



Sources For Anthraquinone And Biphenyl In Coconut Oils

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Introduction

Substituted polycyclic aromatic hydrocarbons (SPAHS) occur ubiquitously in the whole global environment as a result of their persistence and widely-spread sources. They are produced from their corresponding PAHs. Biphenyl (BP) accrues naturally in coal tar, crude oil (up to 0,4 mg/g) and natural gas (3- 42 g/m³) and it is also used as a wood preservative [1]. Anthraquinone (AQ) or 9,10-Anthracenedione is an oxidizing product of anthracene, one of the light polycyclic aromatic hydrocarbons (PAHs). Therefore AQ is an OXY-PAH, but because it is possible to use it as a bird repellent, its residue is controlled, like biphenyl, by the Regulation (EC) 396/2005 [2].

Methods and Results

Because the both substances are regulated in [2] we used our standard method for pesticides. This new accredited in-house developed method, based on liquid/liquid extraction, which is much faster and cheaper than other common methods. This method allows extraction of ca. 700 pesticides (LC and GC) including some SPAHS at the same time in less than one hour (see figure 1). The results are summarized in the figure 2.

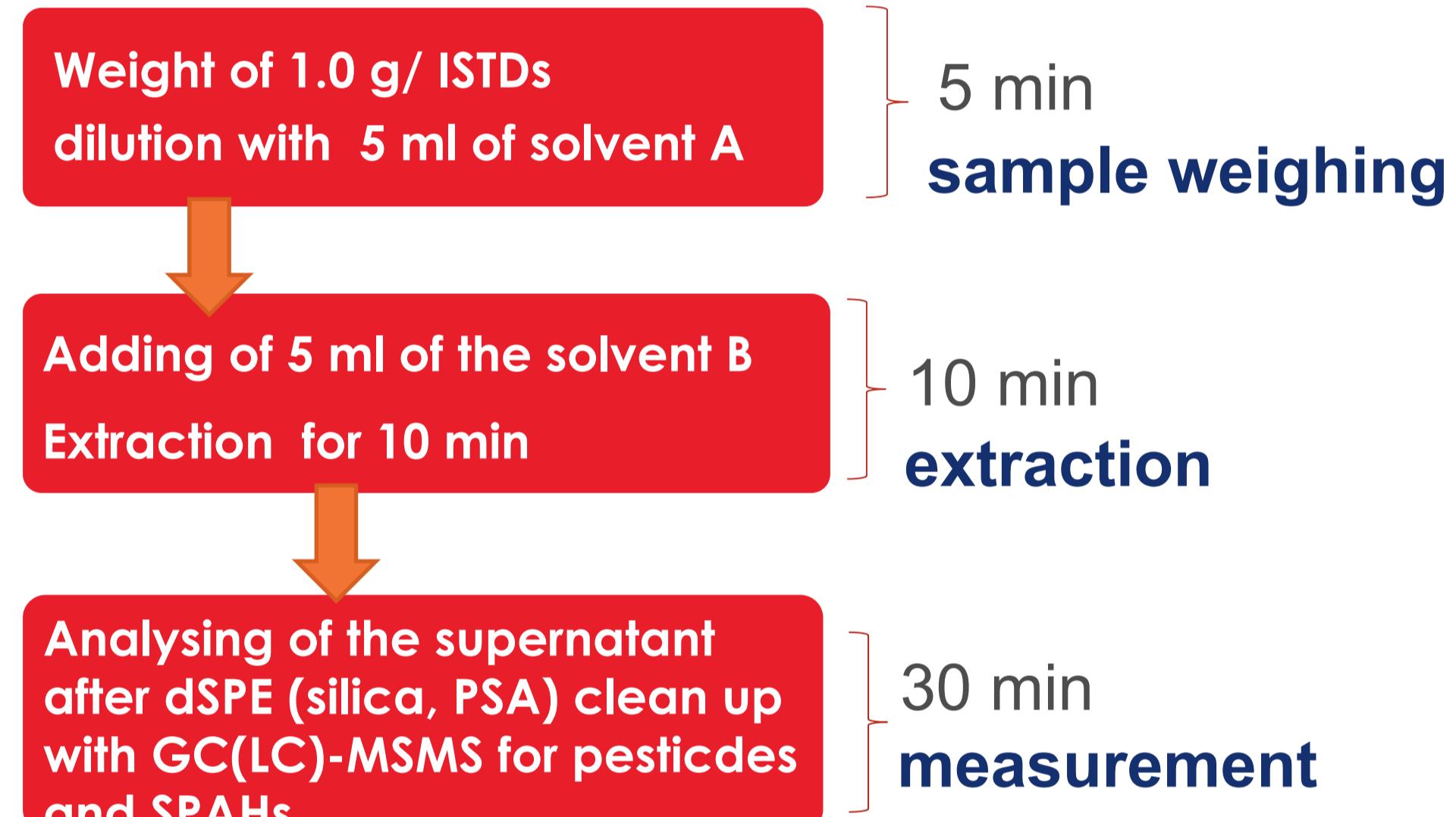


figure 1. sample preparation

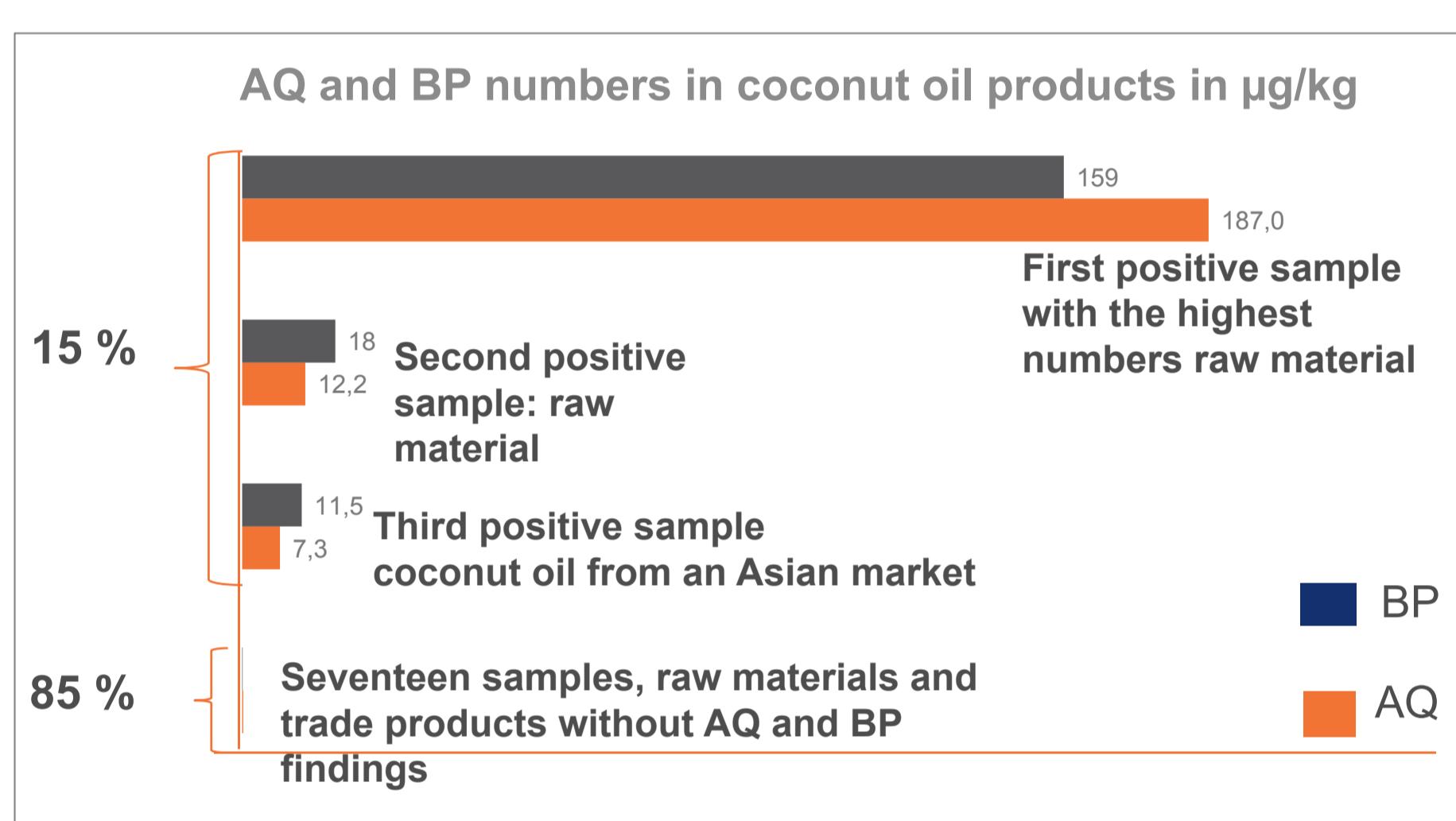


figure 2. numbers for AQ and BP findings

For some compounds of two types of the most frequently occurring SPAHS, oxygenated-PAHs (OXY-PAHs), methyl-PAHs (MPAHs) and Biphenyl were investigated in our study.

Altogether we measured 20 different coconut oil products directly from the market and raw materials from different countries and made with different production processes. Most of the products were free of any critical findings. But three products showed significant amounts of AQ and BP. To find the source of both of these chemicals, we looked into the drying procedure used in processing. We burned the coconut shells and analyzed their smoke for AQ and BP.

15 % (3 samples out of 20) were positive for AQ and BP. In 85% of the samples we didn't see positive signals (below 0.005 mg/kg for each of AQ and BP).

Except for the AQ and BP in the highly contaminated sample we also found small traces of 9-Flurenone and 2-Methyl AQ (see figure 3).

