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# Behavior of PAH/mineral associations during thermodesorption: impact for the determination of mineral retention properties towards PAHs

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**Keywords:** Evolved gas analysis; Thermal desorption; Bentonite; Silica sand; Polycyclic aromatic hydrocarbon; Sorption

## Abstract

Polycyclic aromatic hydrocarbons (PAHs) associated with two minerals (silica sand and bentonite) presenting opposite retention properties were analyzed with a thermodesorption (Td)-GC-MS coupling in order to validate this technique as a new and rapid way to evaluate the solid sorption properties. Two analysis modes were used, evolved gas analysis (EGA) and Td with cryo-trap. EGA allowed a real-time monitoring of the compounds desorbed during a temperature program and gave a first screening of the samples while Td gave more precise indications on compound abundances for selected temperature ranges. When associated with silica sand, PAHs were released at relatively low temperatures (<300 °C) close to corresponding boiling point, whereas for the PAH/bentonite mixture, PAHs were desorbed at much higher temperatures; they were also present in much lower abundance and were associated with mono-aromatic compounds. With bentonite, the PAH abundances decreased and the mono-aromatics increased with the increasing PAH molecular weight. These results indicated a clear PAH retention by the bentonite due to polymerization, followed by a thermal cracking at higher temperatures. The Td-GC-MS was proven to efficiently underline differences in retention properties of two minerals, and this study highlights the great potential of this technique to evaluate compound/matrix bond strength and interaction.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have drawn some attention during the past decades due to their toxic and carcinogenic properties [1]. Their presence in soils can be caused by atmospheric deposition or spilling of contaminated materials such as coal tar which is frequently encountered in sites housing coal-related activities [2]. PAH fate in the soils implies either degradation or stabilization [3]. Biotic and abiotic degradations infer that the compounds are available for such processes, and stabilization involves most of the time strong sorption on mineral or organic surfaces. Consequently, soil constituents and especially minerals will have strong influence on the PAH fate. Indeed, some minerals, especially clay minerals, have strong sorption properties towards PAHs [3–6] and are known to participate in organic matter (OM)—including PAHs—stabilization in contaminated soils [7, 8]. Most of the time, the evaluation of retention properties of a given matrix towards a specific compound or family of compounds is made via sorption batch experiments [9]. Such experiences are time consuming since the solid/solution ratio (at least 1:10) and sufficient contact times (at least 24 h) need to be determined before the definite sorption and desorption experiments [10]. Another possibility is to determine the compound mobility/ availability which depends on the solid retention properties. For example, thermal desorption is applied in the Pollut-Eval technique—based on Rock-Eval pyrolysis—to obtain indications on the type of contamination encountered in soils and sediments (e.g., light oil hydrocarbons, heavy oil, or PAHs) [11]. These distinctions between contaminants are based on the vaporization temperatures. Another more precise way is to use thermal analysis to correlate the solid retention property with the temperature at which the compound is released. Such philosophy was applied by Cuypers et al. [12] and Siewert [13]. They used thermogravimetric analyses (TGA) and associated different loss weight temperatures to different types of OM according to its mobility and structure. Owing to the type of analyses (TGA), their OM description was very general (i.e., easily biodegradable, humified soil OM, condensed graphite-like substance) and they did not reach a molecular level. However, this molecular information is necessary to determine a solid-binding property towards specific compounds. Therefore, we propose to use thermodesorption (Td)

associated with a gas chromatograph–mass spectrometer coupling (GC-MS). Such techniques were already developed for the determination of organic contaminants in waters [14, 15] and in air particulate matter [16–18]. The compounds of interest, in these cases PAHs, organochlorides, and volatile organic compounds (VOCs), were sorbed or collected on filters before being desorbed and analyzed with Td-GC-MS. This coupling was also used to evidence the presence of organic contaminants in river sediments or sludge from wastewater treatment plants [19–21] and was proven to be an efficient first screening for contaminant detection. This technique was mostly developed in order to avoid time-consuming sample preparation and to get rapid results avoiding, at the same time, artifacts and especially losses related to extraction or concentration steps. However, the idea of connecting desorption temperature of given compounds to their binding strength with the solid was never explored until now.

The objectives of this study were to investigate the behavior of PAHs sorbed on different minerals during thermodesorption and to test if the retention properties of a solid towards organic compounds can be determined using the compound desorption temperature. In order to fulfill these purposes, PAHs were sorbed on two mineral surfaces presenting different retention properties, a silica sand and a bentonite. Bentonite was chosen over other clay minerals for its higher specific area, possibly resulting in higher retention capacities. The compounds were then analyzed with Td using two different modes, the evolved gas analysis (EGA) mode, consisting in a Td-MS coupling allowing a first screening of the compound desorption temperatures and the Td-GC-MS coupling with cryo-trap mode to obtain the molecular distribution and allowing an abundance estimation of the compound thermodesorbed during defined temperature ranges.

