

Analytical pyrolysis as a tool for the characterization of natural organic matter—A comparison of different approaches

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Abstract

A substantial fraction of natural organic matter (NOM) consists of complex mixtures of macromolecular compounds. As a result, high-molecular weight fragments liberated during the pyrolysis of NOM often carry the most significant structural information. Their diagnostic value, however, is commonly limited by the preferential transfer of lower-boiling pyrolysis products to the GC column, compared to larger fragments.

Non-discriminating pyrolysis is a technique that minimizes transfer losses of larger fragments, which is the problem with most conventional pyrolyzers. It allows a range of sample sizes from ~15 mg for the study of samples of low organic carbon content to estimated sub-microgram sizes for bacterial biomass.

In this study, the performance of the non-discriminating pyrolysis system in the characterization of natural organic matter (NOM) was compared to the performance of a conventional Pt-filament pyrolyzer. In addition, a more limited comparison was carried out with a Curie-point system. A variety of organic materials were selected to serve as NOM models: chitin, peat, and organic matter isolated from tertiary sands. Non-discriminating pyrolysis-GC/MS allowed for the observation of larger molecular fragments, such as traces of cholesterol in the pyrolysis of chitin. Also, the distribution of the homologous series such as that observed for alkyl benzenes was shifted towards higher molecular weight fragments with the non-discriminating system. Overall, the macromolecular structures within NOM were more pronounced when using non-discriminating pyrolysis, as shown by the higher abundance in the pyrograms of higher molecular weight fragments of various polyaromatic and long-chain aliphatic compounds. Characterization of NOM using non-discriminating Py-GC/MS reduces the ambiguity caused by mass discrimination against higher mass fragments compared to other pyrolysis approaches. This provides a better fingerprint of the organic material present in different sample types, including soils and sediments.

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1. Introduction

Natural organic matter (NOM) is defined as a complex mixture of organic material that is found in water, soils and sediments [1,2]. Aqueous polymeric NOM consists chiefly of fulvic and humic acids, whereas soils/sediments are character-

ized by high concentration of humin (operationally defined as being insoluble in diluted acids and bases) and humic acids. NOMs play a vital role in different environments such as soils, sediments and natural waters [3]. In soils, organic matter can improve physical properties such as water retention, and also provides a major sink and source of carbon and nitrogen. NOM in soils and sediments is known to influence speciation form, transport behavior and toxicity and bioavailability of hazardous organic chemicals [4]. This is due to NOM either acting as a sorbent towards both hydrophobic organic compounds [5] and heavy metals [6], or participating in chemical reactions, e.g., by acting as electron shuttle in redox processes, especially in anaerobic aquifers [7,8]. These properties are strongly related

Abbreviations: Py-GC/MS, pyrolysis-GC/MS; NOM, natural organic matter; EI, electron ionization; ASE, accelerated solvent extraction

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to NOM's structure. For a better understanding of the interactions that involve NOM, it is necessary to understand the building blocks and linkages between them in the polymeric network.

The knowledge of the chemical structure of soil organic matter and other polymers in the environment is very limited, but necessary for true understanding of soil formation, diagenesis, or retention of water and contaminants. In spite of the importance of organic matter in soil characterization, it continues to be “molecularly uncharacterized” due to its complex, heterogeneous nature. Analytical pyrolysis is one of the few degradative methods for the analysis of NOM that has shown an acceptable degree of success [9–12].

Pyrolysis combined with modern analytical instruments, such as gas chromatographs and/or mass spectrometers (often referred to as Py-GC/MS), is a powerful tool for characterizing biopolymers [13,14]. This is due to its speed, convenience, and ability to provide complementary information to wet chemical degradation methods. In general, analytical pyrolysis has been used in most studies of environmental materials as a qualitative method, since pyrolysis-GC produces a “fingerprint”. However, it can also be used as a quantitative technique.