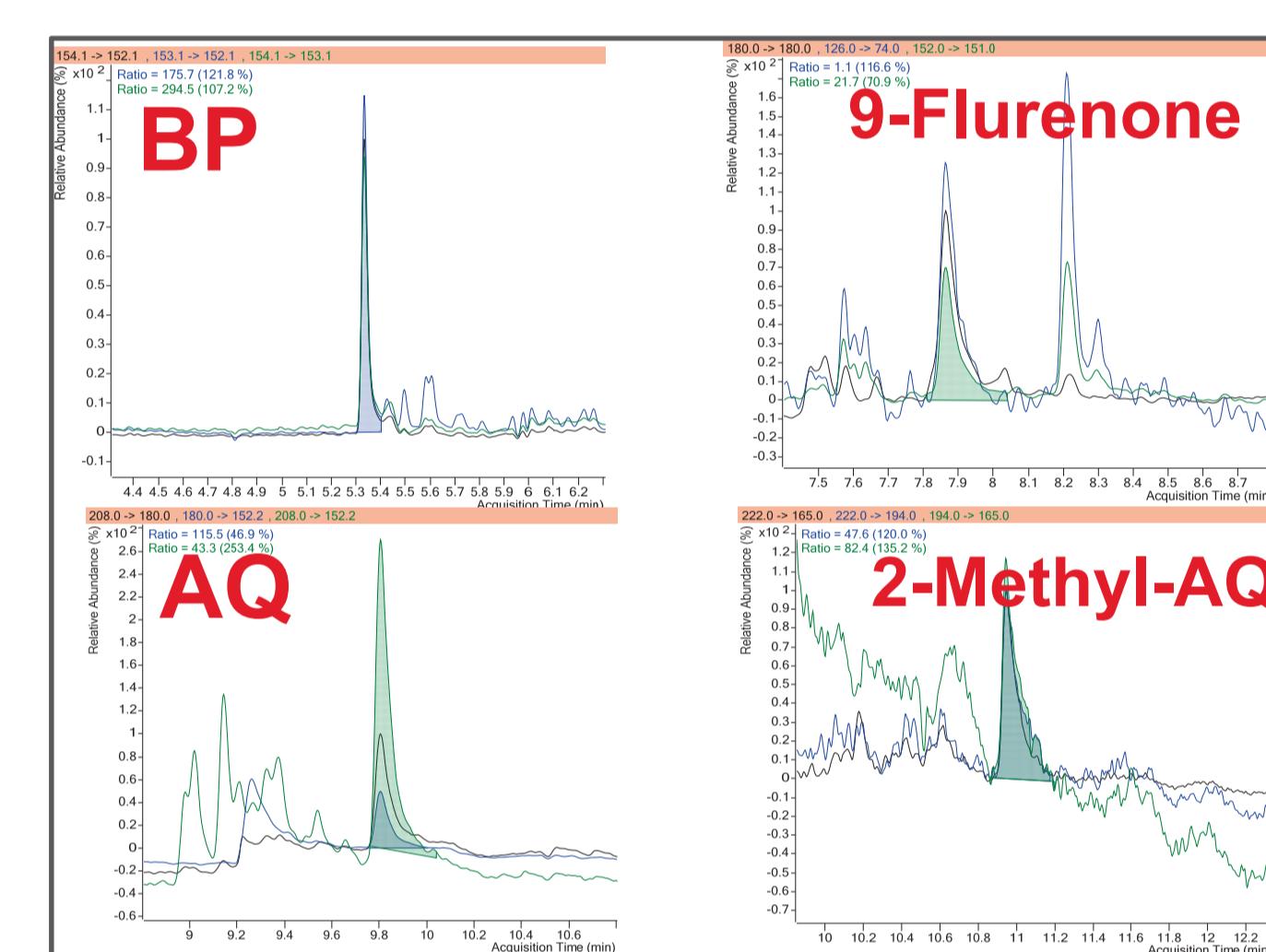


figure 3. signals of AQ, BP, 9-Flurenone and 2-Methyl-AQ in the positive coconut oil sample

Further Research

The drying technique for coconut oil production is the keystone. For heat production the burning of fossil fuels like gas, crude oil, coal, wood or coconut shells and saw dust can be used. By burning any organic matter, like coconut shells or coconut shell charcoal [3], PAHs and their SPAHS are developed. Some coconut