## **2. Materials and methods**

### *2.1. Samples*

#### *2.1.1. PAHs*

Experiments were performed on individual PAHs and on PAH mixture. Phenanthrene, pyrene, and perylene were selected for the individual PAH experiments as they present various molar masses (178, 202, and 252 g/mol, respectively) and different boiling points (Table 1). They were supplied by Sigma-Aldrich with a purity >98 % for phenanthrene and pyrene and >99% for perylene. PAH solutions were prepared to reach a 500 µg/mL concentration by weighing 2.5 mg of PAH crystals and dissolving them in dichloromethane (DCM) adjusted to 5 mL in a volumetric flask. The PAH mixture was supplied by Dr. Ehrenstorfer GmbH (PAH mix-64) and consisted in the 16 listed PAHs (Table 1) and carbazole (a nitrogenated-PAH) at 2000 µg/mL.

**Table 1:** Abbreviations, molar masses and boiling points of the PAHs used in this study

Name	Abbreviation	Molar mass (g/mol)	Boiling point (°C)
Naphthalene*	Na	128	218 <sup>a</sup>
Acenaphthylene*	Acy	152	280 <sup>a</sup>
Acenaphthene*	Ace	154	279 <sup>a</sup>
Fluorene*	Fl	166	295 <sup>a</sup>
Phenanthrene*	Phe	178	340 <sup>a</sup>
Anthracene*	An	178	340 <sup>a</sup>
Carbazole	Car	167	355 <sup>a</sup>
Fluoranthene*	Fluo	202	384 <sup>a</sup>
Pyrene*	Py	202	404 <sup>a</sup>
Benz[ <i>a</i> ]anthracene*	BaA	228	438 <sup>a</sup>
Chrysene*	Chry	228	448 <sup>a</sup>
Benzo[ <i>b</i> ]fluoranthene*	BbF	252	481 <sup>b</sup>
Benzo[ <i>k</i> ]fluoranthene*	BkF	252	480 <sup>a</sup>
Benz[ <i>a</i> ]pyrene*	BaP	252	496 <sup>b</sup>
Perylene		252	350-400 <sup>c</sup>
Indeno[1,2,3- <i>cd</i> ]pyrene*	IP	276	536 <sup>c</sup>
Benzo[ <i>ghi</i> ]perylene*	BghiP	276	550 <sup>b</sup>
Dibenzo[ <i>a,h</i> ]anthracene*	DBahA	278	797 <sup>d</sup>

\*PAHs listed by the US-EPA as priority pollutants

<sup>a</sup>from Handbook of chemistry and physics [21]

<sup>b</sup>from The international program on chemical safety [22]

<sup>c</sup>from Toxnet [23]

<sup>d</sup>from NIST Chemistry WebBook [24]

### 2.1.2. Mineral phases

The silica sand was Fontainebleau sand (180 to 500 µm) provided by Carlo Erba and was used as a non-reactive reference.

Bentonite was obtained from a purified bentonite from Georgia provided by IBECO, S&B Industrial Minerals GmbH. The structural formula was obtained from chemical and electron microprobe analyses:  $(\text{Si}_{3.928}\text{Al}_{0.072})^{\text{IV}}(\text{Al}_{1.383}\text{Mg}_{0.404}\text{Fe}^{3+}_{0.213})^{\text{VI}}\text{O}_{10}(\text{OH})_2\text{Na}^{+}_{0.379}\text{K}_{0.098}$

The cationic exchange capacity is close to 126 meq/100 g. The bentonite texture was characterized in the dry state using conventional step-by-step volumetric adsorption equipment (B.E.T.) in order to perform complete nitrogen gas adsorption–desorption cycles for the specific area determination. The specific area of the bentonite is 78.1 m<sup>2</sup>/g.

Both minerals were washed with a methanol/chloroform 1:1 (v/v) mixture in a Soxhlet apparatus for 24 h in order to remove any potential organic contamination, and the solids were left in a ventilated oven set at 60 °C for 24 h to ensure the complete evaporation of the solvents. Analyses of control samples, i.e., the washed and dried mineral matrices, were carried out and confirmed that no trace of solvent remained (see Electronic Supplementary Material, ESM).

## *2.2. Mineral spiking*

Fraction of minerals (1 g) was spiked with isolated PAH (240 µL) and PAH mixture (60 µL) solutions in order to reach a concentration of 120 µg of individual PAH per gram of solid. DCM (c.a. 1 mL) was added to the mixture in order to spread the PAHs evenly on the solid surface. The mixtures were left in a ventilated hood until complete evaporation of the solvent and stored at –18 °C.

