The Complex Nature of Organic Matter in South Africa’s Water Systems

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Presentation Outline

• Introduction
• Changes in Water Quality
• Analytical Techniques
• Effect of treating water containing organics
• Progress to date
• Research questions that still need to be answered
• Conclusion
Presentation Outline – Analytical Techniques

• Analytical Techniques
  • Oxygen Absorbed (OA)
  • Total Organic Carbon (TOC)
  • Gas Chromatography (GC)
  • High Performance Liquid Chromatography (HPLC)
  • Infrared Spectroscopy
  • Liquid Chromatography – Organic Carbon Detection (LC-OCD)
  • Fluorescent Excitation Emission Matrices (FEEM)
Introduction

• Complexity of organic compounds in natural water (dissolved, suspended, different oxidation states which change, seasonal)

• Knowledge of organic compound type

• Disruption of water treatment processes

• Sand filters (fouling)

• Ion exchange resins (reduced capacity)

• Analytical techniques
Changes in water Quality
Analytical Techniques

- **Oxygen Absorbed**

- **Principle of Oxygen Absorbed:** When a water sample is mixed with potassium permanganate in acid solution, a certain amount of oxygen is taken up from the permanganate by oxidisable matter in the sample.
  
  - Very pure waters absorb little oxygen
  
  - Waters polluted with animal or vegetable organic matter absorb considerable quantities.

- **Total Organic Carbon**

  - Three methods: Wet oxidation (Not suitable for VOC’s)
  
  - High Temperature Combustion
  
  - Persulfate-Ultraviolet or Heated-Persulfate Oxidation method (10 * more sensitive)
In GC a mobile phase and a stationary phase are used to separate individual compounds.

When the sample solution is introduced into the column, the organic compounds are vaporised and moved through the column by the carrier gas (mobile phase).

They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phases.
Block diagram showing the components of an HPLC instrument
Advantages and disadvantages of GC

• **Advantages**
  - Rapid analysis
  - High efficiency leading to high resolution
  - Sensitive detectors (ppb)
  - Non-destructive, enabling coupling to mass spectrometry
  - High quantitative accuracy (typically <1% RSD)
  - Rugged and reliable techniques
  - Well established with extensive literature and applications

• **Disadvantages**
  - Limited to volatile samples
  - Not suitable for samples that degrade at high temperatures
  - Requires MS detector for analyte characterisation
Advantages and Disadvantages of HPLC

Advantages

• There are no volatility issues, however the analyte must be soluble in the mobile phase

• Can analyse samples over a wide polarity range and can analyse ionic samples

• HPLC is normally performed at room temperature, hence samples that are thermally labile can be analysed.

Disadvantages

• It is a much slower technique than GC

• It is subject to a greater peak or band broadening and therefore lower resolution than GC
Molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.
LC-OCD Instrument
Liquid Chromatography – Organic Carbon Detection

- This instrument has 3 detectors namely: The first detector after chromatographic separation is nondestructive, fixed wavelength UV-detection (UVD 254 nm, typeS-200, [6,7]) and thereafter the organic carbon detector (OCD, [6,7]). For nitrogen detection a side stream is diverted after UVD with a restricted flow rate 0.1 mL/min (back pressure-driven) for nitrogen analysis.

- The nitrogen detection is carried out by passing through a capillary UV lamp (DONOX converting N containing compounds to nitrate) and 2\textsuperscript{nd} UV detection measuring at 220 nm (DON).

- LC-OCD separates chromatographable organic carbon (CDOC) into fractions of different molecular weights. The nonchromatographable organic carbon is referred to as hydrophobic organic carbon (HOC).
LC-OCD (contd)

• CDOC is fractionated into:
  • biopolymers (BP) - non-ionic, hydrophilic fraction with a high molecular weight ($\geq 10,000$ g/mol)
  • humic substances (HS) - (450-1000 g/mol), which are a heterogeneous fraction of similar chemical composition but varying molecular size and aromaticity
  • Building blocks (BB) - degradation products of HS, which is HS-like material of lower molecular weight (300-450 g/mol)
  • Low Molecular Weight (LMW) neutrals - low molecular weight and a low ion density and the fraction is hydrophilic to amphiphilic
LC-OCD (contd)
LC-OCD output

![LC-OCD Graph]

- **Building Blocks**: 300 µg/L, 20%
- **Humics**: 665 µg/L, 43%
- **LMM Acids and HS**: 17 µg/L, 1%
- **Biopolymers**: 98 µg/L, 6.0%
- **Neutrals**: 331 µg/L, 22%
LC-OCD Organic carbon detector

• Principle used is (SEC) Size Exclusion Chromatography

• Comprised of:
  • Graentzel Thin-film detector – Separates inorganic carbon dioxide (released) from organic carbon dioxide
  • Organic carbon then enters Vigreux condensers – removes moisture
  • Non-dispersive IR Detector - used for detection of organic carbon
  • Doc Labor
## Table 1: Excitation and Emission Wavelengths for different groups of organic compounds

<table>
<thead>
<tr>
<th>Group of Compounds</th>
<th>Excitation wavelength (nm)</th>
<th>Emission wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic proteins</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Soluble microbial by-products</td>
<td>280</td>
<td>380</td>
</tr>
<tr>
<td>Humic acid-like organics</td>
<td>250</td>
<td>280</td>
</tr>
<tr>
<td>Humic Acids, Hydrophobic acids</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>Fulvic acid-like molecules</td>
<td>214</td>
<td>400</td>
</tr>
</tbody>
</table>
Fluorescent Excitation Emission Matrices (FEEM) continued
Effect of treating water containing organics

- Chlorination – harmful disinfection by-products
  - Trihalomethanes (THMs)
  - Halo-acetic acids (HAA)
- NOM inhibits the formation of precipitation precursors which are required in drinking water treatment
- Aesthetics of water
- NOM also promotes bacterial growth
Progress to Date

• Building up a database of organic profiles using FEEM (UJ) and LC-OCD (Eskom)

• Comparison between FEEM and LC-OCD results

• Looking at alternative water treatment methods based on organic analyses, however there are huge cost implications, hence progress is slow.
Research Questions which still need to be answered

• Should the amount and composition of the natural organic matter (NOM) be changed at the beginning of the water treatment process?

  • Research has been carried out using different pre-treatment techniques such as ion exchange in fluidised form (FIX) to modify the character of NOM which did alter the downstream treatment [10] but this has not been done on South African waters.

• The development of a fully integrated water treatment regime, taking organics, inorganics and bacterial contamination into account.
Conclusion

- Complexity of raw water treatment
  - Inconsistency of composition
  - Organic contamination not fully understood
- Worst case scenario
  - Over design
  - High expense
- LC-OCD in conjunction with FEEM
Thank you

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