oil producers use coconut shells/-charcoal for heat production. This can be the most important sources for AQ and BP as well as for PAHs in coconut products. We proved that by analyzing the ambient air after burning the coconut shells (see figure 4).

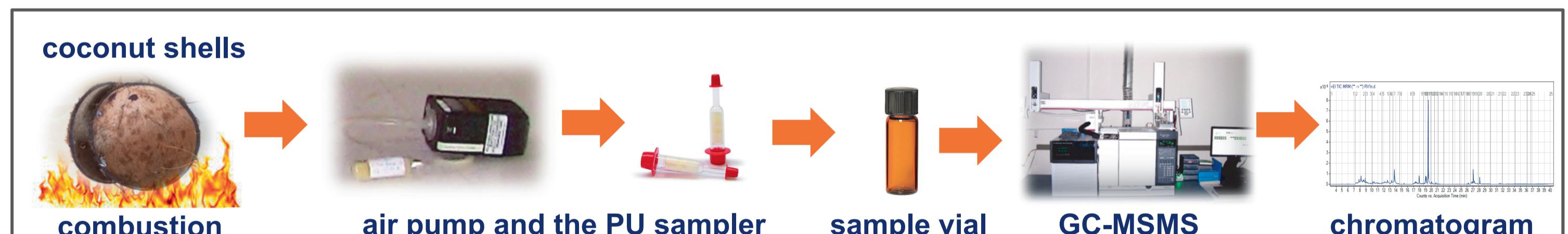


figure 4. sample approach for the burned coconut shell air sample

The air sample was analysed for PAHs, OXY-PAHs, some MPAHs and BP. We could detect the following substances:

