

THE USE OF MODIFIED CARBON AS SELECTIVE ADSORBENTS FOR OLIVE OILS AROMA EXTRACTION

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Introduction

The most used extraction technique for volatile compounds is dynamic headspace sampling followed by GC analysis (DHS-GC) ^[1]. Two main trapping materials are usually used, Tenax and charcoal. The low production of artefacts, due to its high thermal stability associated to its low water retention makes Tenax usually the adsorbent of choice when thermal desorption is used for sample introduction into the GC system. Tenax, however mainly retains medium to high boiling points compounds whilst carbon shows a very strong adsorbent power to all classes of compounds ^[2]. If retroextraction involving a solvent is used, artefacts due to high desorption temperatures might be avoided ^[1]. For these reason carbon was the adsorbent used. To “tailor made” its adsorption properties, carbon surface was oxidized using HNO₃ and H₂O₂. The effect of acid groups on carbon surface, was study for olive oils aroma extraction.

Experimental

The starting carbon materials were two commercially activated carbon (Merck and Norit GAC1210).

The Merck carbon samples were submitted to treatments in HNO₃ and H₂O₂, 1M at 90°C during 1hour. Norit carbon was treated in HNO₃ 13M 90°C, 6h and in H₂O₂ 5M, 90°C during 2 hours. After each treatment, the samples were washed in water, till neutral pH and dried overnight at 110°C.

All samples were characterized by TPD (Temperature Programmed Desorption) using experimental conditions previously reported ^[3]. Textural characterization was carried out using physical adsorption of N₂ at 77K on a Micromeritics ASAP2010 instrument. Olive oil volatile were adsorbed on carbon by means of a controlled nitrogen flow bubbling through the olive oil sample (43°C) and collected on a adsorption tube filled with 0,14g of carbon. After adsorption the carbon was extracted with diethyl ether. The solutions were used for GC

after concentration under a gentle stream of nitrogen.

GC was performed on a CE Instrument Mega series using a DB-Wax capillary column 50m x 1.0 m i.d. Temperature program was 40°C for 10 min followed by a linear increase of 2.4°Cmin⁻¹ until 80°C and then 3.7°Cmin⁻¹ up to 210°C. Detector was 375°C and injector 250°C.

To evaluate extraction yield, four different compounds with different functional groups were chosen: 1-pentene-3-one; hexanal; trans-2-hexenal; 1-hexanol.

The GC calibration curves of the above mentioned compounds were performed by diluting their known increasing quantities in a mixture of pentane:ether. Isobutyl acetate was used as internal standard.

All compounds showed significant linear correlation. The regression coefficients ranged from 0.997 to 0.999. To verify recovery of each component, when the different carbons were used, a mixture of the compounds under study were added to fresh refined olive oil in increasing concentrations. Samples were submitted to volatile extraction by DHS, adsorbed in the different carbons, retroextracted with ether and analysed by GC. Recovery was calculated from the ratio of the slopes of the regression straight, of each analyte extracted from the oil, and the corresponding calibration straight line.

Results and Discussion

The results of textural characterisation are presented on table 1. Norit and Merck carbons are essentially microporous carbons however the Norit carbon showed some mesoporosity, which is not present for the Merck carbon. The TPD analysis (figure 1) has shown, that Merck carbon when treated with HNO₃ 1M presents more carboxylic acids, anhydrides and lactones (CO₂ decomposition) and phenols (CO decomposition) whilst the one treated with H₂O₂ has less acidic anhydrides and phenol sites. The untreated sample has no acidic groups on the surface exhibiting basic properties.

Oxidation of Norit carbon with HNO₃ 13M shows a pronounced increase in the content of acidic groups namely carboxylic, anhydrides, lactones and phenols. This carbon exhibits a strong acidic character when compared to the same carbon treated with H₂O₂ (Figure 2).

Among all carbon samples (Norit and Merck), the carbon treated with HNO₃ (13 M) exhibits the strongest acidic character (Figure 1 and 2).

When olive oil samples were added with increasing amounts of the selected compounds, extraction yield was different. According to table 2 two compounds are preferentially extracted, 1-pentene-3-one and trans-2-hexenal. Both compounds have an insaturation which suggests that the presence of a double bond is determinant for adsorption. The basic characteristic of the surface seems to improve 1-pentene-3-one and trans-2-hexenal adsorption. When Hexanal and hexanol are compared we might conclude that hexanol is not affected by any of the different groups present at the carbon surface whilst hexanal (with an electrophilic carbon) behaves differently.

