



Method Development to Optimize TPH/O&G Analysis by FTIR for Bitumen in Water

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Problem Statement

‘Bitumen in Water’ analyses are widely used with SAGD produced water to aid in process control, but:

- The actual methods used vary across and even within producer facilities.
- Methods are not always practically useful.
- Lack of clear evidence that the results obtained are correlated with de-oiling process performance or boiler protection.
- Not possible to compare methods across labs/producers for industry-wide efforts at improving plant performance and evaluating de-oiling technology performance.

Introduction – Project Goals

Develop a practical (central-lab) method to measure Free & Emulsified Bitumen in Water

- **Free and emulsified** ‘oil’ content in produced water was seen as the most relevant predictor of boiler upset.
 - Current methods, due to their nature, may under-report free and emulsified oil but incorrectly include a significant component of dissolved hydrocarbon.
- For this project, the ASTM D7678 method was investigated/modified to target free and emulsified ‘oil’ measurement in SAGD samples.
- Two method options resulted:
 - FTIR method with cyclohexane (CH) extraction
 - FTIR method with tetrachloroethylene (TCE) extraction

Overview of Proposed Method:

Extraction with either CH or TCE with FTIR detection

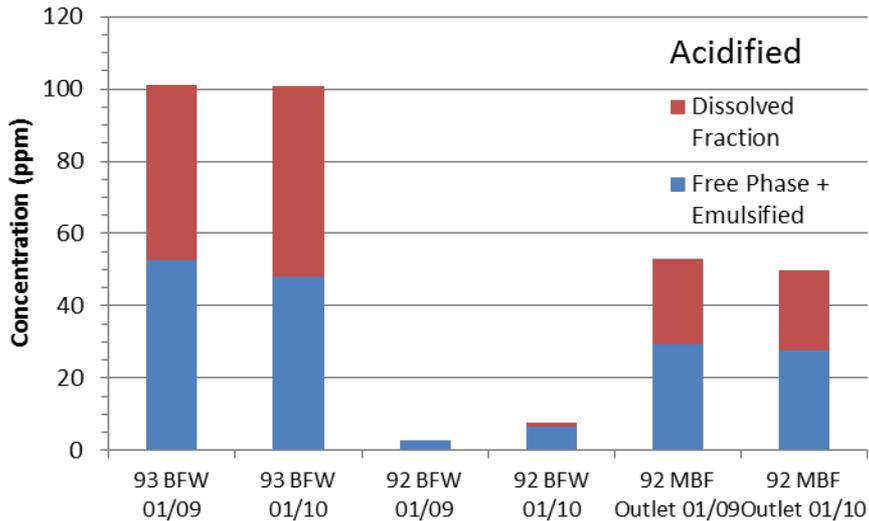
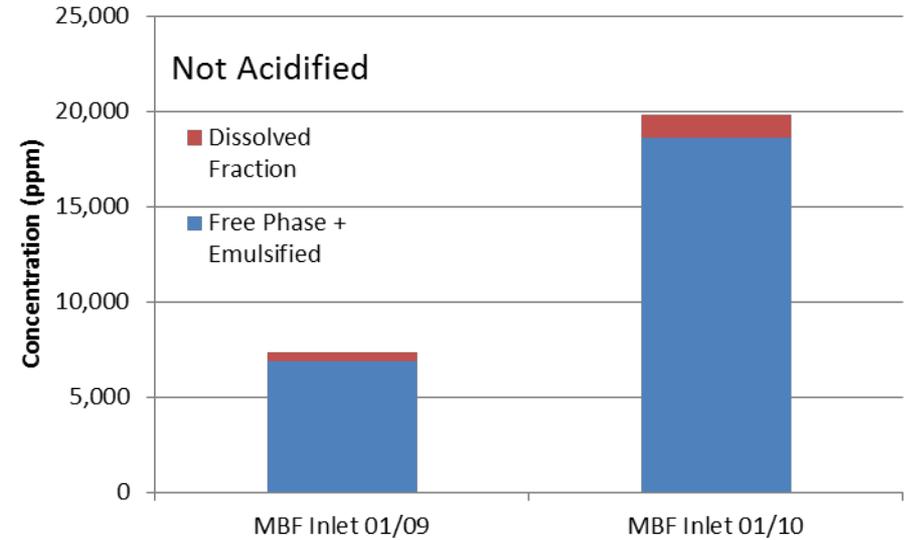
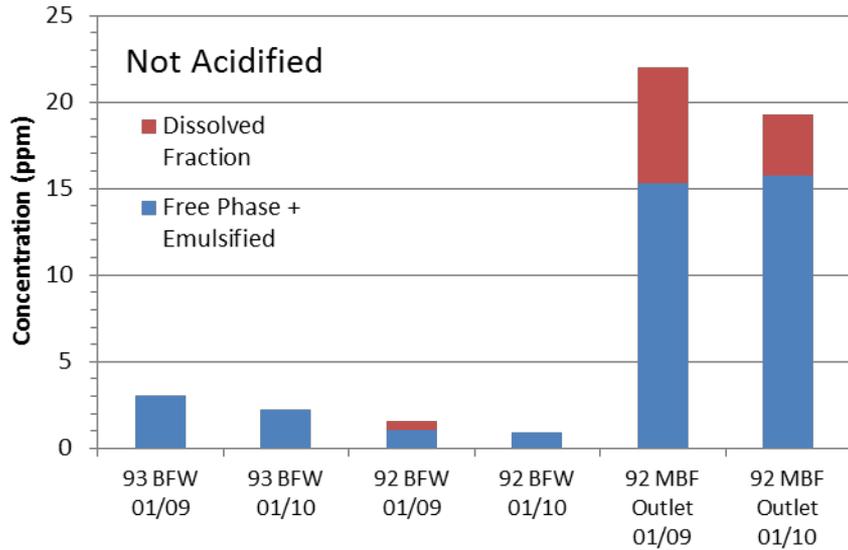
- Small sample volume, 50 mL with CH extraction, 200 mL with TCE extraction.
- No acidification, no extract sulphate drying or filtration.
- Short, low energy extraction (gentle inversions, 1-2 min.) followed by vigorous 30 min. standard extraction. Measure extracts separately.
 - First extract approximates free/emulsified oil
 - Second extract approximates dissolved hydrocarbons
- Dilute extract as necessary to bring into calibration range.
- Calibrate either to tetradecane or to bitumen with a correction factor to correlate to tetradecane equivalent.
- Calibration Ranges:
 - TCE: 1 – 125 mg/L, MDL 0.1 mg/L
 - CH: ~2-2000 mg/L, MDL ~0.5 mg/L with larger cell or larger sample