- 1- and 2-Methylnaphthalene (MPAHs)
- all possible Dimethylnaphthalenes
- 2-Methylanthraquinone (OXY-PAHs)
- 9-Flurenone and other OXY-PAHs
- One of the highest signals is for BP
- The highest signal for AQ (OXY-PAHs)
- Phthalimide, 1,4-Naphthoquinone
- Phthalic acid anhydride
- all PAHs (EPA16), especially Anthracene → precursor for AQ!
- Traces of the other SPAH

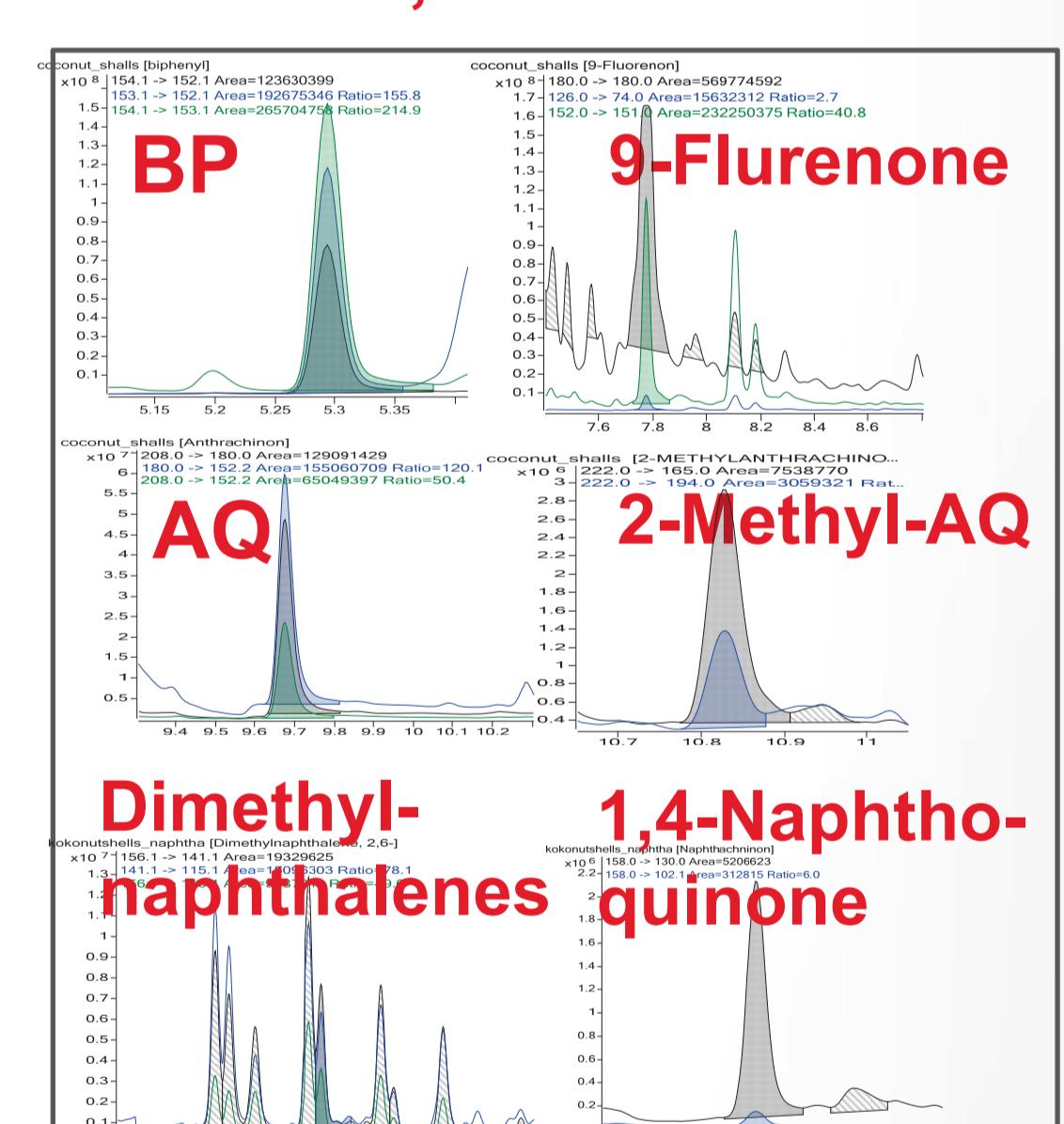


figure 5. some positive findings in the smoke of burned coconut shells

Through this analysis of the coconut shell smoke we could prove that AQ and BP as well as other SPAHS can be developed during the combustion or drying process in coconut oil production.

