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Report

Sodium isobutyl xanthate attachment onto flotation feed

Determination of partitioning coefficient (Kd) in freshwater and desorption in seawater in samples from April 2020.

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ABSTRACT

For this project, SINTEF Ocean determined the rates of adsorption and desorption of the flotation chemical sodium isobutyl xanthate (SIBX) to mine flotation feed in freshwater and seawater, respectively. The client provided SIBX and flotation feed. SINTEF Ocean set up adsorption and desorption tests. Small aliquots of the water phase were sampled throughout both tests and SIBX was measured by liquid chromatography mass spectrometry. We conclude that 93.3% of SIBX is adsorbed during the industrial process prior to release, corresponding to a Kd value of 256 l/kg. Thereafter, 1.27% of SIBX is desorbed back into the aqueous phase.

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1	2020-06-18	Final report
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APPENDICES

1 Background

Xanthates are flotation compounds that belong to the O-alkyl esters of thiolthione carbonate. Alkyl xanthates have been widely used in mining to selectively separate valuable minerals from host rock (*1*). In froth flotation, most of the xanthate reagent is consumed in the process and it degrades rapidly thereafter in aquatic ecosystems (*2*). Nevertheless, it is important to determine the amount of xanthates released into the environment because they are toxic to aquatic organisms at low (<1 mg/l) concentrations and because they decompose into toxic compounds (*2*, *3*).

The quantification of xanthates has traditionally been achieved by measuring the UV absorbance at 301 nm of aqueous solutions, both with and without HPLC (*4*, *5*). However, the detection limit for UV spectrophotometry is too low to measure xanthates in sub 1 mg/ml concentrations. One way to overcome this limitation is to induce oxidation of the xanthate analyte to dixanthogen using *e.g.* potassium iodine, followed by HPLC-UV detection at 254 nm, yielding detection limits in the order of 10 µg/l (*6*). Another strategy is to employ mass spectrometry (LC-MS/MS) for detection, which provides a similarly low detection limit in addition to higher specificity.

For this project, SINTEF Ocean was tasked with simulating a froth flotation to determine the rates of adsorption (partitioning coefficient, Kd) and desorption of sodium isobutyl xanthate (SIBX) onto mining flotation feed (FF). The adsorption was carried out briefly in freshwater, followed by addition of seawater in a liquid/solid ratio reflecting field values. The desorption was carried out in seawater. An LC-MS/MS method was established to quantify SIBX in fresh- and seawater.

2 Samples

Upon receipt at SINTEF Ocean Sealab in Trondheim, the samples were checked and registered. Samples for analysis were stored at -80 °C. Partitioning experiments were performed with SIBX in FF (three replicates), SIBX and FF in the presence of a frother (Dowfroth400; polypropylene glycol, PPG) (single replicate). FF without SIBX (single replicate) and SIBX without FF (three replicates) were used as controls. Samples to determine SIBX adsorption/desorption were taken at t = 0, 2.5, 5, 7.5, and 10 min for the freshwater adsorption test, followed by t = 0, 20, and 24 h after each seawater addition. A total of 79 samples were analyzed, an overview of which is given in Table 1.

Table 1: Samples taken during partitioning study.

SINTEF-ID	Replicate	Contents	Step	Time
2020-5151	1	SIBX + FF	Adsorption in freshwater	0 min
2020-5152				2.5 min
2020-5153				5 min
2020-5154				7.5 min
2020-5155				10 min
2020-5156			Addition of seawater	0 h
2020-5157				20 h
2020-5158				24 h
2020-5159			Desorption in seawater	0 h
2020-5160				20 h
2020-5161				24 h