Comparison of New Method to Existing Methods

New TCE/FTIR method was compared to several existing field and lab methods

- Suncor/Surmont hexane extraction / Turner Designs fluorescence
- Suncor Total Petroleum Hydrocarbons (TPH) by FTIR
- Suncor Oil & Grease (O&G) by FTIR
- Maxxam TPH (C10 – C50) GC/FID method

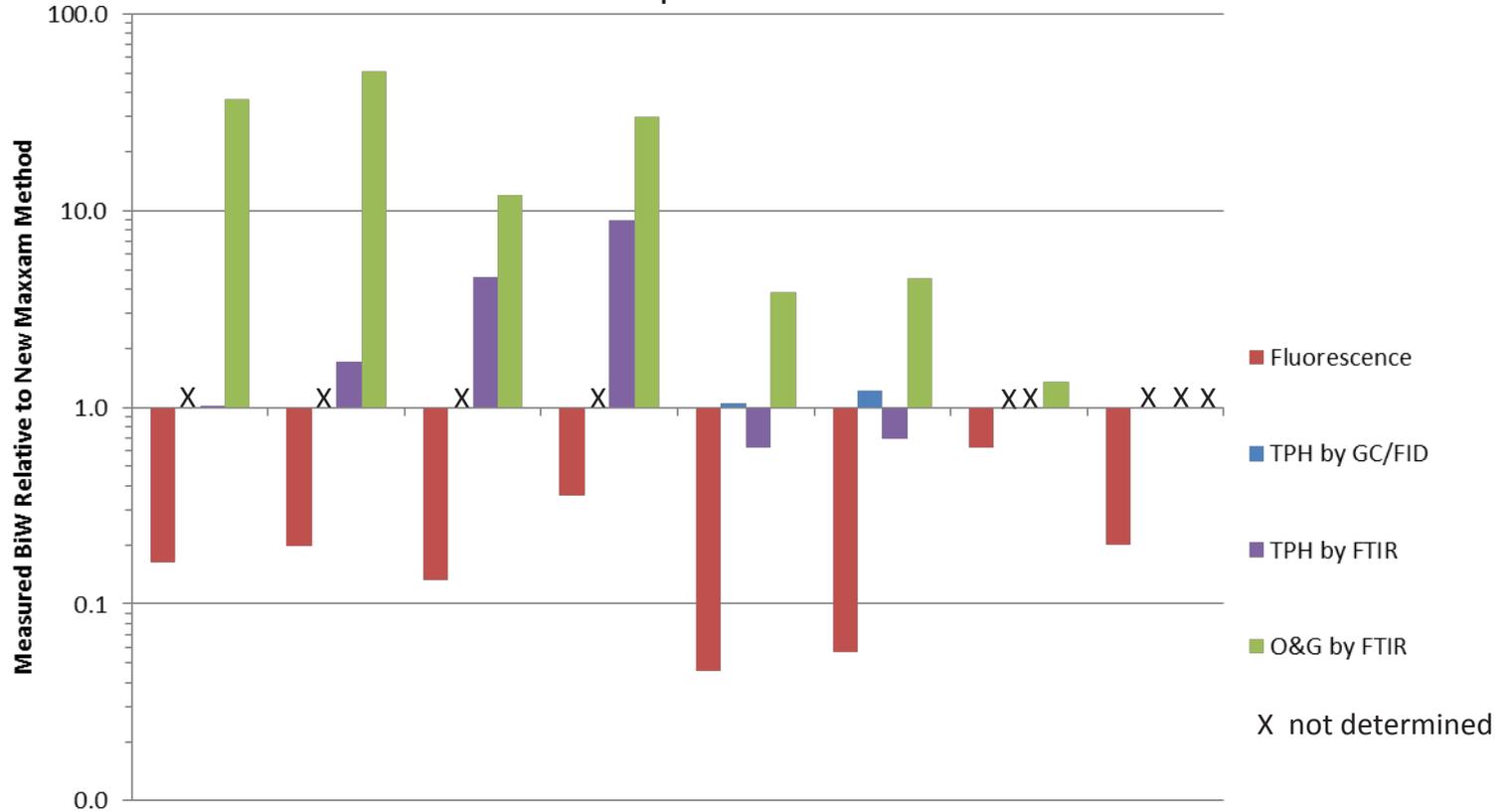
Firebag – Maxxam FTIR Method Results



Significant overall increase in measured