The answer to why anthracene is so much more easily oxidized than other PAHs lies in its particular linear 3-ring structure with double symmetry, which is the cause of two delocalized π-electrons in central ring pos. 9 and 10, see figure 6 [4].

The formation of AQ from 1,4-Naphthoquinone is also possible [5]. The strong lipophilic property of coconut oil explains the absorption effects of SPAHS. A big amount of AQ- and BP-free coconut oils shows that „cleaner“ production is possible.

On another hand, the current environmental situation in Southeast Asia and Africa [6] is the other well-known cause for the air contamination with aromatic contaminants because of the wide using of fossil fuels.

Conclusions

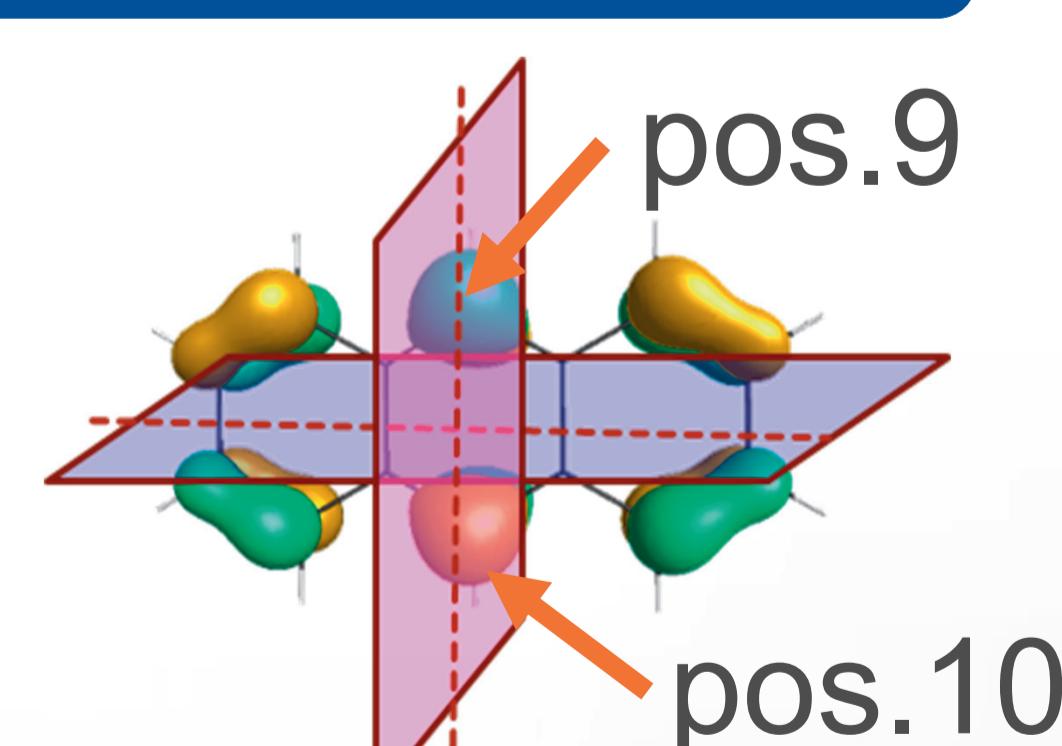
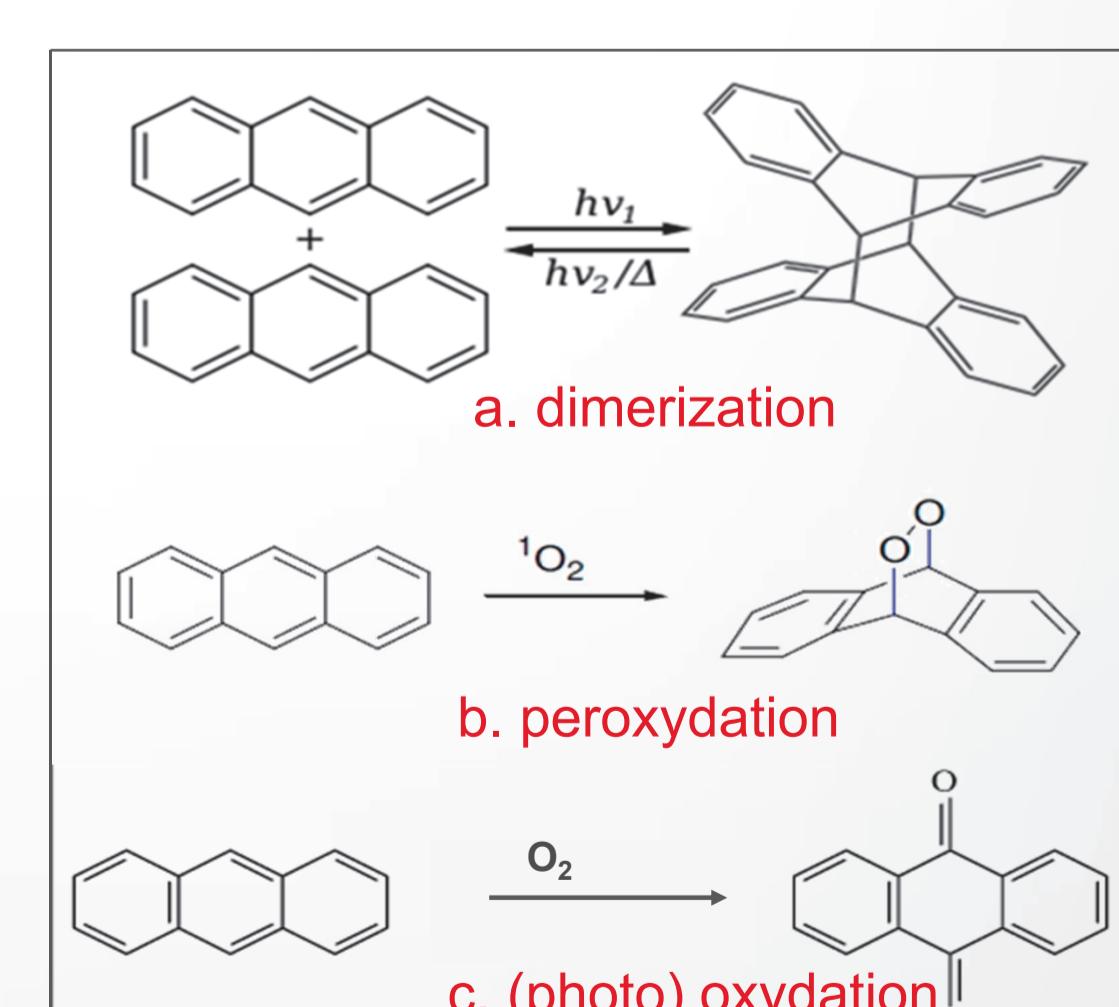


figure 6. π-electrons model and symmetric plain of AC and the typical reactions



References

- [1] Bohncke et al., Concise International Chemical Assessment Document 6. Biphenyl, WHO, 1999
- [2] Annexes Reg. 396/2005, Regulation (EC) 2015/401, Annex IIIA, Applicable from: 01/11/2014
- [3] <http://www.usessofcoconut.com/coconut-shell-charcoal/>
- [4] Fox, M., Olive, S., Photooxidation of Anthracene on Atmospheric Particulate Matter, SCIENCE, VOL. 205, 10 AUGUST 1979
- [5] <https://en.wikipedia.org/wiki/1,4-Naphthoquinone>
- [6] WHO's Ambient Urban Air Pollution –Database Update 2016 http://www.who.int/topics/air_pollution/en/