2020-5162	2	SIBX + FF	Adsorption in freshwater	0 min
2020-5163				2.5 min
2020-5164				5 min
2020-5165				7.5 min
2020-5166				10 min
2020-5167			Addition of seawater	0 h
2020-5168				20 h
2020-5169				24 h
2020-5170			Desorption in seawater	0 h
2020-5171				20 h
2020-5172				24 h
2020-5173	3	SIBX + FF	Adsorption in freshwater	0 min
2020-5174				2.5 min
2020-5175				5 min
2020-5176				7.5 min
2020-5177				10 min
2020-5178			Addition of seawater	0 h
2020-5179				20 h
2020-5180				24 h
2020-5181			Desorption in seawater	0 h
2020-5182				20 h
2020-5183				24 h
2020-5184	1	SIBX + FF + PPG	Adsorption in freshwater	0 min
2020-5185				2.5 min
2020-5186				5 min
2020-5187				7.5 min
2020-5188				10 min
2020-5189			Addition of seawater	0 h
2020-5190				20 h
2020-5191				24 h
2020-5192			Desorption in seawater	0 h
2020-5193				20 h
2020-5194				24 h
2020-5195	1	FF only	Adsorption in freshwater	0 min
2020-5196				2.5 min
2020-5197				5 min
2020-5198				7.5 min
2020-5199				10 min
2020-5200			Addition of seawater	0 h
2020-5201				20 h
2020-5202				24 h
2020-5203			Desorption in seawater	0 h
2020-5204				20 h
2020-5205				24 h

2020-5206	1	SIBX only	Adsorption in freshwater	0 min
2020-5207				2.5 min
2020-5208				5 min
2020-5209				7.5 min
2020-5210				10 min
2020-5211			Addition of seawater	0 h
2020-5212				20 h
2020-5213				24 h
2020-5214	2	SIBX only	Adsorption in freshwater	0 min
2020-5215				2.5 min
2020-5216				5 min
2020-5217				7.5 min
2020-5218				10 min
2020-5219			Addition of seawater	0 h
2020-5220				20 h
2020-5221				24 h
2020-5222	3	SIBX only	Adsorption in freshwater	0 min
2020-5223				2.5 min
2020-5224				5 min
2020-5225				7.5 min
2020-5226				10 min
2020-5227			Addition of seawater	0 h
2020-5228				20 h
2020-5229				24 h

3 Methods

3.1 Analytical chemistry

All chemicals and solvents used were HPLC grade or higher. Water was obtained from a milliQ water system.

3.1.1 Sample clean-up

Filtered water samples were subjected to solid phase extraction (SPE) prior to analysis. For samples in freshwater, weak anion exchange (WAX) columns were used (Waters Oasis WAX 1cc 30 mg sorbent, 30 µm). Columns were preconditioned with 1 ml methanol twice and then 1 ml water twice, after which samples were loaded. The columns were washed with 1 ml 25 mM ammonium acetate and 1 ml methanol and then dried for 5 min. Finally, samples were eluted with 20:80 methanol:acetonitrile containing 2% ammonium hydroxide. For samples containing seawater, hydrophobic-lipophilic balance (WAX) columns were used (Waters Oasis HLB 1 cc 30 mg sorbent, 30 µm). The pH of the samples was first lowered by adding 4 µl 25% ammonium hydroxide per ml sample. The SPE columns were preconditioned with 1 ml methanol twice and then 1 ml water twice, after which samples were loaded. The columns were washed with 1 ml water and the samples were eluted with 1 ml methanol.

3.1.1.1 Analytical method

Samples were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS). The HPLC used was an Agilent 1260 HPLC system using a Supelco Ascentis Express HILIC column (2.1 x 50 mm, 2.7 µm particle size). The autosampler was kept at 6 °C, the column was kept at 30 °C, and the injection volume was 5 µl. The mobile phases were water containing 0.1 % ammonium hydroxide (A) and acetonitrile (B). The 6-

min-long HPLC program was as follows: 95% B for 30 s, ramp to 60% B in 6 s, hold at 60% B for 24 s, ramp to 95% B in 6 s, and hold at 95% B for 5 min.
The HPLC was coupled to an Agilent 6470 triple quadrupole mass spectrometer equipped with an electrospray ion source operating in negative mode. Prior to the mass spectrometer was a UV detector that measured UV absorbance at 301 nm. The source settings were as follows: 260 °C drying gas temperature, 6 l/min drying gas flow, 400 °C sheath gas temperature, 12 l/min sheath gas flow, 45 psi nebulizer pressure, -3500 capillary voltage, -2000 V nozzle voltage, and -70 V ion transfer capillary (fragmentor) voltage. The mass transitions used and their collision energies are given in Table 2.

