have a proton affinity (PA) higher than that of the reagent species (i.e., water):

H_3O^+ + VOC ->VOC?H^+ + H_2O (1)

Unlike gas chromatography, PTR-MS does not require any sample treatment such as drying and/or preconcentration, which makes possible quantitative measurement of alkenes (except ethylene), aromatics, and even oxygenated VOCs. However, the proton transfer in reaction (1) does not occur for alkanes because they have lower PAs than water. Very recently, a method to measure C_{12}-C_{18} alkanes using PTR-MS was demonstrated. They were, however, detected by a series of fragment ions with formula C_nH_{2n+1} and were detected not individually, but as an ensemble.

Reactions of alkanes with NO^+ have been investigated by selected ion flow tube mass spectrometry (SIFT-MS). It was reported that hydride ion transfer is a major channel in the reaction of alkanes (RH) with NO^+.

NO^+ + RH ->R^+ + HNO (2)

Recently, the PTR-MS instrument has been combined with switchable reagent ion capability, which allows for easy and fast switching between H_3O^+ and NO^+ (proton-transfer-reaction *plus* switchable reagent ion mass spectrometry (PTR + SRI-MS)).

In the present study, the detection properties of alkanes by PTR + SRI-MS are investigated. We confirmed that alkanes (RH) were usually detected as R^+ by PTR + SRI-MS using NO^+ as the reagent ion and detection sensitivities were comparable to those of aromatics observed by H_3O^+ ionization. We also demonstrated time-resolved measurements of C_4-C{16} alkanes in automotive exhaust during the Japanese JC08 transient cycle. It can be concluded that sensitive on-line measurement of multiple alkanes is possible by PTR + SRI-MS using NO^+ as the reagent ion.

Keywords: PTR-MS, alkane, NO^+ chemical ionization, Gasoline vehicle, Diesel vehicle, Exhaust gas