Different pyrolyzers have been used for the analysis of NOM, including microfurnace, Curie point, Pt filament and Pt ribbon-based devices [15–19]. Each of these devices has their advantages and disadvantages. For example, with Curie point pyrolyzers, the pyrolysis temperature is limited to the Curie point temperature of the available materials, and there is not much flexibility in choosing different pyrolysis temperatures. In case of Pt filament pyrolyzers with quartz sample tubes, the sample never comes into direct contact with the heating element, the filament. As a result, it is difficult to determine the exact temperature of the pyrolysis reaction. In most of the conventional pyrolyzers, the resulting pyrolyzates do not get flushed from the pyrolysis zone fast enough, which might potentially result in secondary reactions (e.g. defunctionalization, release of low molecular weight analytes including CO and CO₂, formation of carbonaceous residue, etc.). In the pyrolyzer–analytical system interface, there might be poorly swept areas and cold spots, which might prevent some of the pyrolysis products (especially high molecular weight ones) from being transferred to the analytical system. As a consequence, the results of pyrolysis can be ambiguous because of the possible discrimination between large and small molecular weight pyrolyzates on transfer from the pyrolyzer to the GC.

A new technique called in-column pyrolysis was introduced in 2001 to eliminate, or at least minimize, the discrimination of high-molecular weight pyrolysis products [20]. In the design of this system, attempts were made to maintain the advantages of the existing systems, while eliminating or reducing the disadvantages. The design of the non-discriminating pyrolysis system has been continuously evolving since its introduction to make it more robust and user friendly [21]. Forcing inert gas through the sample during pyrolysis causes the pyrolyzates to be flushed from the hot zone, potentially reducing the occurrence of secondary reactions. The small inner diameter

of the pyrolysis capillary tube (0.53 mm) guarantees that the sample is exposed to the same temperature as the heating element. Improved recovery of higher molecular weight pyrolyzates was demonstrated with this device. These fragments often carry very significant structural information, yet their recovery using commercial pyrolyzers is usually difficult or impossible [22–25].

The non-discriminating pyrolysis technique was used to study a variety of environmental samples including synthetic and naturally occurring polymers [26,27]. The aim of this paper was to evaluate the performance of the technique in the analysis of NOM and to compare it with the performance of selected commercially available pyrolysis devices.

2. Experimental

2.1. Instruments

Three different pyrolysis systems were used, including a non-discriminating Py-GC/MS, a Curie point pyrolyzer, and a CDS Pyroprobe. In the case of the non-discriminating pyrolysis, experiments were performed using a GC/MS system (HP6890/HP5973) from Agilent Technologies, Mississauga, ON. Both a 32 m × 0.25 mm × 0.1 μm DB-1 HT (J&W) column and a (30 + 10) m × 0.25 mm × 0.25 μm EZ-guard VF-5 ms (Varian) column were used. The DB-1 HT column was equipped with a 2-m fused-silica pre-column, connected with a glass press-fit connector (Chromatographic Specialties, Brockville, ON). Different temperature programs were used, depending on the analysis, but in general the oven was maintained at 45 °C for 3 min, and then the temperature was programmed to 360 °C or 320 °C at rates varying from 4 to 20 °C/min. The mass spectrometer (MS) was operated in full scan mode with a mass range between 45 and 700 amu or 45 and 650 amu at 70 eV electron ionization (EI).

Fig. 1 presents a schematic diagram of the non-discriminating pyrolysis system. Pyrolysis was carried out in an inert, disposable Silcosteel capillary (0.53 mm i.d.; Restek, Bellefonte, PA). The sample (1–10 mg) was maintained in place inside the capillary by means of two fused-silica wool plugs (Quartz Fiber Filter, F&J, Specialty Products Inc., FL). Further details can be found in Ref. [21].

