Direct insertion analysis of polymer modified bitumen by atmospheric pressure chemical ionization ultra-high resolution mass spectrometry

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Overview

Purpose: characterization of bitumen and polymer modified bitumen (PMB) with thermal analyses without any sample preparation

Method: Direct insertion probe Fourier transform ion cyclotron resonance mass spectrometry with atmospheric pressure chemical ionization

Results: Bitumen and styrene butadiene (SBS) polymer samples were characterized by direct thermal analysis at 400°C and by thermal ramp between 250-450°C. The presence of SBS in the PMB can be proved using DIP-FTMS with heteroatom class distributions and DBE vs #C plots.

Introduction

Bitumen is a very viscous and complex material used in the construction of asphalt pavements and roads. Bitumen chemistry depends on the manufacturing process, and on the use of polymeric additives such as styrene-butadiene-styrene (SBS) to improve bitumen properties [1]. The objective of this work was the development of a new method with a direct insertion probe (DIP) APCI source coupled to FTICR mass spectrometry for the rapid characterization of polymer modified bitumen (PMB) with minimal sample preparation. DIP-APCI allows the controlled pyrolysis of the polymer whereas FTICR offers the high resolution for separation of the high number of signals [2]. By this way it was possible to fully characterize both polymeric additive and bitumen in very simple and fast experiment.

Methods

Solid samples of bitumen, PMB (5% SBS), and SBS were melted in a glass bottle using a heated sand bath (100°C). DIP glass capillary tube was dipped in the melted sample and then fixed to the DIP probe holder before introduction in the ionization source. DIP-MS analyses were performed with a hybrid quadrupole-FTICR instrument (SolariX XR, Bruker) equipped with a 12T superconducting magnet. The operating parameters for direct analyses on the APCI source were a corona needle current of 3000 nA at a nebulizer gas temperature of 400°C.

For the temperature behavior analyses, instead of a fixed nebulizer gas temperature of 400°C, the temperature was ramped between 250 and 450°C. . For these experiments, the temperature was incremented by 2°C per scan.

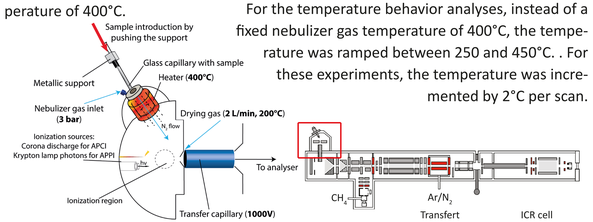


Figure 1. Schematic view of the DIP-APCI source with the FTICR Bruker 12T instrument [3]

Results

Base bitumen direct analysis 400°C

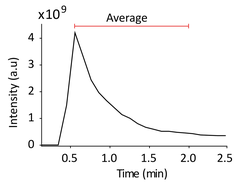


Figure 2. Desorption profile of the base bitumen sample

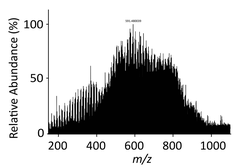


Figure 3. Average mass spectrum of the base bitumen sample

- About 1.5 min is required to analyze a base bitumen sample
- The attributions were dominated by HC compounds and molecules containing sulfur atoms
- Molecules are principally found between C# 20 and 60, and between DBE 10 and 30

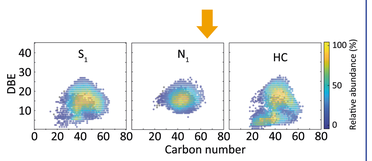
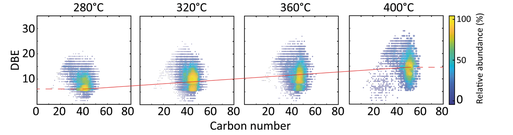


Figure 4. DBE vs C# plots of the major compound classes of base bitumen

Base bitumen analysis thermal ramp analysis (250-450°C)



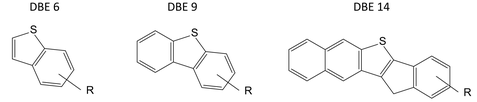


Figure 5. DBE vs C# plots of the S1 compound class at different temperatures, and the corresponding structure

- More time-consuming with about 13 min for a temperature gradient
- The structural complexity of heavy crude oil matrices increases sharply with the boiling point
- This increasing of complexity could be seen with the increasing of DBE and carbon number of the molecules with the temperature (DBE 6 to DBE > 14)