## *2.3. TD-GC-MS analyses*

### *2.3.1. Td-GC-MS coupling*

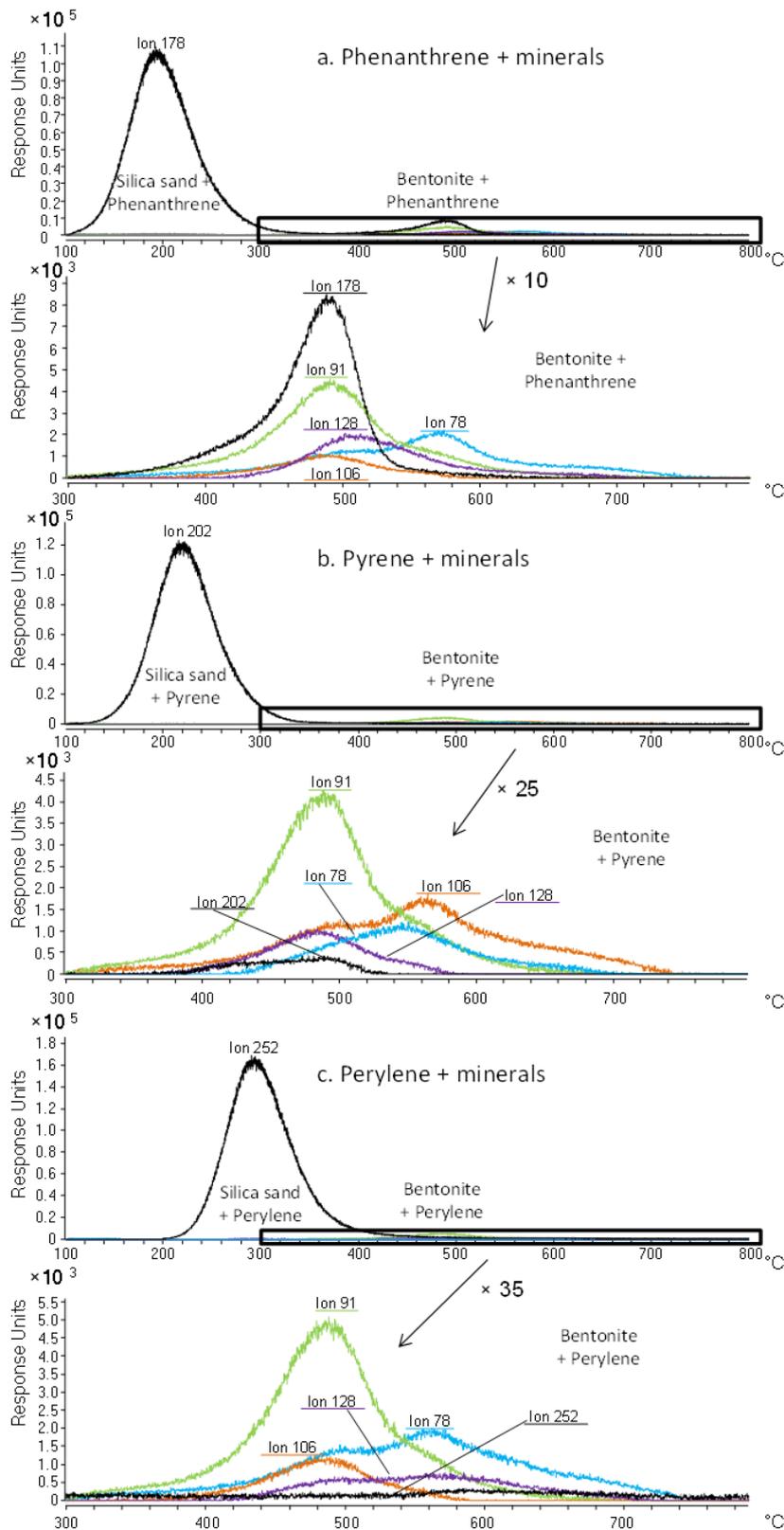
A Frontier Lab Multi-shot pyrolyzer EGA/PY-3030D and a Micro Jet Cryo-Trap MJT-1030Ex were installed on an Agilent GC 7820 coupled with a 7595 MS detector. Helium was used as carrier gas at a constant flow of 1.4 mL/min in all Td-GC-MS measurement. The inlet and transfer line temperatures were set at 320 °C, and the MS quadrupole and ion source were set at 180 and 230 °C, respectively. For all analyses, the MS was used in the full scan mode.