concentration with acidification

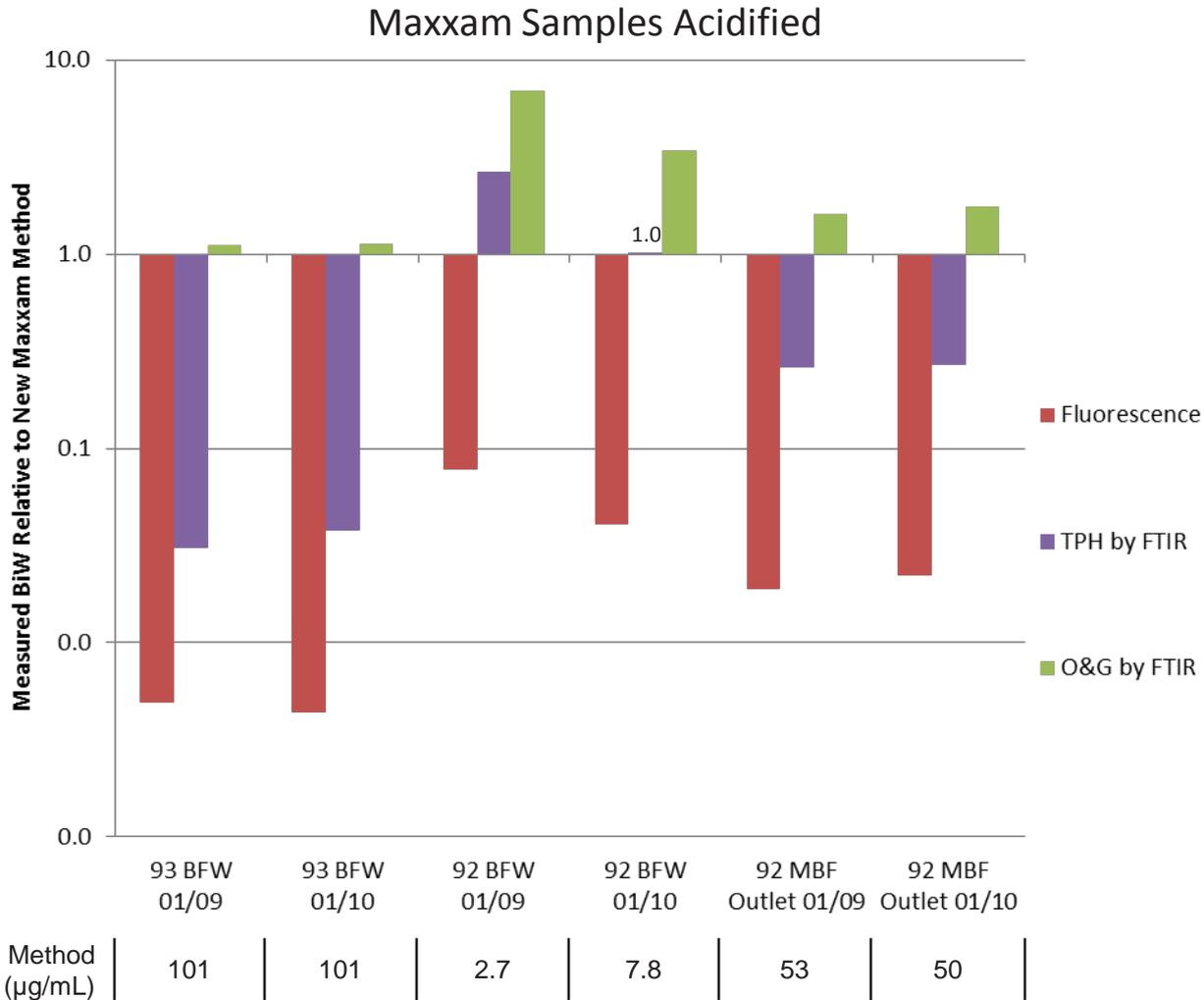
Firebag – Method Comparison

Maxxam Samples Not Acidified

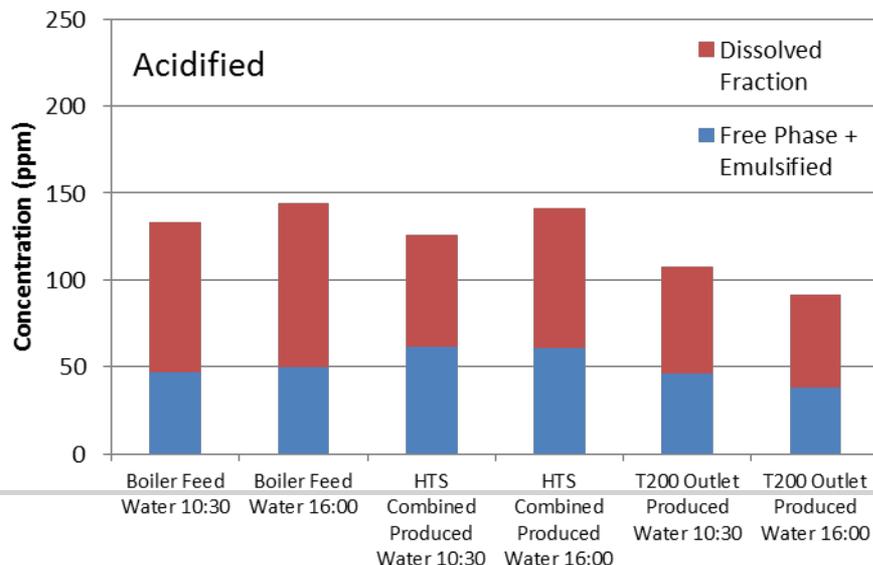
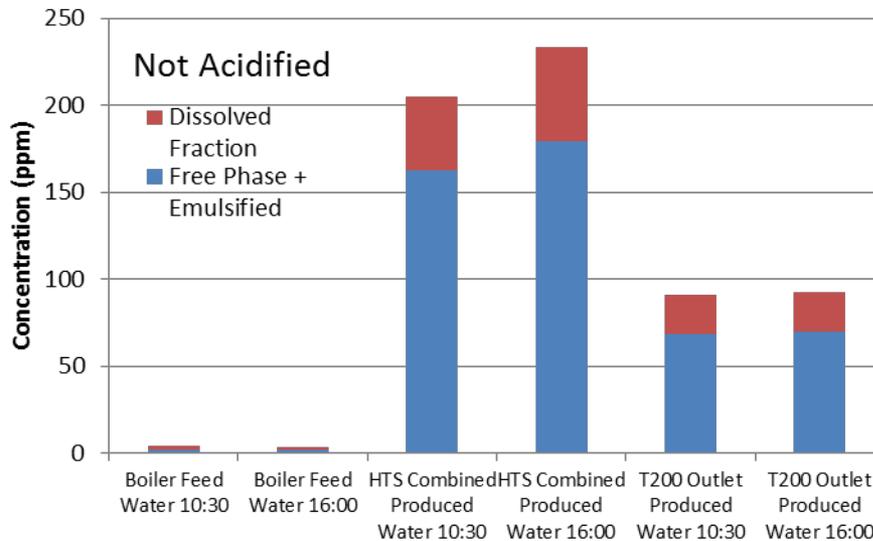


