PRAM: Polarity Rapid Assessment Method

Background

This is intended to provide a rapid method for determining some useful properties for natural organic matter in water.

This approach was first investigated at UMass by Bree Carlson, an MS student working with Dave Reckhow. The work was funded through a 2001 MA WRRC grant. Carlson explored the use of 7 different phases (C18, C8, CN, NH2, Diol, Phenol, and SAX) in 3mL syringe barrel cartridges (500 mL). UV absorbance at 254nm and 272nm was monitored in the SPE effluents (Carlson & Reckhow, 2003). However, it wasn't until Fernando Rosario-Ortiz focused his PhD (completed 2006, advisor: Irwin Suffet) on this approach that the method was developed to a point where it could be published (Rosario-Ortiz et al., 2004, 2007). These authors gave their method the name PRAM. Rosario-Ortiz used the same SPE phases as Carlson, except he included silica, C2 and did not include phenol. He also worked with smaller tubes (100 mg).

Method Description

This method is largely based on the work of Rosario-Ortiz and colleagues (2004, 2007). We have incorporated several departures and clarifications. These are summarized as follows:

- Cartridges are purchased separately as the SPE kit once offered by Alltech is no longer available
- The C2 SPE cartridge has been dropped, because it is no longer commercially available.
- Supelco is used as the supplier rather than Alltech for reasons of convenience and economy
- Larger cartridges 500 mg are used instead of the 100 mg size so that larger sample effluent volumes are available. This facilitates DOC analysis.
- DOC is measured in addition to UV absorbance
- Low pH may be used for some (C18 and possibly C8) whereas neutral pHs for others (e.g, SAX). This is to improve retention and was not fully specified in by Rosario-Ortiz
- We may also use SCX at low pH in an effort to get good base separation

Recommended Cartridges and pH conditions

- Acidic: C-18, C-8, CN, Diol, Ph, Silica, SCX
- Neutral: SAX, NH_2

The recommended method is described below:

Sample Preparation

1. Secure about 500 mL of sample
2. Bring 350 mL of the sample down to a pH of about 2.5 by adding 3.5 mL of a 1M acidic phosphate buffer[1]. Check final pH and record a full UV-Vis scan (~ 3mL used)
3. With the remaining 150 mL adjust pH to 7.0 with 1.5 mL of a 1M neutral phosphate buffer[2]. Check final pH, and record a full UV-Vis scan (~3 mL used)
4. Look for obvious signs of particles or precipitate in either. Filter (GF/C) if there appears to be some.

Setup and Cartridge Preparation

5. Warm up the Agilent Diode Array Spectrophotometer
6. Make a 1:100 dilution of both buffers in Milli-Q water for rinsing purposes
7. Fill a 25 mL glass syringe with methanol
8. Connect it to the red SPE flange and wedge it in to the top of the first cartridge.
9. Attach the cartridge to a clamp pointing down into a waste beaker and force about 20 mL of methanol through
10. Fill a 60 mL syringe with a 1:100 dilution of the acidic buffer and force the full volume though the syringe and into waste

Blank Collection

11. Fill a 60 mL plastic syringe with a 1:100 dilution of the acidic buffer and secure it in place on the KDS100 syringe pump (Cole Parmer 74900 series). Enter the syringe diameter (see table in Manual).
12. Connect the first cartridge to the syringe and connect the cartridge effluent to the influent tube on the flow-through cuvette. Connect the cuvette effluent tube to a waste beaker.
13. Start the syringe pump at 6 mL/min and monitor the absorbance at 200 nm to be sure that the methanol has been completely flushed. Collect a sample for TOC analysis from the effluent line once the 200 nm absorbance has returned to a steady level. Continuing running the pump for another 30 mL and collect a second sample for TOC. Refill the syringe with diluted buffer when needed.

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[1] Acidic buffer prepared by adding 31.4 millimoles of H_3PO_4 to 68.6 millimoles of NaH_2PO_4 (or KH_2PO_4) and dilute to 100 mL with milli-Q water.