### 2.3.2. EGA

The EGA mode, coupling directly Td with MS without GC separation, allowed a real-time plot of the ions released during a temperature program of the pyrolyzer oven and gave a first screening of the samples which was used to determine the temperature ranges used for the Td-GC-MS analyses. The pyrolyzer temperature was programmed from 100 to 800 °C which is the maximum temperature of the device, at a heating rate of 10 °C/min, and 30 mg of samples were analyzed in the EGA mode with a split ratio of 10:1. For the molecular transfer to the mass spectrometer, a Frontier Lab Ultra Alloy-DTM column (2.5 m×0.15 mm i.d.) was installed in the GC. The oven temperature was isothermal at 300 °C.

### 2.3.3. Td with cryo-trap

For this mode, the desorbed compounds were separated by gas chromatography. The use of the cryo-trap (−180 °C) at the column head allowed concentrating the compounds that were desorbed during a given Td temperature program. The samples (1 mg) were heated according to three successive Td temperature ranges which were determined according to the first sample screenings obtained with the EGA: from 100 to 350 °C, from 350 to 550 °C, and from 550 to 800 °C with a heating rate of 10 °C/min. The injections were done in split mode with a split ratio of 200:1. The GC was equipped with an Agilent HP-5MS column (30 m×0.25 mm i.d.×0.25 µm film thickness). The oven temperature program was as follow: 50 °C for 2 min, from 50 to 315 °C to 15 °C/min, then hold at 315 °C for 10 min.



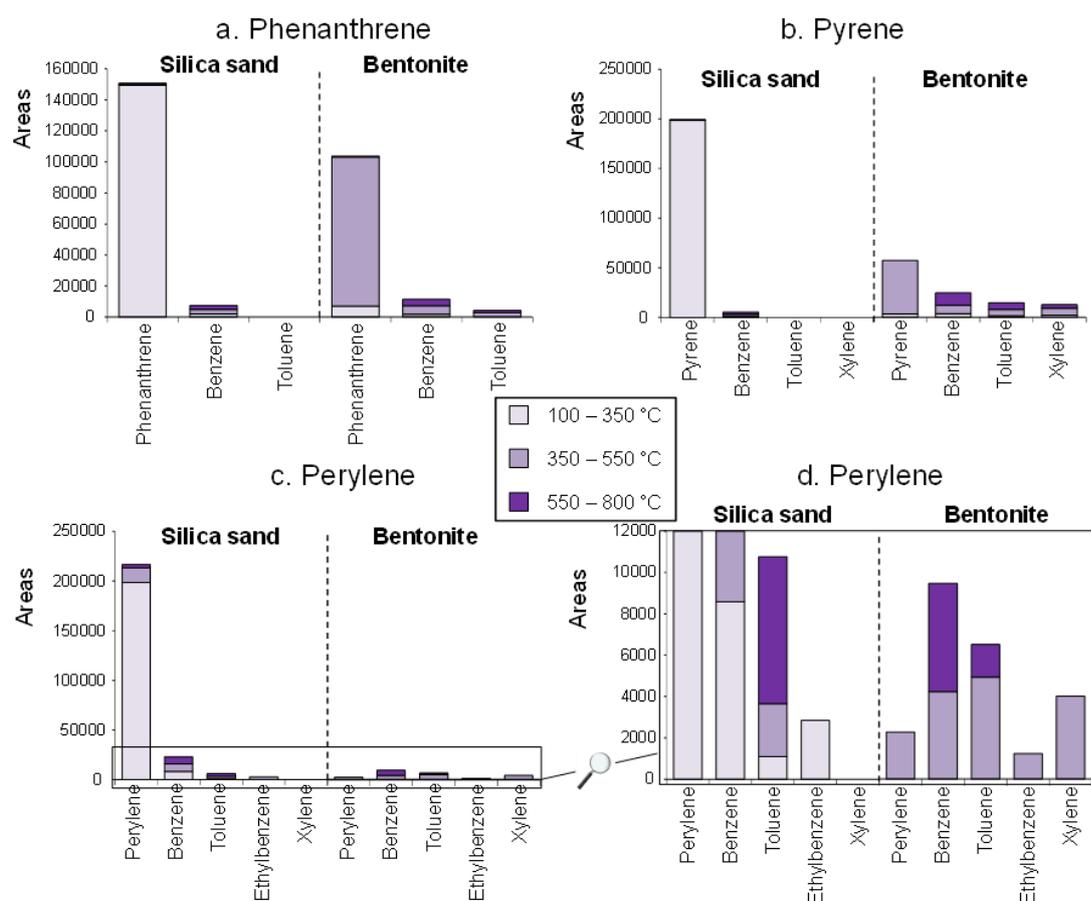
**Fig. 1:** Overlaid extracted ion chromatograms of the EGA of (a) the phenanthrene/mineral (b) pyrene/mineral and (c) perylene/mineral mixtures ( $m/z$ : 178, 202, 252, 78, 91, 106, 128 ions were identified as phenanthrene, pyrene, perylene, benzene, toluene, ethylbenzene/xylene and naphthalene, respectively, by mass spectra comparison with the Wiley275 library)