SBS analysis: 400°C and ramped 250-450°C

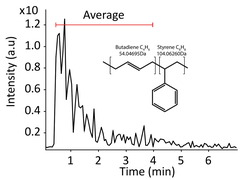


Figure 6. Desorption profile of the SBS sample

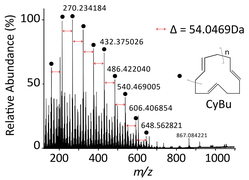


Figure 7. Average mass spectrum of the SBS sample

- Main ions series with mass difference of 54.0469 Da (C_4H_6) was attributed to radical cations of butadiene cyclic species (CyBu)
- Twice more attributions were obtained using the ramp, but main ions remained the same
- These major signals corresponded to SBS markers

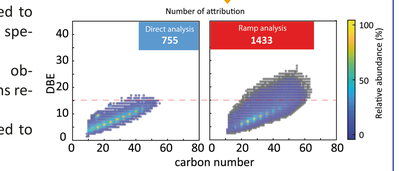


Figure 8. DBE vs C# plots of the HC classe of SBS in direct and ramp analyses

PMB direct analysis 400°C

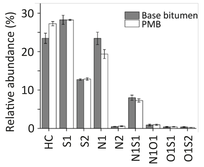


Figure 9. Heteroatom class distribution of base bitumen and PBM samples

- Logically, the HC class of the PMB presented a higher abundance compared to the base bitumen, due to the presence of SBS pyrolysis fragments
- The most intense signals in the PMB were the same as those found on the SBS
- Interestingly, the biggest ions in the PMB were not found in the SBS plot. It could be due to the sample of polymer which was in pure form and could cause ion suppression for the high masses

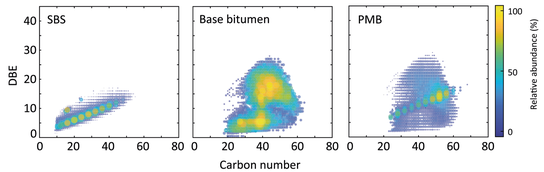


Figure 10. DBE vs C# plots of the HC classe of SBS, base bitumen, and PMB in direct thermal analyses at 400°C

Mass recalibration

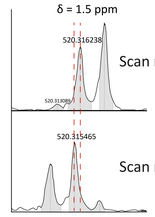


Figure 10. Enlargements of base bitumen mass spectra corresponding to scan 1 and 2 of the desorption profile

- A self-written Matlab interface (Matlab R2018b, CERES – computing enhanced resolution mass spectra) allowed to recalibrate each scan individually
- This approach is correcting peak shifts during the acquisition caused by the substantial variation in ion abundance transmitted to the ICR cell, during the thermo-desorption process

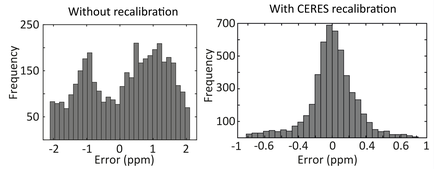


Figure 11. Error plot distributions of all assignements obtained before and after CERES recalibration

Conclusion

In this study, DIP-MS allowed to fully characterize both polymeric additive and bitumen in very simple and fast experiment, without any sample preparation. Indeed, DIP-APCI allowed the controlled pyrolysis of the polymer whereas FTICR offers the high resolution for separation of the high number of signals. DIP-MS, which consists in thermal analyses, was carried out with fixed or ramped temperature. Even if temperature behavior analysis drastically increased the chemical coverage and the number of assigned formulas, analysis with fixed temperature, which allowed faster analysis, was sufficient to characterize the presence of polymer in PMB. It can be evidenced using DBE vs C# plots on the HC compound class or heteroatom class distribution.

References

[1] S.-p. Wu, L. Pang, L.-t. Mo, Y.-c. Chen, G.-j. Zhu, Construction and Building Materials 2009, 23, 1005-1010.
[2] A. G. Marshall, R. P. Rodgers, Proc. Natl. Acad. Sci. 2008, 105, 18090.
[3] C. Castilla, C. P. Rüger, S. Marcotte, H. Lavanant, C. Afonso, Journal of the American Society for Mass Spectrometry 2020, 31, 822-831.

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