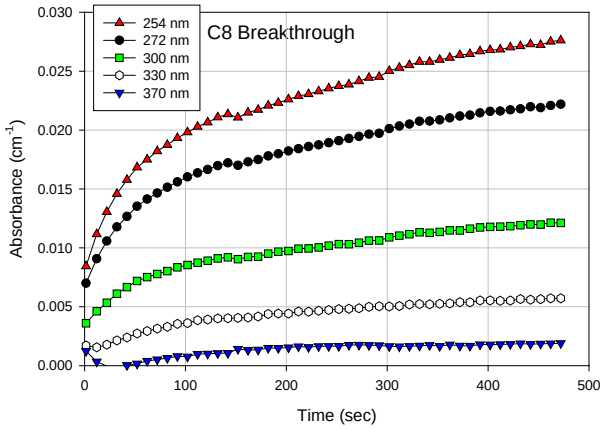
[2] Neutral buffer prepared by adding 61.3 millimoles of NaH_2PO_4 (or KH_2PO_4) to 38.7 millimoles of Na_2HPO_4 (or K_2HPO_4) and dilute to 100 mL with milli-Q water.

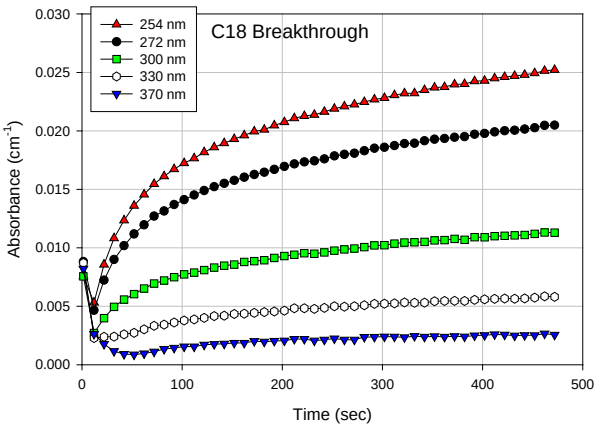
Sample Processing and Data Collection

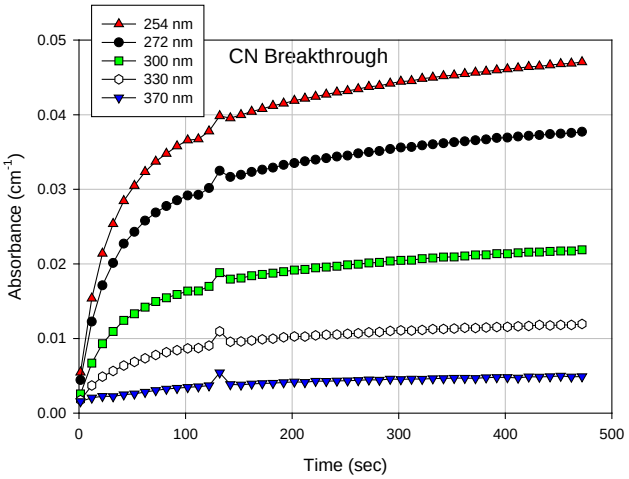
14. Replace the 60 mL syringe with another one that contains the acidified sample to be tested.
15. Run the syringe pump at 6 mL/min for 4 minutes, monitoring the absorbance at 10 second intervals (kinetics mode). Save absorbance traces at 254 nm, 272 nm, 300 nm, 330 nm and 370 nm.
16. After 4 minutes place the cuvette effluent line into a receiving vessel and collect the effluent for subsequent TOC analysis for the next 4 minutes.
17. After the full 8 minutes of pumping, stop the test and repeat the full procedure with the next cartridge starting with the methanol rinse. Use the appropriate buffer (buffered sample and rinse water) for the particular cartridge (neutral for SAX and NH_2, acidic for all others).