### 3. Results and discussion

#### 3.1. Overview of the compound desorption temperatures with EGA

Ions corresponding to the compounds of interest ( $m/z$  178, 202, and 252 for phenanthrene, pyrene, and perylene, respectively) were extracted from the chromatograms obtained with EGAs of the PAH/mineral mixtures (Fig. 1). According to the mineral and for the three target compounds, a difference in the maximal desorption temperature was obvious. When associated with silica sand, phenanthrene, pyrene, and perylene were, respectively, desorbed at c.a. 200, 220, and 300 °C which represent temperatures lower than their respective boiling points (Table 1). These lower observed values can easily be explained by the fact that the equilibrium is constantly shifted by the helium flowing through the oven. For the phenanthrene/bentonite mixture, the maximal desorption temperature for the ion  $m/z$  178 was about 500 °C. Even if the EGA profile did not give absolute quantitative results, it should be noted that the response intensity was ten times lower for the phenanthrene/bentonite mixture than for the phenanthrene/silica sand (Fig. 1a). This trend was observed to a greater extent for the pyrene and perylene associated with bentonite. The maximal desorption temperature for the ion  $m/z$  202 was between 400 and 500 °C, with lower response intensity, and the ion  $m/z$  252 corresponding to perylene was not detected for the perylene/bentonite mixture (Fig. 1c). For the PAH/bentonite mixtures, the low response intensity of the targeted PAH ions was associated with the presence of other fragments appearing between 400 and 600 °C. They corresponded to smaller units such as benzene ( $m/z$  78), toluene ( $m/z$  91), xylene ( $m/z$  106), and naphthalene ( $m/z$  128). As already mentioned, clay minerals present strong sorption properties towards PAHs [3–5] that could be responsible for these relatively high desorption temperatures. Clay minerals are also known to interact with OM during pyrolysis causing aromatization and polymerization of organic compounds [26–28]. Indeed, it has been demonstrated that kerogen pyrolysis [29] and coal thermal maturation [30] in the presence of clay induced retention of the volatilized compounds on the clay mineral surfaces. A tar-like coating presenting pre-graphitic structure is observed around the clay grains, which is consistent with the

polymerization/polycondensation of the retained compounds. Kopinke and Remmler [28] also observed the formation of a bound residue during thermal analyses of organic compounds (including PAHs) associated with sediments and sediment mineral matrix and named this phenomenon “charring”. They also observed that increasing temperatures (>450 °C) cause a thermal decomposition or thermal cracking of the newly formed residues, which would lead to the release of low molecular weight aromatic hydrocarbons. During the PAH/bentonite Td experiments and unlike the PAH/silica sand experiments, the PAHs were strongly retained on the mineral surfaces and polymerization likely occurred with the increasing temperature, possibly through radical reaction [28], leading to more thermally stable compounds. When the thermal cracking zone was reached (c.a. 500 °C [31]), low molecular weight aromatic structures such as benzene, toluene, xylene, etc. were produced either from the sorbed PAH or, more likely, from the polymerization products.