On the other hand, the C₅ molecule is rather adsorbed by the more microporous carbon (Merck) which suggests that molecule size has an important role.

Conclusion

Different charcoals showed different adsorption towards the different compounds (table 2). Recoveries ranged from 5% to 40% for the C₆ compounds depending on the presence of insaturation and/or the functional group. For the C₅ ketone recoveries ranged from 82 to 100% and differences seem to be related to the increasing of microporous area of carbon samples (table 1) and decreasing of surface oxygen content (Figure 1 and 2).

References

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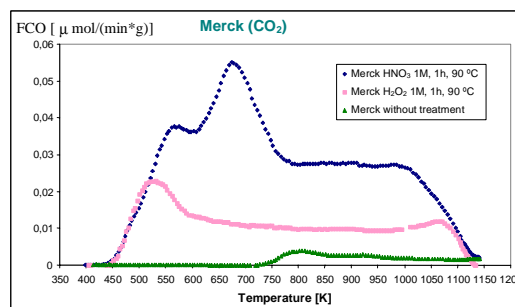
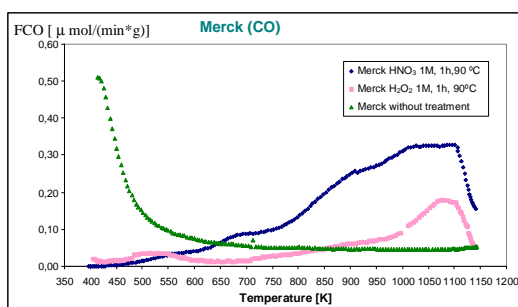


Figure 1 - TPD spectra of Merck carbon

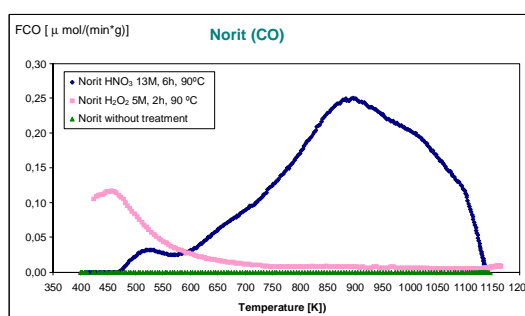
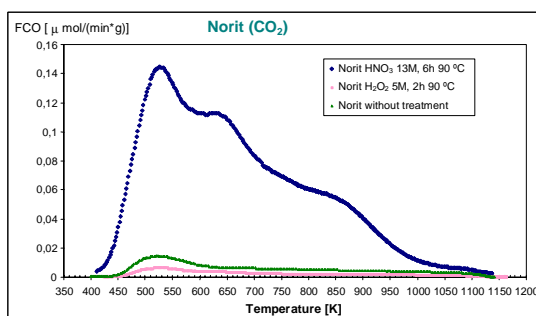


Figure 2 - TPD spectra of Norit Carbon

Table 1 – Carbons Textural Characterization

| Carbon | Total pore volume (cm ³ /g) | Surface Area (BET) (m ² /g) |
|--|---|---|
| Merck without treatment | 0,73 | 1399 |
| Merck HNO ₃ 1M | 0,61 | 1260 |
| Merck H ₂ O ₂ 1M | 0,66 | 1168 |
| Norit without treatment | 0,54 | 888 |
| Norit HNO ₃ 13M | 0,53 | 847 |
| Norit H ₂ O ₂ 5M | 0,50 | 854 |

Table 2 - % Extraction yield found for the selected compounds with the different carbon samples

| | 1-pentene-3-one | Hexanal | Trans-2-hexenal | 1-hexanol |
|--|-----------------|---------|-----------------|-----------|
| Merck without treatment | ~100% | 22% | 32% | 9% |
| Merck HNO ₃ 1M | 82% | 5 % | 27% | 7% |
| Merck H ₂ O ₂ 1M | ~100% | 8% | 40% | 10% |
| Norit without treatment | 55% | 11% | 21% | 9% |
| Norit HNO ₃ 13M | 30% | 15% | 39% | 10% |
| Norit H ₂ O ₂ 5M | 64% | 20% | 21% | 10% |