Table 2: Mass transitions used in the analysis.

Analyte	Precursor ion	Product ion	Collision energy (V)
SIBX quantifier	149.0	73.1	9
SIBX qualifier 1	149.0	71.1	17
SIBX qualifier 2	149.0	77.0	5

3.2 Partitioning set-up

Adsorption: The experimental apparatus was set up as shown in Figure 1, and pictures of representative set-ups are shown in Figure 2. An overview of volumes, masses, and concentrations used is provided in Table 3. Freshwater (233 ml) from the tap and SIBX (1 mg) were first added to a glass beaker and set to stir vigorously with air bubbling at a flow rate of 5.5 l/min. Dowfroth 400 (1.5 mg), consisting of polypropylene glycol (PPG), was added in the relevant samples at this point. Two 1 ml samples were taken. Next, 100 g flotation solids were added (30% final solid content). The slurry was stirred with air bubbling for 10 min, after which bubbling and stirring were shut off (Figure 2A). Two 1 ml samples were taken after 2.5, 5, 7.5, and 10 min. Small (<100 µl) aliquots were taken at t = 10 min for pH measurement on litmus paper. After sampling, the final water volume was therefore 10 ml (4.3%) lower than at the start of the test.
First seawater addition: After the last sample was taken, seawater (1615 ml) was added to the samples (5.16% final solid content). Seawater was obtained from the Trondheim fjord at a depth of 80 m and filtered. Two 1 ml samples were taken directly after seawater addition. The samples were subjected to stirring for 20 h and then sedimented for 4 h (Figure 2C, E). Two 1 ml samples were taken directly at 20 and 24 h. Small (<100 µl) aliquots were taken at t = 24 h for pH measurement on litmus paper. After sedimentation, most the water was removed from the bottom of the flasks by aspiration through a vacuum flask (Figure 2D). The remaining water was then decanted through a GF/C glass fiber filter.
Desorption: The GF/C filters were inverted, and any sediment retained thereon washed back into the beakers with 1838 ml seawater (5.16% final solid content). Sampling and stirring was then carried out identically to the first seawater addition.

