Fingerprinting bitumen from archaeological sites using 2-Dimensional Flow-Modulated Gas Chromatography

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INTRODUCTION

Biomarker analysis by means of GC-MS has been the standard for years in oil-spill analysis, sourcing unknown hydrocarbons, and in environmental assessments. The techniques developed for this practice, however, do not limit themselves to present-day issues: the same analytical techniques have proven to be very useful to acquire archaeological and historical knowledge. Bitumen, currently mainly a by-product of petroleum exploration and -drilling, has been used by mankind extensively for over six thousand years. It was commonly used to either glue or waterproofing items, ranging from the smallest type of objects such as jewellery, to ships and monumental architecture.

Figure 1: Several examples of artefacts where bitumen was used. Bitumen used as a sculpting material to fabricate pottery and stoppers are a commonly found item on archaeological sites (left). The Royal Cemetery of Ur (right image, ca. 1900 B.C.). The Standard of Ur (right image, ca. 2500 B.C.) was excavated from the Royal Cemetery and consists of a second core to which shell and lapis lazuli elements were glued with bitumen.

SOURCING ARCHAEOLOGICAL BITUMEN

Bitumen surfaces naturally at specific locations (e.g., in southeast Iran and in Iraq) where it could be easily collected. Already in the Palaeolithic period there is (rare) evidence of the usage of bitumen by mankind’s ancestors. However, it is from around 5000 B.C. onwards that the material becomes exploited on large scale and shipped over long-distance and overseas. By analysing bitumen found on archaeological sites and determining where it originated, archaeologists obtain valuable knowledge on trade networks and interregional contacts. This holds especially true for bitumen, as there was an extensive trade in this specific product.

Figure 2: Map of the Near East highlighting the areas were bitumen extraction occurred in Antiquity. These areas are: 1. The Mesoite Area (Iraq), 2. The N Africa (Iraq), 3. The Desert Luran Plain (Iran), 4. Susiana Plain (Iran). Almost all bitumen excavated from Archaeological sites in the Near East can be traced back to one or several of these areas.

2-DIMENSIONAL GC IN BITUMEN RESEARCH

Two-dimensional comprehensive Gas Chromatography is more and more becoming embedded in petro-chemistry for the detailed analysis of biomarkers1-2. Its main advantages over the more traditional one-dimensional GC include:

- potential for higher peak capacity,
- easier compound separation from matrix interferences,
- signal enhancement due to analyte refocusing on the modulator3.

However, this is generally achieved by employing cryogenic modulation and time-of-flight mass spectrometry (TOF MS). Analyses using these techniques are relatively complex and costly to operate. We are here presenting an experimental setup using a Forward Hi/flush flow modulated system with FID and Quadrupole MS detector in parallel.

SETUP

For this research, a combination of a 30m HP-5MS and 2m DB-17MS column was used. A glass Y-splitter and deactivated fused silica tubing was used to achieve a 1:12 split (MSD-FID) prior to detection (see Figure 3). This was necessary due to the high flow rate of the second dimension (25mL/min), which would be problematic when introduced directly into the MSD. Employing one-dimensional GC, generally m/z 191 is targeted for specific compound identification rather than the total ion chromatogram (Figure 4A). The FID data provided by our setup presents well-separated peaks and the ability to easily determine molecular ratios, both with MSD and FID. The additional MSD data can be used to identify individual compounds based on their mass spectra. However, this setup has one major disadvantage; small trace compounds visible in the FID data could often not be identified on the MSD. This is the result of the split introduced right after the second column. To resolve this issue, possible solutions included more concentrated samples, a higher injection volume, or the usage of cryogenic modulation.

ARCHAEOLOGICAL SAMPLES

Five archaeological samples originating from two different archaeological sites were selected to investigate the potential of flow-modulated comprehensive GC for sourcing ancient bitumen. Both sites are located in the Persian Gulf (see Figure 2):

- F6 on Failaka Island in Kuwait
- Tell Abraq in the Sharjah Emirate (U.A.E.)

Bitumen was found in considerable quantities on both sites, despite the absence of nearby seaports, indicating import.

Figure 4: (A) Traditional GC-MS chromatogram (m/z 191) of an archaeological bitumen sample. Figure 4B exhibits several molecular ratios commonly used in biomarker analysis. It is evidently evident that only the sample from F6 Failaka shows the presence of the chemical compound Oleasane, which is indicative of oils coming from the Tertiary Padlaf Source Rock formation (in case of this geographical area). Molecular ratios support this hypothesis, e.g. a with a significant higher 29ab/30ab ratio than any other sample. The ratios in figure 4B are:

1. α(H)/β(H)
2. (H22S)/22(R)
3. 17β(H)/17α(H)
4. 22(R)/22(S)
5. 17ββ/17αα (H)
6. 17ββ/17αα (E)

Figure 4C shows the structures of the compounds: 17α(H)-hopenone (C1), 17β(H)-hopenone (C2), and 17ββ-22,29,30-trinorsesane (C3).

CONCLUSION

- Comprehensive flow-modulated two-dimensional GC has shown to be a useful tool for biomarker targeting in archaeological bitumen.
- The setup is quite straightforward and easy to operate.
- The parallel operation of an FID and Quadrupole MSD offers flexibility in data processing and makes compound identification possible.
- The analysis on the samples used in this test-case makes clear that both archaeological sites were supplied with bitumen from at least two different source areas.

REFERENCES