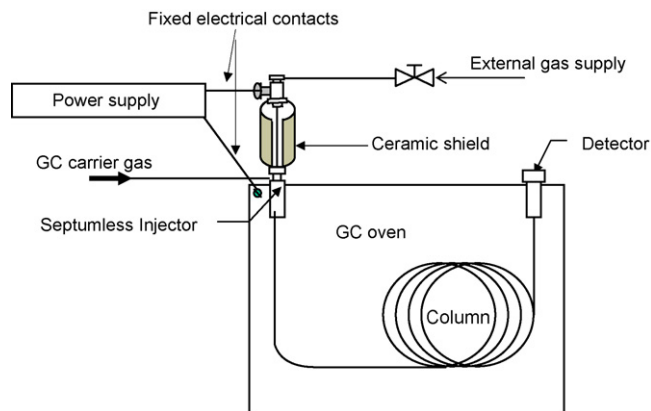


Fig. 1. Schematic diagram of the non-discriminating pyrolysis system [26].

A Curie point pyrolyzer with a ferromagnetic wire with a Curie temperature of 610 °C was used. Curie point Py-GC/MS analyses were carried out using a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a FOM-3LX unit for pyrolysis (FOM, Amsterdam, The Netherlands). A VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range of m/z 50–800 was interfaced with the GC system. This Py-GC/MS system was accommodated with a cryogenic unit which was programmed from 0 °C to 300 °C at a rate of 3 °C/min. Separation was achieved using a fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5CB (film thickness 0.4 μm). For further information refer to references [28,29].

A CDS pyroprobe 100 series solids pyrolyzer with Pt filament (coil) was used. Interface temperature was set at the maximum value of 300 °C. The upper interface temperature is limited by the materials of the seals (septum and o-ring). Pyrolysis interval was set at 20 ms and a heating rate of 10 °C/ms was applied. Experiments were performed using a GC/MS system (HP6890/HP5973) from Agilent Technologies, Mississauga, ON. The mass spectrometer (MS) was operated in full scan mode with a mass range between 45 and 700 amu at 70 eV (EI). A (30 + 10) m × 0.25 mm × 0.25 μm EZ-guard VF-5 ms (Varian) column was used in all experiments. Injection was carried out using split ratio of 20. The oven was programmed from 45 °C to 330 °C or 320 °C at a rate of 8–10 °C/min.

3. Samples and standard

The chitin standard was bought from Aldrich (Cat. No. 41,795-5 Chitin, from crab shells). The peat sample analyzed by pyrolysis-GC/MS was subjected to an intense “degearing” procedure using accelerated solvent extraction (ASE) with benzene at 100 °C for 15 min. The tertiary sandy sediment samples were selected from an area located in the eastern part of the Netherlands near a drinking water production site ‘t Klooster. The samples were treated first with 10% HCl, than with 38% HF to be decarbonated and demineralized. The HCl and HF procedures were repeated multiple times until no evidence of reaction was apparent. Finally, samples were treated with 30% HCl to remove any potential fluoride gels and

were washed using distilled water to pH 7. Studies have indicated that treatment of the sediment samples by HCl and HF removes 81–99% of the mineral matrix with no significant effect on the bulk composition of the organic matter isolated [30,31].

4. Results and discussions

The objective of this study was to assess the performance of non-discriminating Py-GC/MS in the characterization of NOM from aquifer sediments, and to compare the results to those obtained with a Pt filament pyrolyzer and a Curie-point pyrolyzer. The latter comparison was limited in scope.

The study was initiated with the pyrolysis of chitin, one of the most commonly occurring polymeric NOM compounds. Chitin, which is one of the most abundant macromolecules on Earth, is produced by a variety of animals, insects, and fungi. It is a linear polysaccharide containing β(1–4)2-acetamido-2-deoxy-D-glucopyranose residues. This molecule has been well studied and characterized, therefore was a reasonable choice for the first phase of this study. The expected pyrolysis products of chitin are documented in many publications [32–37].