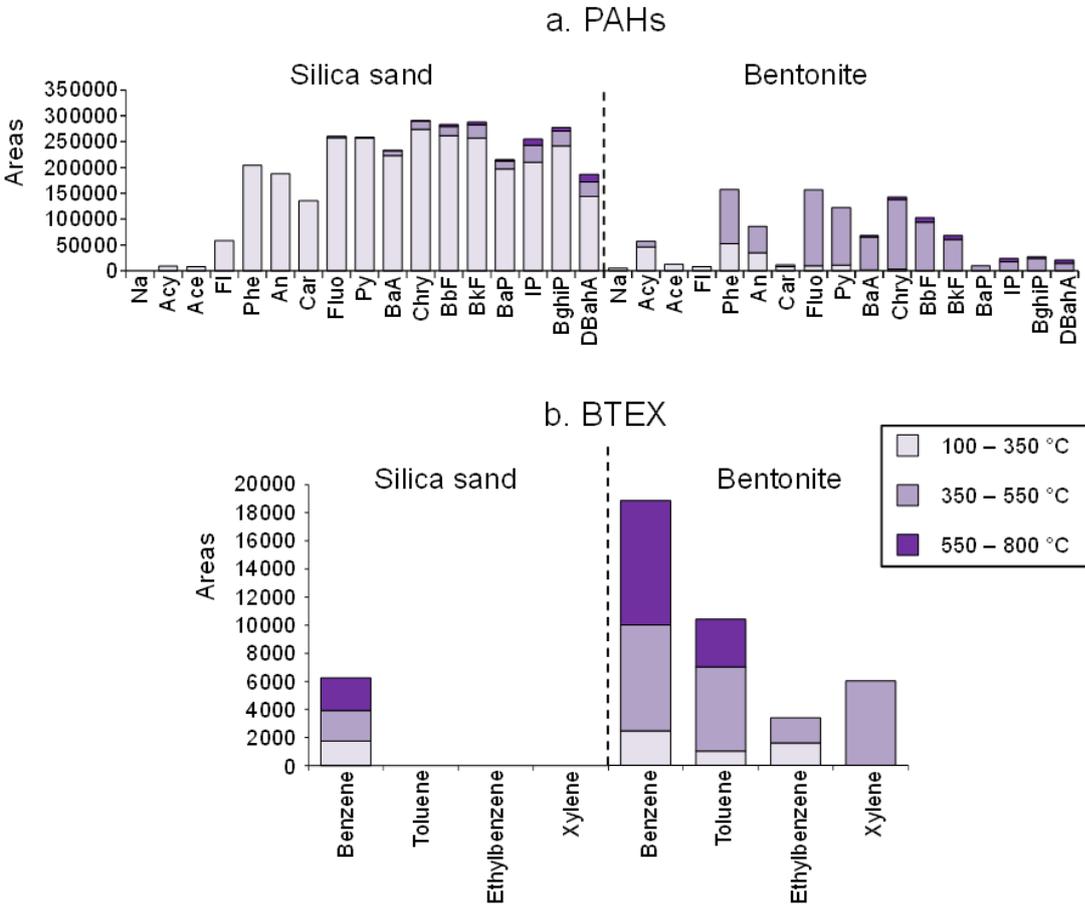
**Fig. 2:** Areas of the GC-MS peaks corresponding to the compounds detected during the 100 - 350 °C, 350 - 550 °C and 550 – 800 °C thermodesorptions of (a) the phenanthrene/mineral (b) pyrene/mineral and (c, d) perylene/mineral mixtures (d is a magnified portion of c)

### *3.2. Temperature-related compound discrimination with Td/cryo-trap analyses*

Td analyses allowed targeting specific temperature ranges, determined after EGA, for which the thermodesorbed compounds were concentrated in the cryo-trap and subsequently analyzed with GC-MS. The first zone (100–350 °C) corresponded to the thermodesorption of most of the PAHs associated with silica sand, the second one (350–550 °C) was related to the detection of most of the small aromatic units formed with the PAH/bentonite associations, and the last one (550–800 °C) was used to report the last thermal cracking events. The integration of the GC-MS peaks gave better indication of the abundance of the different compounds released during the Td steps. Td analyses confirmed the observations made with EGA (Fig. 2), but the differences observed between silica sand and bentonite were less intense. For the PAH/silica sand associations, most of the compounds were desorbed during the first temperature zone (100–350 °C). Mono-aromatic compounds were also detected for the perylene/silica sand mixture, but their intensity can be considered as negligible compared to the parent compound (Fig. 2c, d). When associated with bentonite, most of the parent compounds were detected during the 350–550 °C Td. Their areas were lower than with the PAH/silica sand association which confirmed the difference of behavior of the minerals and the resulting higher retention property of bentonite towards PAH than the silica sand. The areas of the parent compounds decreased with increasing molar mass to reach values 100 times lower for the perylene/bentonite than for the perylene/sand mixture, confirming the bentonite strong sorption properties possibly related to catalyzed polymerization. The thermal cracking products, i.e., BTEX, were also mostly detected during the 350–550 °C Td of the PAH/bentonite mixtures, and their relative intensities compared with parent compounds increased with the PAH molecular weight. Mostly, mono-aromatic compounds resulting from thermal cracking were detected during the 550–800 °C Td but in relatively low intensity.

The results obtained for the PAH mixture and mineral association showed the same trend than isolated PAHs (Fig. 3). For the PAH mix/silica sand mixture, most of the compounds were released from 100 to 350 °C. It is worthwhile noting that, as observed for the isolated PAH experiment, the intensity of the compounds detected during the higher temperature Td increased with the PAH molecular weight (Fig.

3a). Again, when associated with bentonite, most of the PAH were released during the 350–550 °C Td and their relative intensity decreased with increasing molecular weight, which was not observed with the silica sand. Only benzene was detected during the PAH mix/silica sand mixture Td (Fig. 3b) whereas benzene, toluene, xylene, and ethylbenzene were generated during the PAH mix/bentonite mixture Td mostly from 350 °C. These observations underlined once again that the important retention property of the bentonite is likely associated with a polymerization phenomenon, inducing an immobilization of the PAHs at its surface followed by a thermal cracking of the sorbed compounds at high temperature (>450 °C) rather than a simple volatilization as it was the case for the silica sand.