Maxxam Method (µg/mL)	93 BFW 01/09	93 BFW 01/10	92 BFW 01/09	92 BFW 01/10	92 MBF Outlet 01/09	92 MBF Outlet 01/10	MBF Inlet 01/09	MBF Inlet 01/10
	3.1	2.2	1.6	0.9	22	19	7,333	19,802

Firebag – Method Comparison



McKay River – Maxxam FTIR Method Results

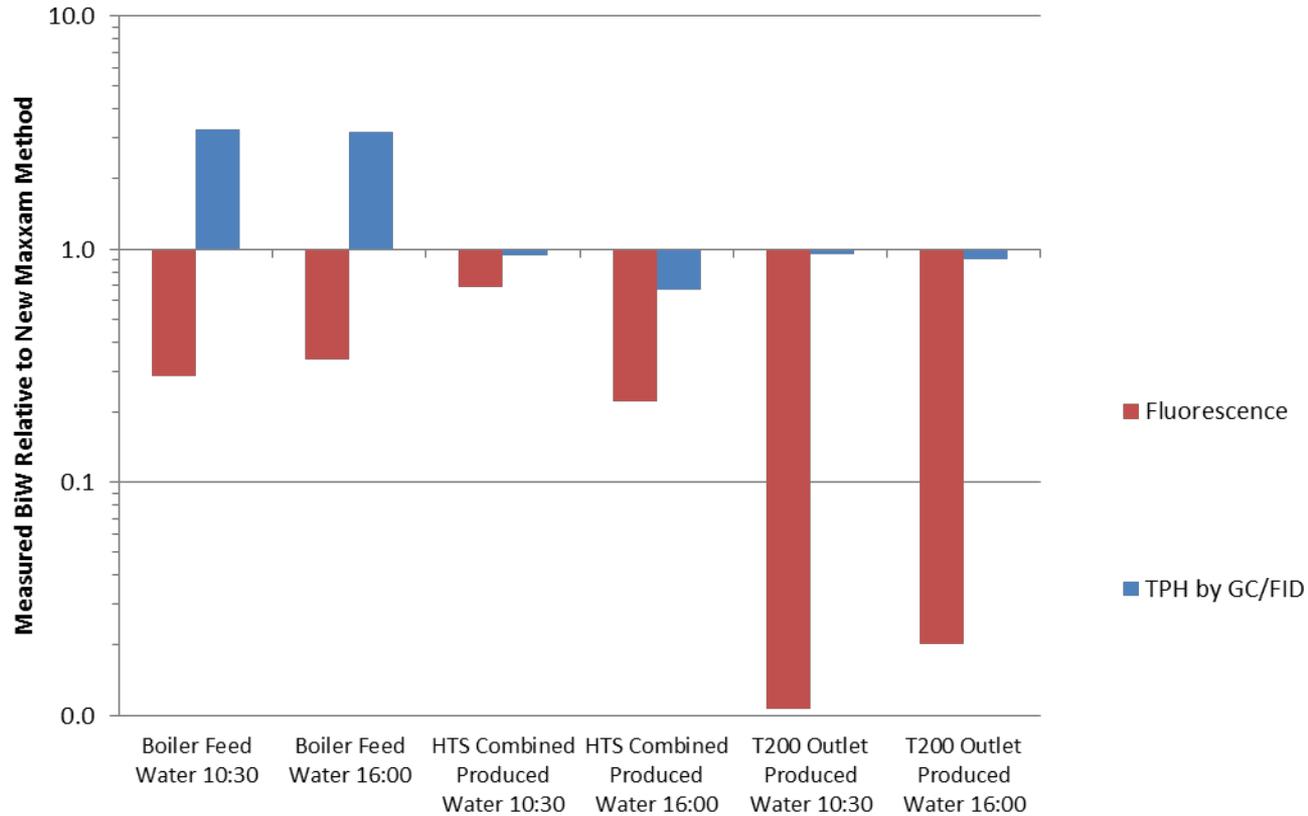


Impact of acidification:

- Variable impact on overall amount
- Significant increase in dissolved proportion

