Thermodesorption/Pyrolysis (TD/Py)-DART – Orbitrap MS for the characterization of fluoropolymers in environmental matrices

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Résumé

Direct analysis in real time (DART) coupled with high-resolution mass spectrometry (HRMS) provides valuable insights into the chemical structure of fluoropolymers, including the determination of repeat unit(s), end-groups, and the identification of additives (1). However, DART is primarily effective for small oligomers, as its desorption/ionization efficiency favors the most volatile compounds. Furthermore, it is not well-suited for directly analyzing powdery samples, such as soils contaminated with polymers. To address these limitations, DART can be coupled with a thermodesorption/pyrolysis (TD/Py) device (2), enabling more comprehensive fluoropolymer characterization and improving sensitivity, particularly in complex environmental matrices.
A sand sample spiked with 2% (w/w) polyvinylidene fluoride (PVDF) was investigated using TD/Py-DART Orbitrap mass spectrometry in negative ion detection mode. The sample was heated from 35 to 600 ∘C at a rate of 100 ∘C.min-1 and held at 300 ∘C for 2 minutes. Kendrick plots were used to visualize the complex mass spectra obtained, and the results were compared with those from a bulk PVDF sample.

The thermogram revealed two distinct steps: thermal desorption (35–300 ∘C) and pyrolysis (300–600 ∘C). The mass spectra displayed ions differing by the number of VDF units, along with various adducts such as NO2–, NO3– and HCO3–. Different products were observed across temperature program, with pyrolysis yielding more unsaturated compounds. The products detected in the spiked sand matched the most intense signals observed in the bulk sample, allowing the identification of PVDF. This study demonstrates that TD/Py-DART-MS is an effective method for characterizing fluoropolymers and for the direct analysis of soils contaminated by polymeric materials.

(1) Pacholski, P. et al. (2023). *J. Am. Soc. Mass Spectrom. 34*(10), 2278-2288.
(2) Cody, R. B. et al. (2020). *Rapid Commun. Mass Spectrom. 34*, e8687.

Mots-Clés: high resolution mass spectrometry, direct analysis in real time, pyrolysis, polymers, polyvinylidene fluoride

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