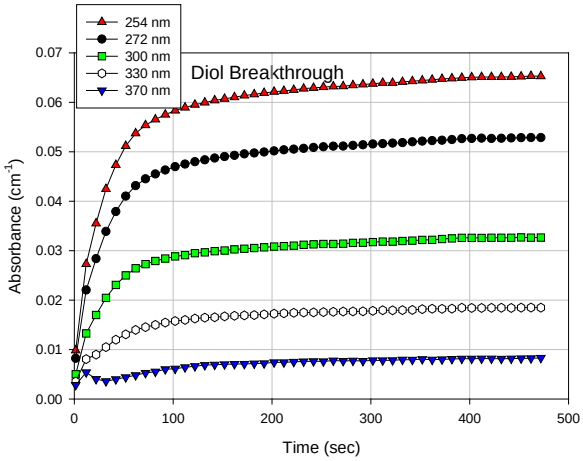
DOC Analysis and Data Presentation

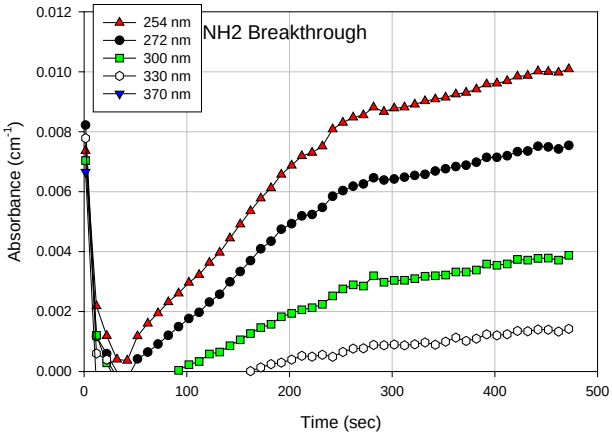
18. Measure DOC on all samples (including the original buffered samples) using the TOCV analyzer
19. Determine steady state absorbance values for each resin and each wavelength. This will first require you inspect all absorbance vs time graphs and note any anomalies. In most cases you should see relatively consistent values between 4 and 8 minutes. In this case you should average these values to determine the breakthrough absorbances
20. Calculate fraction retained for all 9 resins at all 5 wavelengths and for DOC (54 values)
21. Present these in tabular and graphical form (bar charts)

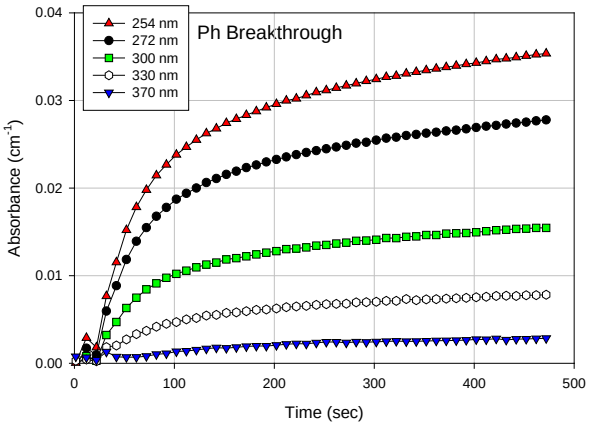


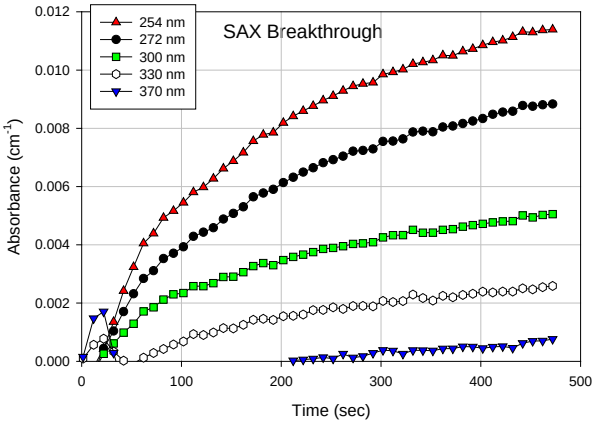


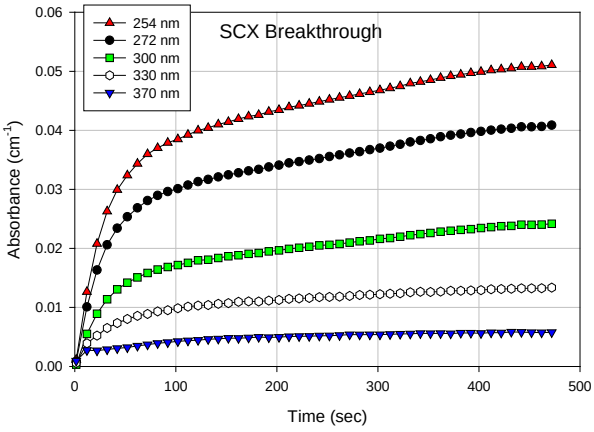

254 nm
272 nm
300 nm
330 nm
370 nm
CN Breakthrough
Absorbance (cm-1)
Time (sec)