**Fig. 3:** Areas of the GC-MS peaks corresponding to (a) the PAHs and (b) the BTEX detected during the 100 - 350 °C, 350 - 550 °C and 550 - 800 °C thermodesorptions of the PAH-mix/mineral mixtures (see Table 1 for PAH abbreviation meanings)

#### **4. Conclusion**

Td and EGA were tested as a simple and rapid way to evaluate the retention properties of silica sand and bentonite towards PAHs. EGA allowed a first screening; it underlined major differences between the two matrices and evidenced the bentonite catalytic properties. Indeed, the results suggested that PAHs were strongly retained on the bentonite surface, which was likely enhanced by a temperature-induced polymerization, followed by thermal cracking as temperatures increased, releasing smaller units. The Td analyses allowed getting more precise indications on the abundance of the compounds released during defined temperature range. These results are encouraging and underline the potential of such instrument for the study of organic compound–solid matrix interactions and the evaluation of matrix retention property controlling the compound availability. A method for compound quantification, which is necessary to validate the use of Td for the determination of the contamination available fraction, is currently being developed.

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## Supplementary material

### Behavior of PAH/mineral associations during thermodesorption: impact for the determination of mineral retention properties towards PAHs

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#### **Control samples**

Control samples, i.e. sand and bentonite washed with solvent with no PAH, were analyzed in thermodesorption mode with cryogenic trap and were heated from 100 to 800 °C at 20 °C/min. Chromatograms of the control samples did not show any trace of remaining solvent (Figure S1). Two peaks were above the baseline and were also present on the blank analysis which was done under the same conditions but with no sample (only the stainless steel cup, Figure S1). They were identified as polysiloxanes by comparison with the NIST mass spectrum database (Figure S2) and originate from the column or septa bleeding.