McKay River – Method Comparison

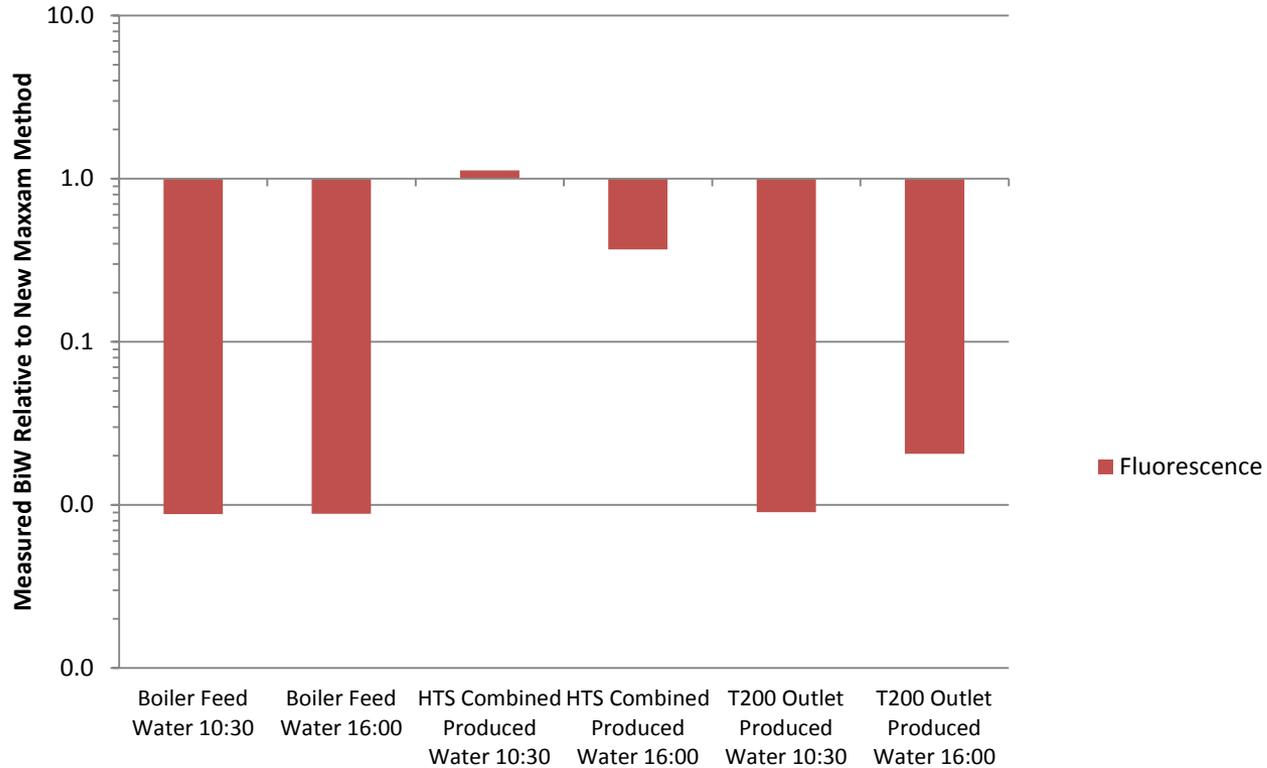
Maxxam Samples Not Acidified



Maxxam Method (µg/mL)	4.1	3.8	205	233	91	93
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McKay River – Method Comparison

Maxxam Samples Acidified

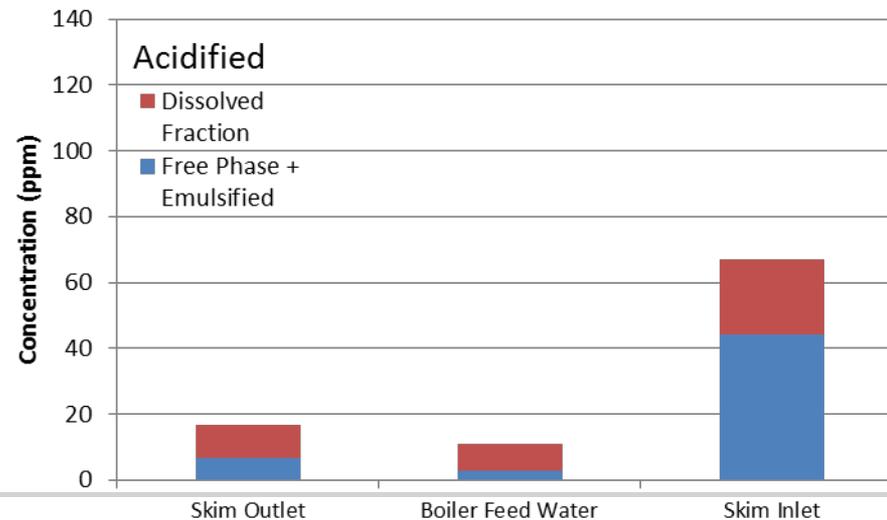
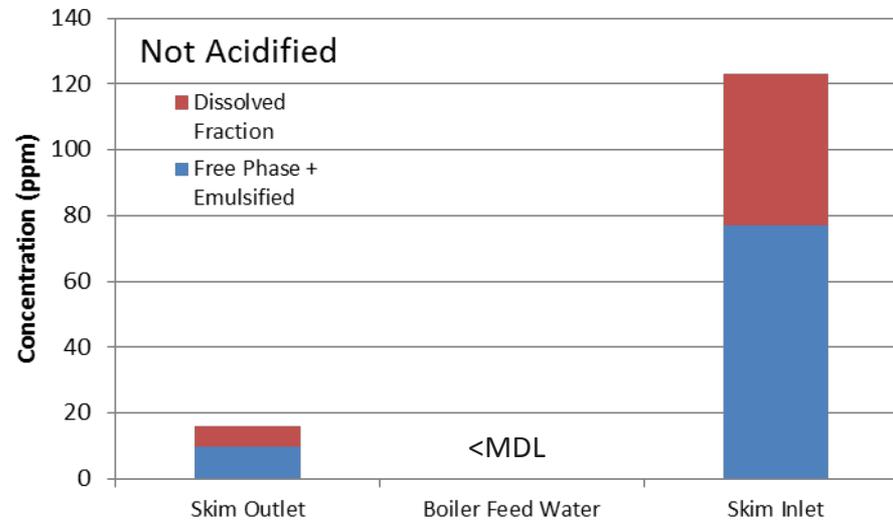