The pyrolysis of chitin often produces additional compounds in the pyrograms, which are caused by contaminants. It is difficult to purify chitin from its source [37], therefore different contaminant peaks might be observed for chitin samples from different manufacturers. Fig. 2 illustrates the pyrogram (pyrolysis at 650 °C) of a chitin standard obtained using non-discriminating Py-GC/MS. One of the impurities detected in the sample was cholesterol, which could not be observed when using the same amount of the sample with the commercial pyrolyzers. Transferring trace amounts of compounds like cholesterol (C₂₇H₄₆O) from conventional pyrolyzers to the GC/MS system is challenging, and the associated results are often difficult to interpret. To be able to detect cholesterol in this sample with conventional pyrolyzers, a significantly larger amount of the sample would most likely have to be loaded. In general, lack of clear evidence of large contaminant molecules in the pyrograms obtained with conventional systems does not necessarily mean that the chitin standard is contaminant-free.

A peat sample was analyzed next by non-discriminating Py-GC/MS. The complexity and diversity of the chemical structure

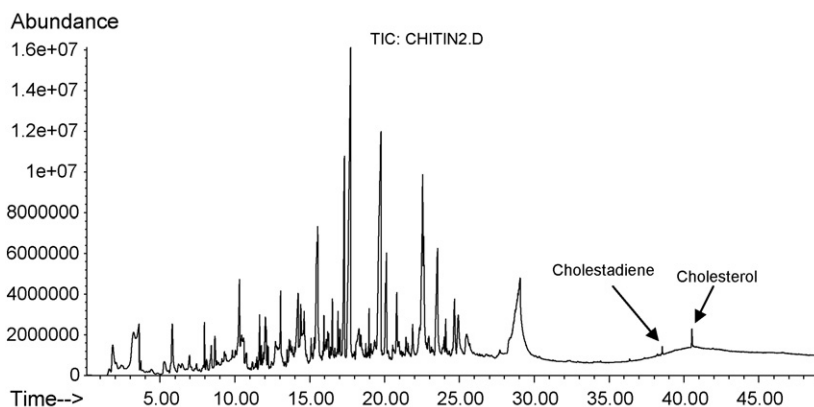


Fig. 2. Pyrogram of chitin standard obtained using the non-discriminating pyrolysis system at 650 °C.

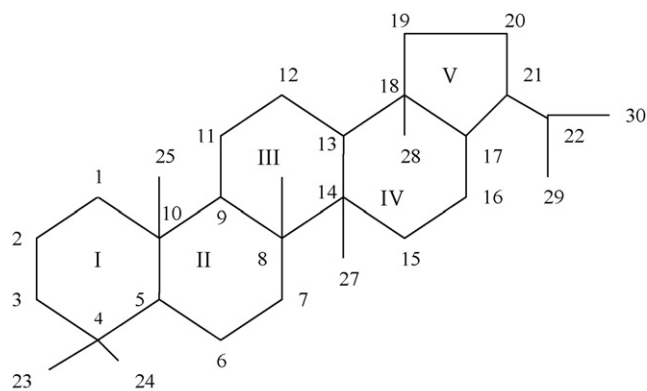


Fig. 3. Hopane structure.

of peat make it a good example of complex samples. Prior to pyrolysis, the sample was subjected to intense degreasing procedure using accelerated solvent extraction (ASE) to eliminate loosely bound lipidic residues, so that the pyrogram was representative of the macromolecular structure of the matrix. Alkanes, alkylbenzenes and steranes/hopanes were identified among other products (characterized by lower molecular weight, thus, of lower diagnostic value) with this approach. Fig. 3 illustrates the general structure of hopanes, originating most likely from methanotrophic bacteria. During the humification process, biohopanoids are defunctionalized, then getting incorporated into the HA polymeric network. Transfer of such large products from the pyrolysis unit to the analysis system is usually inefficient when using conventional systems [38,39]. As a result, the pyrograms obtained might not provide a correct fingerprint of the sample with the conventional pyrolysis approach. Fig. 4 illustrates a comparison of extracted ion m/z 191 traces in the peat pyrograms obtained from the pyrolysis of the peat sample at 700 °C using the non-discriminating Py-GC/MS and Pt filament- Py-GC/MS systems. The m/z 191 fragment characteristic for hopanes and hopenes is formed through the cleavage of rings I and II in the molecule. The pattern of hopanes and hopenes was similar in both cases, with high abundances of tris-nor-hopene (MW 368 amu), nor-hopenes (MW 396 amu) as well as C2-hopenes

(MW 438). However, the S/N ratio with non-discriminating Py-GC/MS, especially for later eluting, less volatile compounds, was better.

