Analytical separation

Approximately 30 mg of WSOCE was separated according to a technique, first described by Davis et al. (2000).

We used a Tosoh TSK-DEAE-SPQ gels column (7.5mmID, 7.5cm length). The mobile phase was deionized water. From 0.2 minutes to 2 minutes, the solvent composition was linearly increased to 0.1M NaClO4/0.02M TRIS, 10% methanol. The eluent was kept constant until 10 minutes when the eluent was linearly changed to the final composition at 15 minutes of 0.1M NaClO4/0.02M TRIS and 10% methanol. The pH was constant at 8. The HPLC system used was a AB 1050 system with a Diode Array Detector. The detection wavelength was set at 254nm.

Results

We obtain the results very similar to the example by Davis et al. for WSOCE extracts of aerosol samples from Yosemite National Park and for California fog samples.

Separations of WSOCE samples from Yosemite National Park show 3 fractions with fraction 3 having the highest absorbance peak. Interestingly, there are some minor differences in the depicted chromatograms with the sample from August 14 resuming more distinct peaks in the second fraction than the sample from July 30. In both fractions, the neutral/basic fraction absorption peak is much smaller than the other fractions.

Problems?

Because few results have been published showing retention times of individual compounds analyzed by this approach, we conducted tests for several atmospherically relevant organic compounds. Unfortunately, results of these tests often appear to contradict the usual published classification scheme: neutral/basic, meso-diarylcarboxyl acid, and polysaccharide fractions.

Based on the chromatograms of the California fog samples, the neutral/basic fraction (fraction 1) is the largest fraction, followed by fraction 2 and then fraction 3. The results for the WSOCE samples from Yosemite National Park are similar, with fraction 1 being the largest, followed by fractions 2 and 3. The polysaccharide fraction (fraction 3) is the smallest fraction in both cases.

Summary

The separation appears to give similar results for different studies.

1. The classification of the observed fractions as neutral/basic, meso-diarylcarboxyl acid, and polysaccharide appears incorrect. Single compounds taken from fractions without carbohydrates often elute in the second or third fractions.

2. Charged separation might not be the only factor determining retention times as indicated by the long retention times of cationic polyaromatics.

3. UV detection to determine the fractions is problematic due to low absorption efficiencies at 254nm of many important organic compounds, including carbohydrates. On the other hand, phenolic compounds, which might elute in wrong fractions, present very high absorption efficiencies at 254nm.

4. Although classification problems might exist for fog samples due to the abundance of small molecular weight carbohydrates and carboxylic acids, the separation technique might give more reasonable picture for aerosol extracts.

5. Large, polyaromatic molecules like the modular humic acids compounds, do not elute completely off the column and might explain the losses in the experiment with two low molecular weight compound losses due to purging of the eluent prior to TOC analysis.

Further testing is warranted to evaluate the uncertainties of these techniques.

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References


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