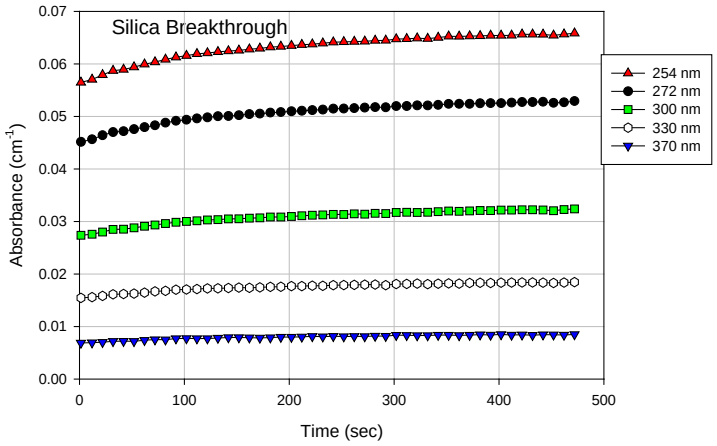

254 nm
272 nm
300 nm
330 nm
370 nm
Diol Breakthrough
Absorbance (cm-1)
Time (sec)


254 nm
272 nm
300 nm
330 nm
370 nm
NH2 Breakthrough
Absorbance (cm-1)
Time (sec)