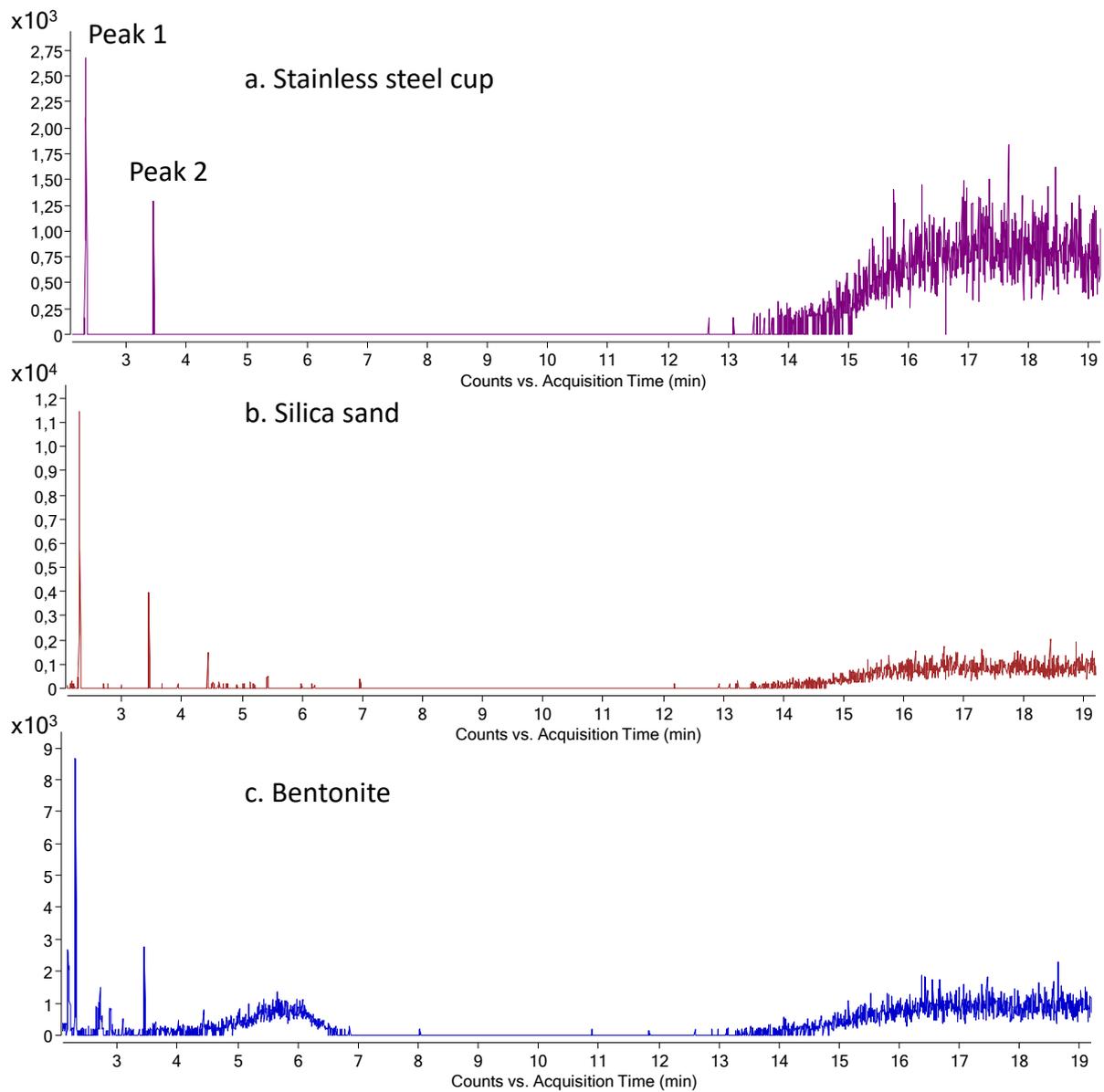


Figure S1: Chromatograms of a. the blank sample (the stainless steel cup alone), b. and c. the sand and bentonite control samples, respectively

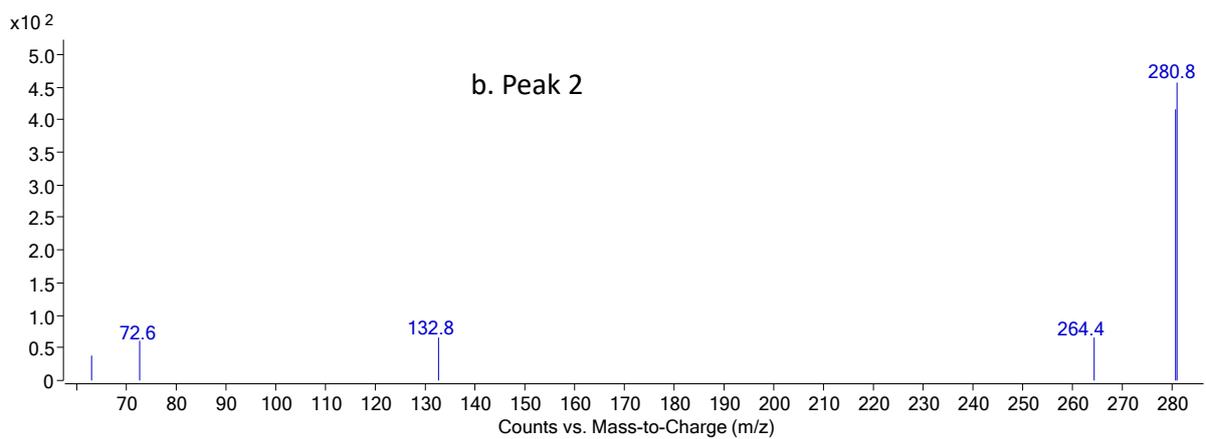
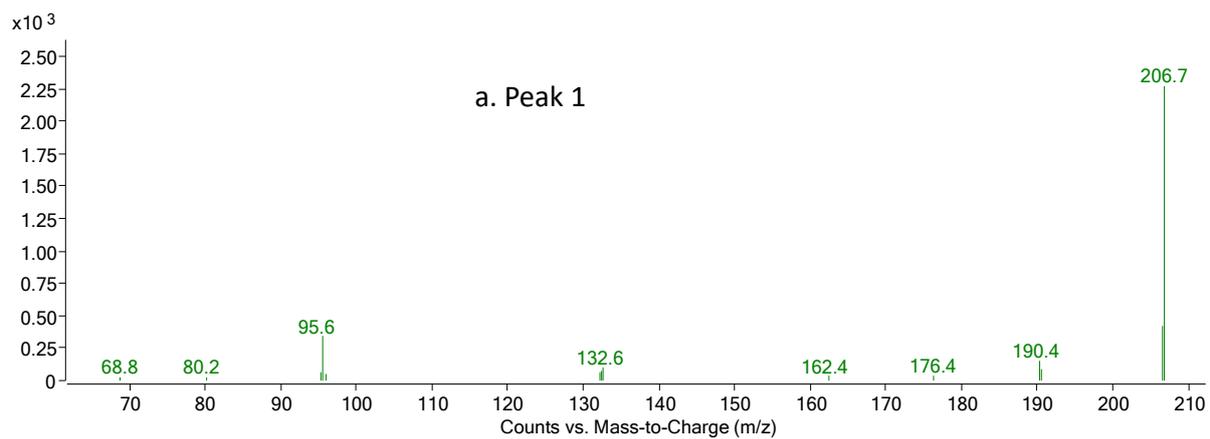


Figure S2: Mass spectra of the peak 1 and 2 from the control chromatograms identified as polysiloxanes by comparison with the NIST mass spectra database