The pattern of polycyclic aromatic hydrocarbons (PAHs), in particular phenanthrene/anthracene and fluoranthene/pyrene, was similar for both systems (not shown), but the abundances of the PAHs under study obtained using the Pt-filament pyrolyzer were somewhat higher compared to those obtained with the non-discriminating Py-GC/MS system. Since these compounds might be formed during pyrolysis through secondary reactions, this observation might indicate that non-discriminating-Py-GC/MS system is somewhat “gentler”, most likely owing to faster removal of the products from the hot pyrolysis zone by the forced flow of the carrier gas through the pyrolysis capillary.

The profiles of methyl naphthalenes (142 amu), C2-naphthalenes (156 amu), and C3-naphthalenes (170 amu) seemed less discriminated with the non-discriminating approach. More interestingly, hydroxybiphenyl (170 amu) peak had a significantly higher abundance in comparison with methyl naphthalenes when applying the non-discriminating approach, whereas the peak areas of 142 amu for methyl naphthalenes and 170 amu for OH-biphenyl were very similar with the Pt-filament pyrolyzer (Fig. 5). This might indicate that OH-biphenyl likely underwent partial defunctionalization with the Pt-filament pyrolyzer. Consequently, the latter might not mirror precisely the content of functional groups in HOM-polymers. These groups account for environmental significance of HOM, e.g., chelating characteristics, electron-shuttle function, etc. Similar observations were made for levoglucosan (characteristic fragments at m/z 60 and 73), which is a marker for carbohydrates. The abundance of levoglucosan was higher with the non-discriminating Py-GC/MS system, which indicates again that diagnostic markers might be partly destroyed when using Pt-filament pyrolyzers.

The last sample used in the comparison was tertiary sandy aquifer sediment from ‘t Klooster (Netherlands). Sample KLO744 was selected for the comparison because it was analyzed previously with a Curie point pyrolyzer. The macromolecular compounds in the original sample were thermally fragmented using pyrolysis to produce among others

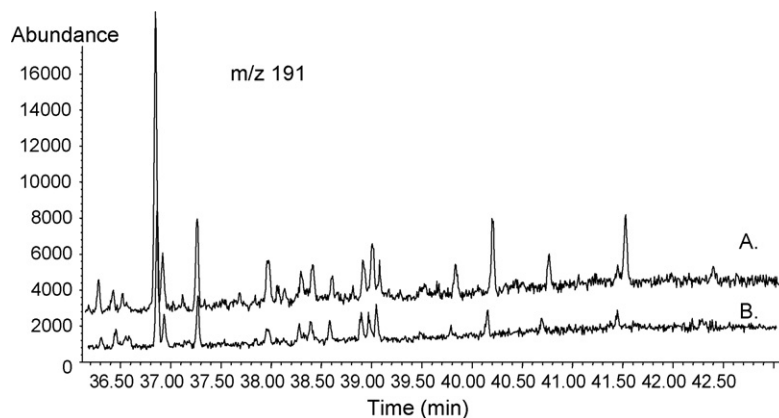


Fig. 4. Hopane patterns (extracted ion chromatograms, m/z 191) obtained from the pyrolysis of a peat sample using the non-discriminating pyrolysis system (A) and a Pt filament pyrolyzer (B) at 650 °C.