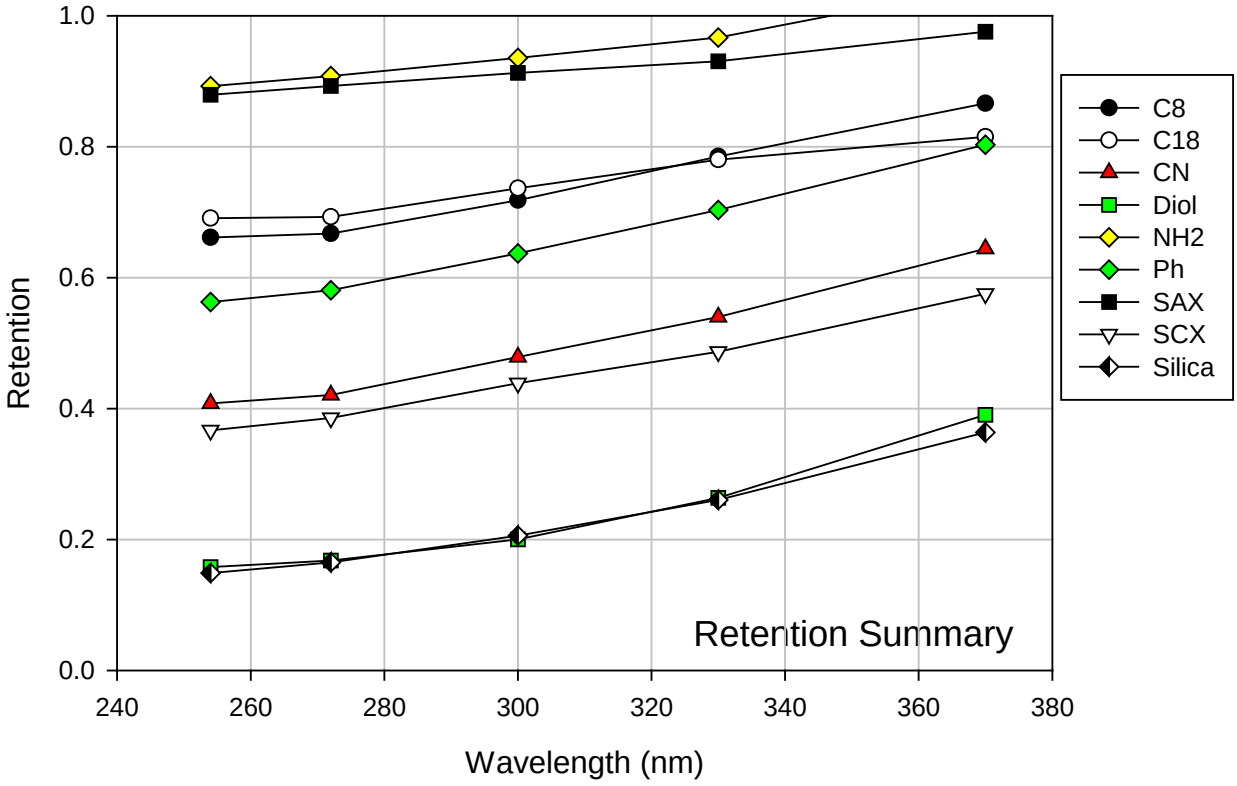

254 nm
272 nm
300 nm
330 nm
370 nm
Ph Breakthrough
Absorbance (cm-1)
Time (sec)


254 nm
272 nm
300 nm
330 nm
370 nm
SAX Breakthrough
Absorbance (cm-1)
Time (sec)

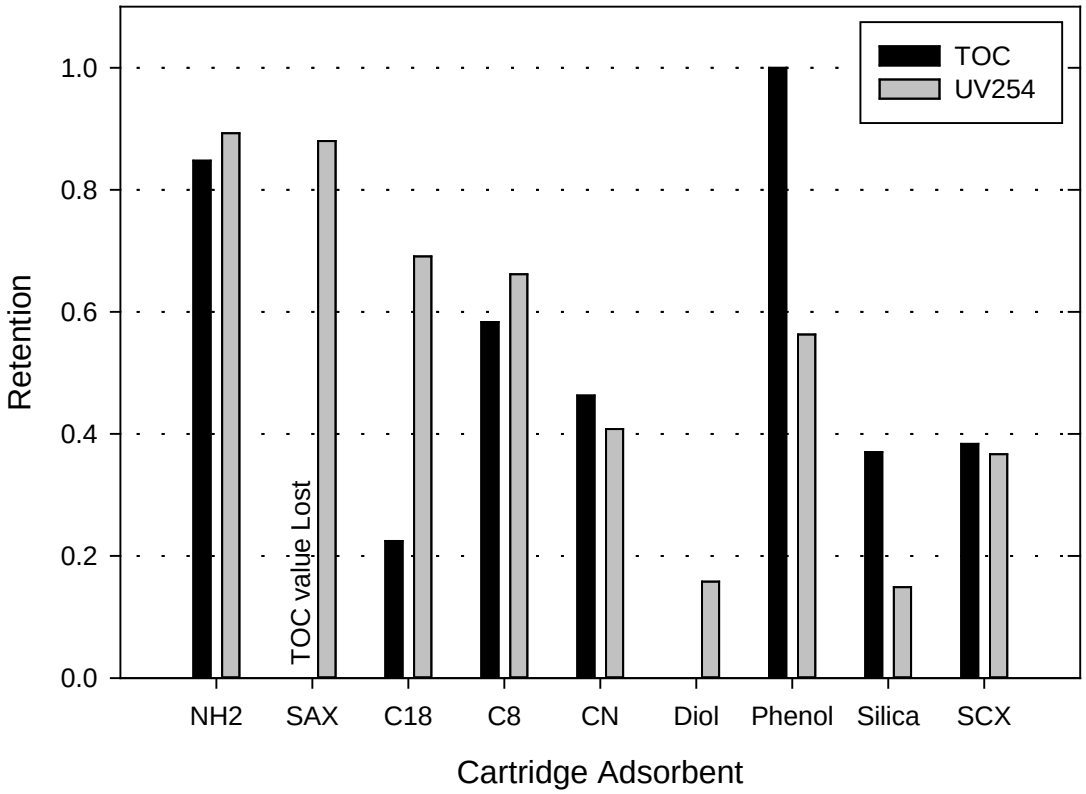

254 nm
272 nm
300 nm
330 nm
370 nm
SCX Breakthrough
Absorbance (cm-1)
Time (sec)



Example Set of Breakthrough Curves



Example Retention Data Summary


TOC
UV254
Retention
1.0
0.8
0.6
0.4
0.2
0.0
TOC value Lost
NH2
SAX
C18
C8
CN
Diol
Phenol
Silica
SCX
Cartridge Adsorbent