GC-MS AND Py-GC-MS: COMPLIMENTARY FINGERPRINTING METHODS FOR COMPLEXLY CONTAMINATED SITES

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Introduction and methods

Industrial chemicals such as petroleum hydrocarbons, creosote or coal tar, and their derivatives are contaminants of concern. Their complex chemical composition makes determination of their origin difficult, especially when different mixtures of products are affecting the soil and subsoil. In this context, one of the main tools of environmental forensics (Morrison, 2000) is chemical fingerprinting, which permits the identification of the nature of the contamination, the differences among sources of analogous contamination, and the weathering degree of the pollutants. A forensic approach requires different methodologies in order to identify distinctive features of site- or source-specific contamination, useful to fingerprint the contamination, and particularly the application of GC-MS and Py-GC-MS qualitative methods (Kruge & Permanyer, 2004; Lara-Gonzalo et al., 2015).

In this work, a set of samples with very different origins from industrial releases have been studied. Two different approaches were followed: firstly, a "classical" extraction approach (SARA fractioning followed by GC-MS of maltene fractions, and Py-GC-MS of asphaltenes), and the second a "non-extraction" approach by means of thermodesorption (TD-GC-MS) for semivolatiles, and double-shot (TD+Py)-GC-MS for heavy fractions. We hypothesized that the second approach may improve upon, or at least complement, the information obtained with common GC-MS fingerprinting methods.

Soil samples were extracted in a Soxtherm system (Gerhardt). Aliquots were fractionated by LC into saturate (SAT), aromatic (ARO), resins (RES), and asphaltene (ASP) fractions subsequently analyzed by gas chromatography-mass spectrometry on a GCMS-QP2010 Plus (Shimadzu). TD and Py-GC/MS were performed using a CDS 5150 pyroprobe coupled to a Thermo Focus DSQ GC/MS.

Results and conclusions

Table 1 shows the main characteristics identified in the seven samples studied and the SARA fractioning results. A comprehensive study of each sample facilitated the acquisition of complementary information from the different analytical approaches. In general terms, the fingerprints obtained are very similar when the main contaminants are oil products (samples F1 and F2), and therefore the non-extracting approach (no sample preparation, rapid and non-expensive) is favoured. On the other hand, the main peaks and their abundances are usually different when studying complex residues (coal tar and others, see for example Figure 1), and thus both approaches are in these cases are complementary.

Table 1 *Samples description and main characteristics*

Sample	Origin	%SAT	%ARO	%RES	%ASP	Main pollutants identified
F1	Soil affected by old heavy fuel spill (25 years)	27.2	37.4	18.2	17.2	Weathered hydrocarbons (C10-C40)
F2	Soil affected by old heavy fuel spill (45 years)	24.3	36.7	21.7	17.3	Weathered hydrocarbons (n-alkanes absent), S-aromatics abundant
W1	Soil mixed with industrial waste (pyrite ash)	28.2	6.9	41.4	23.5	Weathered alkanes and PAHs (4-5 rings predominant)
W2	Soil mixed with Hg-As metallurgical waste	3.1	1.5	9.9	85.5	As-compounds, alkanes, PAHs 3-4 rings predominant)
T1	Soil affected by coke batteries releases	2.9	3.6	9.4	84.1	Coal tar fingerprint (heavy and very heavy PAHs)
T2	Sediments affected by old industrial spills & waste	37.4	12.9	20.2	29.5	Severely weathered hydrocarbons (*n*-alkanes absent) + coal tar fingerprint
PC	Soil affected by petrochemical releases	2.2	11.0	47.5	39.3	Light cycloalkanes, aromatics and olefins predominant

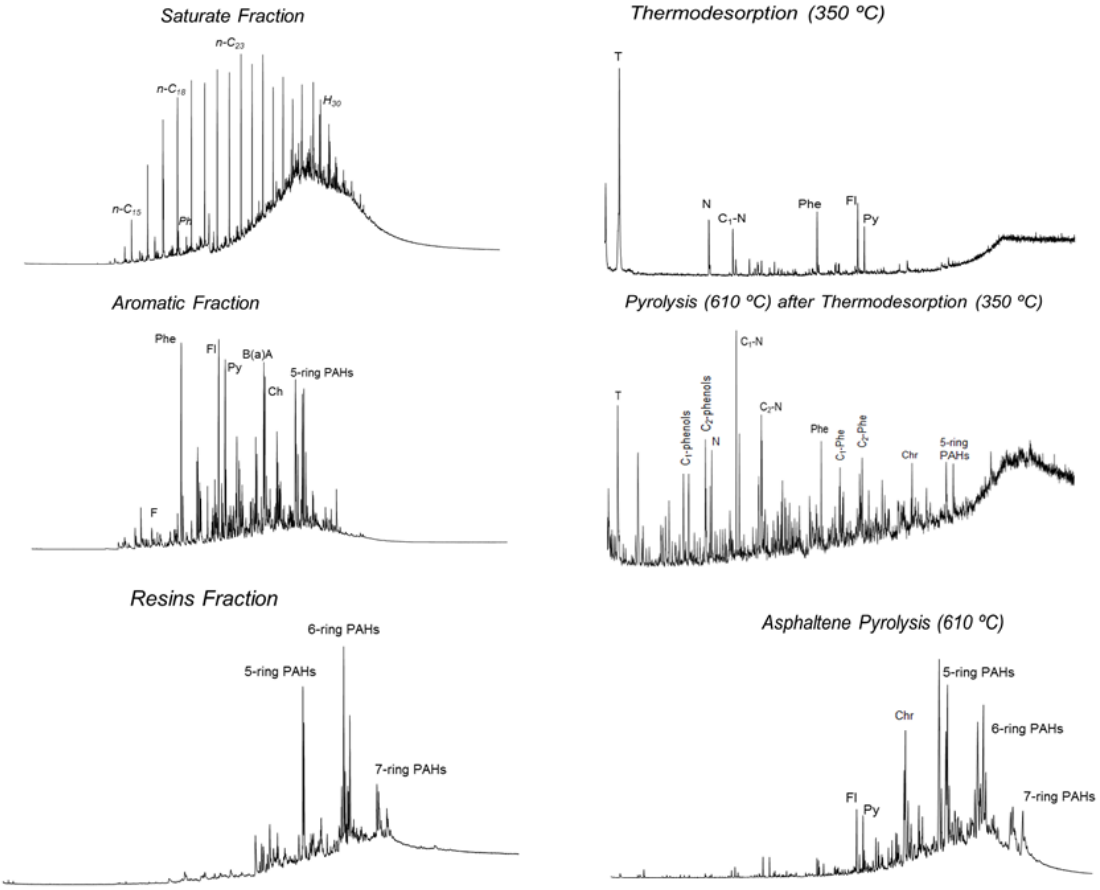

Figure 1 *TIC chromatograms obtained for sample T1*

References

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