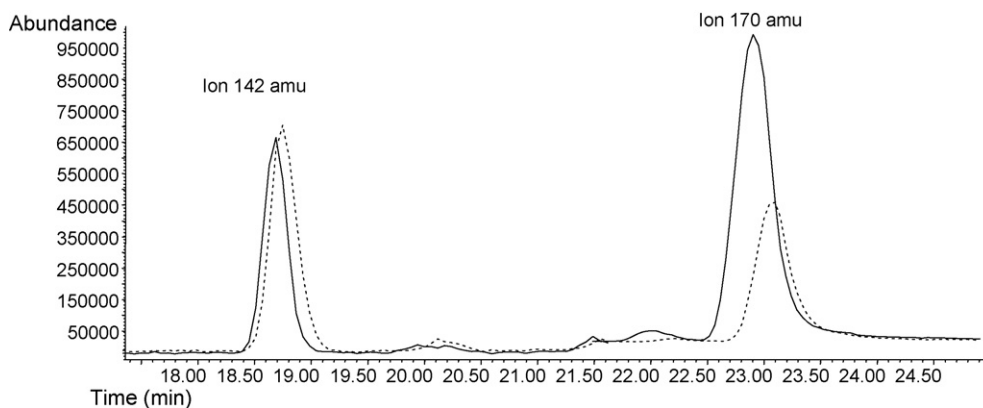


Fig. 5. Overlaid patterns of hydroxy biphenyl (m/z 170 amu) and methylnaphthalenes (m/z 142 amu) obtained from the pyrolysis of a peat sample using the non-discriminating pyrolysis system (solid line) and a Pt filament pyrolyzer (broken line) at 650 °C.

aromatic hydrocarbons such as benzene, toluene, alkylbenzenes, naphthalene, alkylnaphthalenes, indenes, acenaphthene, fluorene, phenanthrene, biphenyl and pyrene. In this study, the alkylbenzene series was selected for comparison of the three pyrolysis systems, because alkylbenzenes are not expected to originate from aromatic HOM-building blocks. Analysis of the distribution of the alkylbenzenes in the pyrolyzates of the aquifer sample is a useful comparison tool, while providing information about the presence and origin of the precursors of these compounds.

The alkylbenzene patterns obtained with the non-discriminating Py-GC/MS system, the Curie point pyrolyzer and the Pt-filament pyrolyzer are presented in Fig. 6 (extracted ion chromatograms for m/z 92 amu). When using the Curie point pyrolyzer, the highest abundances were observed for C₅ to C₉ alkylbenzenes, with a maximum at C₅ and a continuous drop in intensity after that. The last member of the series that could be detected was C₂₉. The alkylbenzene pattern obtained with the Pt-filament pyrolyzer was quite similar, except that the maximum abundance was observed in this case for C₇. In

