Development and application of C and N isotope analysis in investigating alkaline hydrolysis mechanism of 2,4-dinitroanisole

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Compound specific isotope analysis combined with ultrasound assisted liquid-liquid extraction (USALLE) method was developed and validated for determining carbon and nitrogen isotope compositions in 2,4-dinitroanisole (DNAN). USALLE was modified and performed as described in previous research [1]. The efficiency of USALLE for DNAN in liquid samples is 94.3% ± 2.6%. Method detection limits (MDLs) were determined according to the moving mean procedure [2]. The MDLs of C and N isotope analysis in DNAN are 150ng and 2000ng, respectively, with precision of $\delta^{13}C$ and $\delta^{15}N$ values of ±0.3‰ and ±0.5‰.

The kinetics and mechanisms of alkaline hydrolysis of DNAN have been investigated by complementary experimental kinetic measurements and molecular modeling calculations, which implied that methyl group abstraction is one of the suggested pathways of DNAN transformation during alkaline hydrolysis [3-5]. In present research, isotope analysis of C and N was applied to determine the isotopic enrichment factors ($\varepsilon^{13}C$ and $\varepsilon^{15}N$) during alkaline hydrolysis of DNAN, which provides valid evidence for verifying the pathway(s) of this specific abiotic transformation. Alkaline hydrolysis of DNAN in water was a pseudo-first-order reaction with a kinetic rate constant of 24.63±0.09. The ^{13}C enrichment via the alkaline hydrolysis of DNAN ($\varepsilon^{13}C$) was -7.54‰ ± 0.24‰. The corresponding value for ^{15}N enrichment ($\varepsilon^{15}N$) was -2.76±0.12‰. 2,4-Dinitrophenol (2,4-DNP) was identified as the terminal product in alkaline hydrolysis of DNAN. A complete discussion will be done after we finish the calculation of position-specific C and N isotope fractionation factors in DNAN. Future work will focus on deciphering other abiotic and biotic transformation pathways of DNAN in groundwater and soil-groundwater systems by C and N isotope analysis.

[1] Khezeli et al. (2016) *Talanta* **150**, 577–585. [2] Jochmann, et al. (2006) *Rapid Commun. Mass Spectrom* **20**, 3639-3648. [3] Salter-Blanc, et al. (2013) *E S&T* **47**, 6790–6798. [4] Sviatenko, et al. (2014) *E S&T* **48**, 10465–10474. [5] Zhou et al. (2018) *J Mol Model* **24**, 44.