Maxxam Method (µg/mL)	133	144	126	141	108	91

Surmont – Maxxam FTIR Method Results

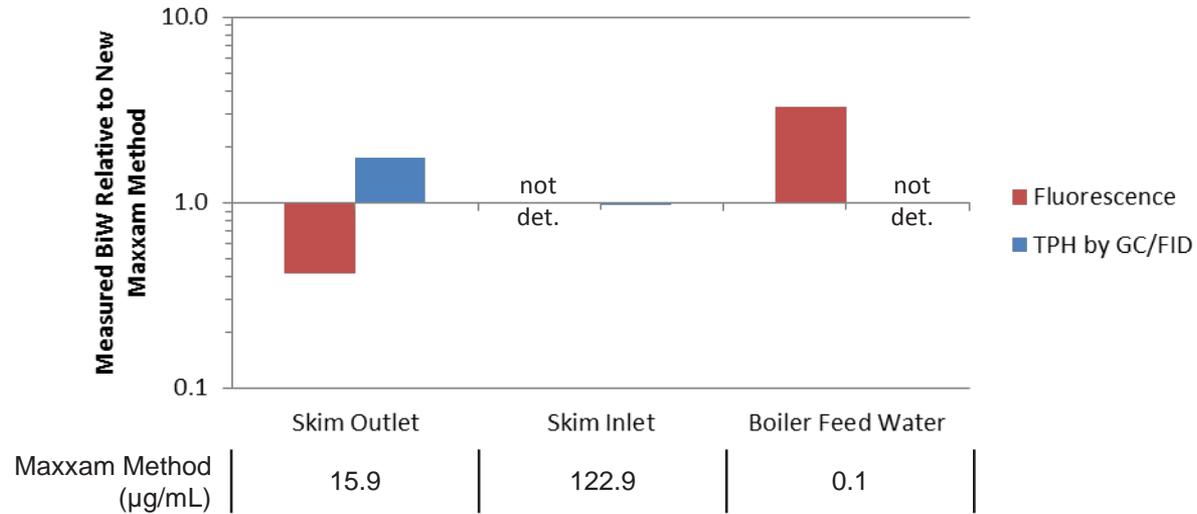
Impact of acidification:

- Variable impact on overall amount
- Variable impact on dissolved proportion

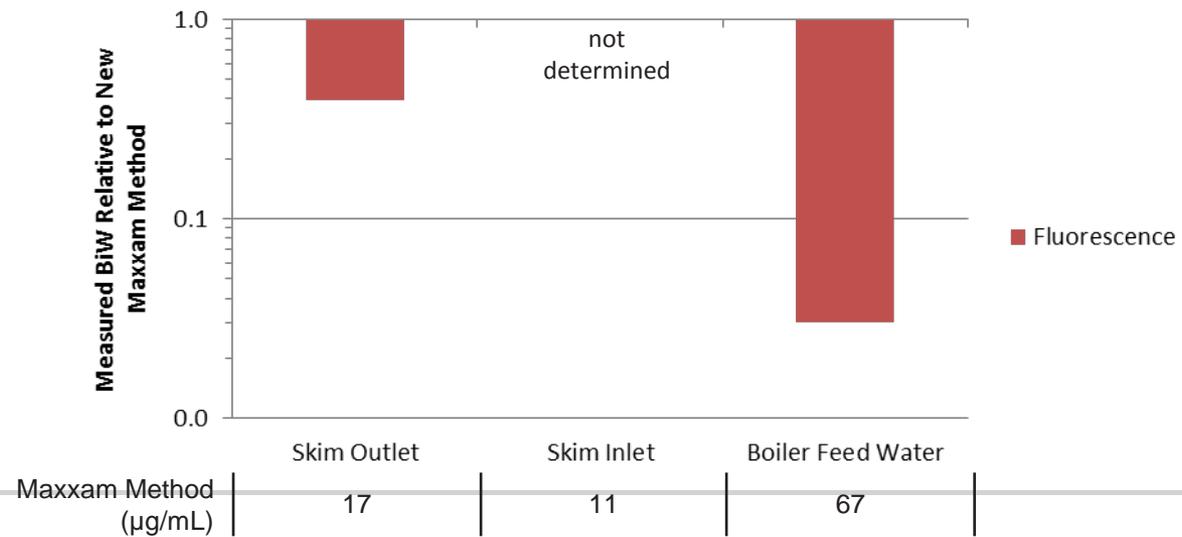


Surmont– Method Comparison

Maxxam Samples
Not Acidified



Maxxam Samples
Acidified



Method Development Findings

Existing Oil in Water methods use a variety of sample preparation techniques – these were investigated from a SAGD perspective

- **Sample Acidification** – used routinely in standard TPH methods, not recommended for SAGD samples
- **Solvent Selection** – different solvents can target different types of hydrocarbons
- **Silica Gel Treatment** – used to remove polar organics from solvent extracts, not recommended for SAGD samples
- **Filtration** – avoid if possible, particulate in extract may bias results, recommend dilution to re-dissolve particulate.
- **Sodium Sulphate Drying** – used to remove water from extracts, not recommended for TCE extracts

Sample Acidification

Acidification is used in routine TPH methods like ASTM D7678 to improve overall hydrocarbon extraction efficiency:

- Protonates acidic hydrocarbons to make them less water soluble.
- Protonated acids are more easily extracted by hydrophobic solvents.

Maxxam advises against sample acidification:

- Project objective is to better evaluate free & emulsified oil, not dissolved hydrocarbons.
- Acidification caused precipitate formation and more significant emulsion problems.
- Standard acidification protocols are typically insufficient to neutralize high pH produced water - final pH is variable
 - Maxxam's acidification protocol (neutral pH) required significantly more acid for these samples than was used in Suncor's FTIR protocol

Solvent Selection – Cyclohexane vs TCE

Due to the use of FTIR, solvent selection is limited to IR Transparent Solvents

Cyclohexane (1378 cm ⁻¹)	TCE (2900 cm ⁻¹)
Better calibration range	Less expensive instrument
Flammable solvent	Not flammable, chlorinated solvent
Standard high purity solvent sufficient	Spectral quality solvent required
Does not respond to cycloaliphatic bitumen components, bitumen has a high proportion of cycloaliphatics	Responds to all aliphatics, possibility of discriminating aliphatic/aromatic
Correction factor = 1 for all bitumens evaluated to date	Correction factor likely required to compare between producers

Method Development - continued

- **Silica gel (florisil) treatment**

- Not recommended - significant proportion of free and emulsified bitumen components are polar enough to be removed by in-situ silica gel

- **Extract Filtration**

- Not required, extracts were generally clear, high concentration extracts clarified on dilution to bring into calibration range.
- Some extracts developed precipitate on 1 month storage.

- **Drying through sodium sulphate:**

- Clear extracts formed precipitate during sodium sulphate filtration!
- Drying through sodium sulphate not recommended
 - If extract drying is needed, in-situ sodium sulphate is recommended

Conclusions

- **Current FTIR methods are generally good for determining total TPH**
 - Fluorescence methods are suspect as they appear to under-report free and emulsified bitumen.
- **Potential wins with a change to determining free/emulsified separately from dissolved:**
 1. Primary potential win is that a link between free/emulsified oil and PW cooler and/or OTSG fouling may be observed.
 2. Secondary potential win - chemical optimization (chemical type & dose):
 - i. EB/REB
 - ii. De-oiling polymer
 - iii. WLS coagulant
 3. Tertiary potential win if the industry standardizes to a common method: Results between facilities can be more accurately compared.

Operating company would need to do side-by-side testing to determine the value of differentiating the free vs emulsified oil content in the produced water.

Thank You!

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