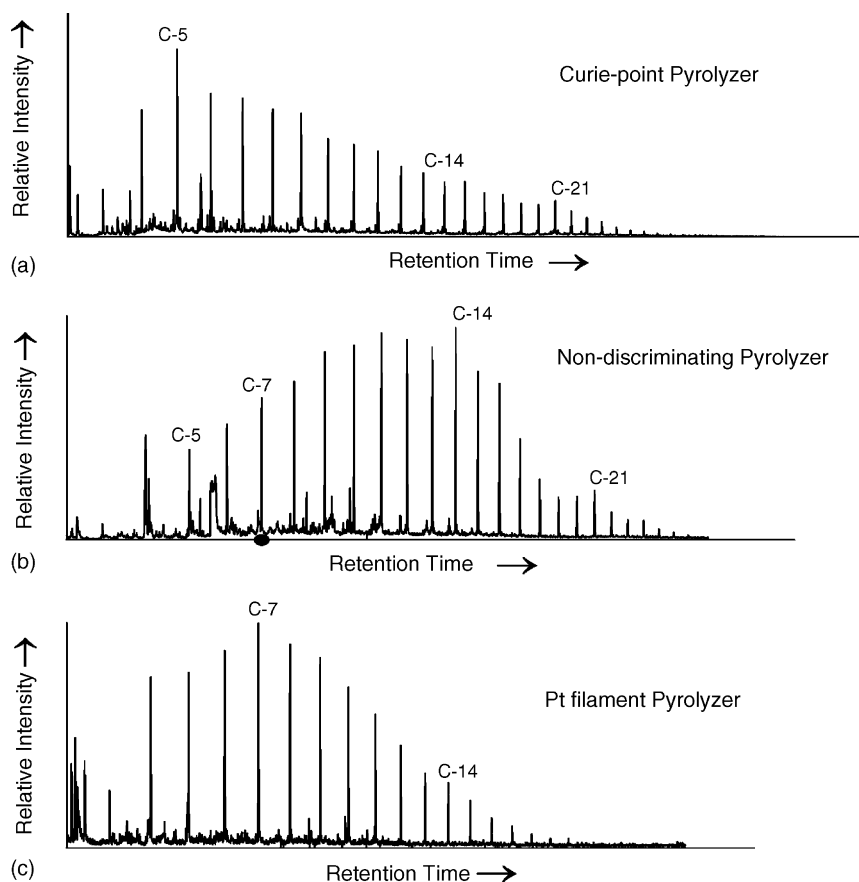


Fig. 6. Alkylbenzene pattern (m/z 92) obtained from the pyrolysis (650 °C) of a tertiary sandy aquifer sediment using Curie point pyrolyzer (a), non-discriminating Py-GC/MS system (b) and a Pt filament pyrolyzer (c).

contrast, the non-discriminating Py-GC/MS exhibited a different pattern, with the abundances of alkylbenzenes increasing from C₅ to C₁₁–C₁₄, followed by a gradual drop in intensity towards C₂₉. Also, the absolute abundances of the alkylbenzene peaks were higher. This is a strong indication that discrimination of larger alkylbenzenes occurred during the transfer of the analytes from the conventional pyrolyzers to the analytical system, since, it is quite certain that the amount and relative distribution of the alkylbenzenes in the pyrolyzate were similar in all cases.

The largest alkylbenzene found with all three pyrolysis systems was C₂₉. The absence of higher molecular weight members of the series in the pyrolyzate could be due to several reasons. It is possible that molecules beyond C₂₉ were absent in the pyrolyzate, or were present in too low abundances to be detected. However, it could also be the result of the limitations of the chromatographic system, or it may have resulted from strong sorption of larger molecular weight fragments to the carbonaceous residue left after pyrolysis of NOM. Such strongly sorbed molecules most likely could not have been thermally desorbed using any of the three systems.

The results indicate that the non-discriminating Py-GC/MS approach effectively reduces analyte discrimination on transfer from the pyrolysis unit to the GC column. The very small volume of the “interface” between the pyrolyzer and the separation system (the pyrolysis capillary itself) combined with the forced removal of the pyrolysis products from the pyrolysis zone with the help of forced flow of auxiliary carrier gas through the sample in the capillary significantly reduce the time which the pyrolyzates spend in the hot zone compared to other pyrolyzers. In the two systems used for the comparison in this work, the carrier gas is directed around rather than forcefully through the sample, and analyte transfer out of the pyrolysis zone is propelled by thermal expansion and molecular diffusion, which increases the dwell time in the hot pyrolysis zone. As a result, the extent of side reactions in the non-discriminated pyrolysis system is reduced.

The system requires smaller sample sizes compared to Pt filament or Curie point pyrolyzers. Consequently, a reliable fingerprint of the precursor molecules can be obtained with smaller sample mass, resulting in increased confidence in pattern recognition and characterization of the original sample. Discrimination of high-molecular weight compounds was observed previously in all types of conventional pyrolyzers, including filament and Curie point systems [23,25,40,41].

5. Conclusions

Structural characterization of natural samples of environmental significance by current pyrolysis approaches has significant analytical limitations. Non-discriminating Py-GC/MS eliminates or significantly reduces one of those limitations, analyte discrimination on transfer from the pyrolysis unit to the GC (along with reduced formation of artificial by-products formed in secondary reactions). As a

result, larger molecular weight pyrolyzates are usually more pronounced in the pyrograms obtained by this method, and the interpretation of the results can be less biased. Consequently, non-discriminating pyrolysis seems to be more useful than conventional pyrolysis if the sample of interest contains macromolecular structures.

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