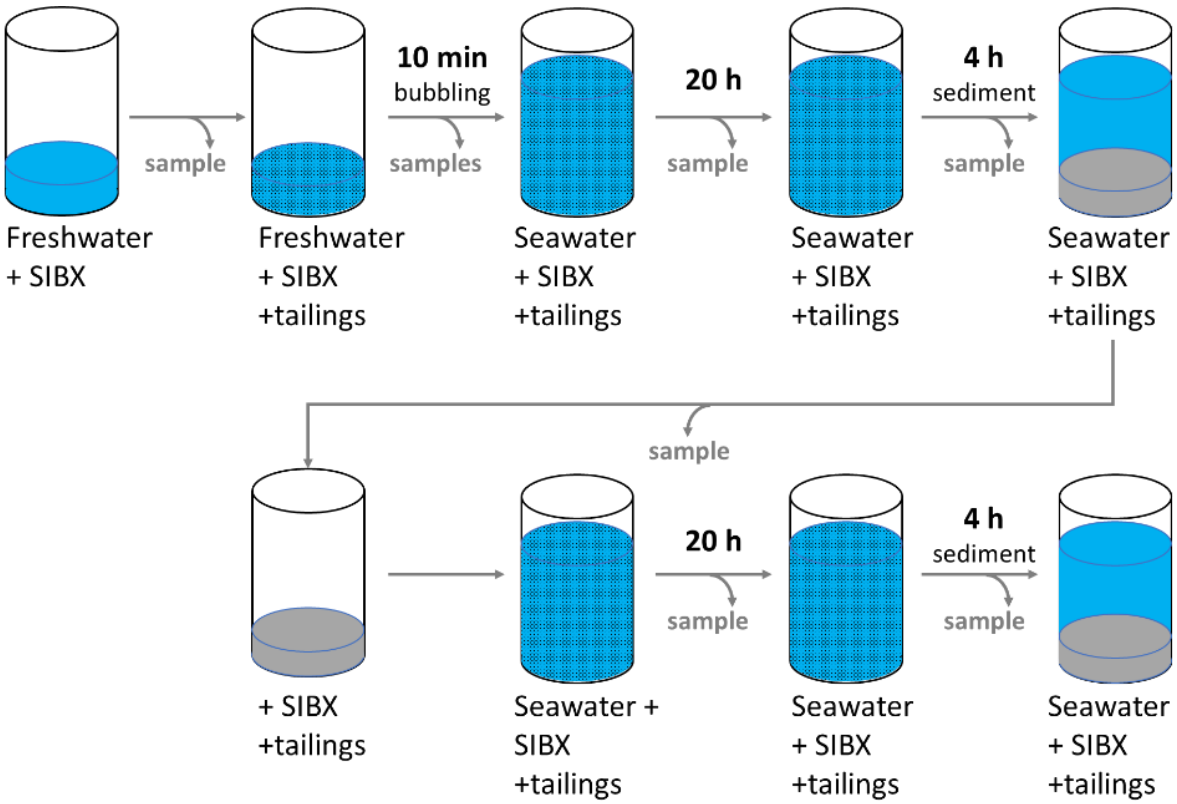
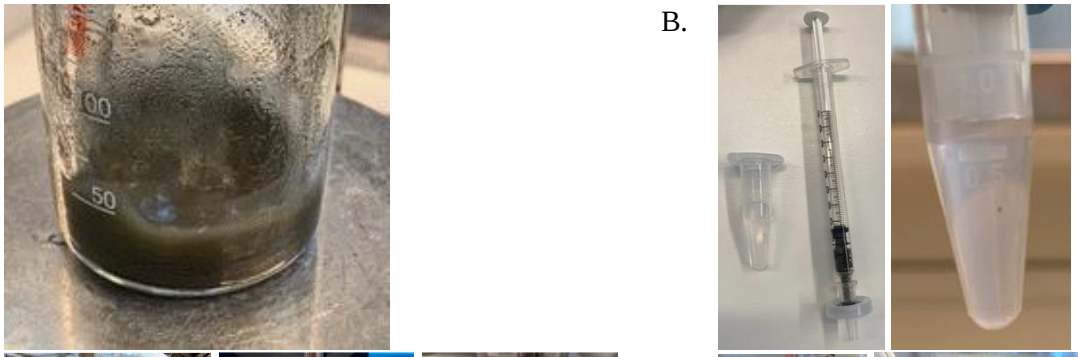


Figure 1: Schematic of partitioning experiment set-up.

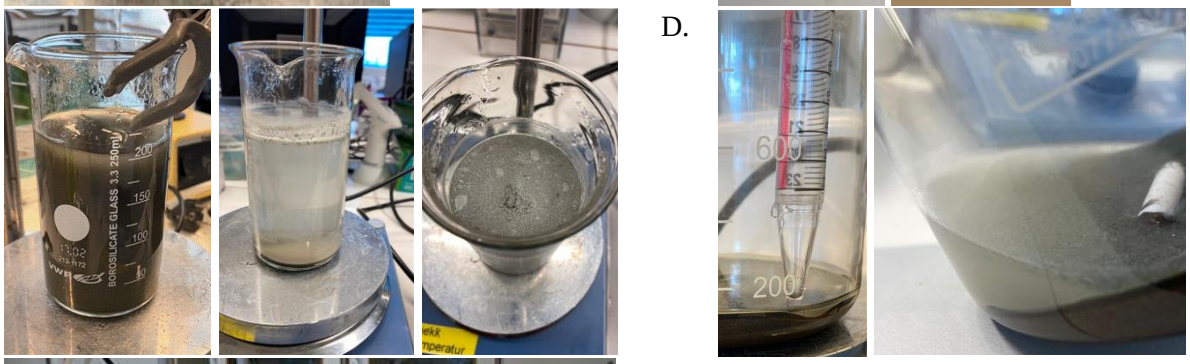
Table 3: Partitioning test parameters.

Parameter	Amount	Units
Adsorption		
Mass of float test sample	100	g
Solids % in float	30%	
Water in float	233	ml
SIBX Addition		
SIBX dosage	10	g/t
SIBX added	1	mg
SIBX concentration	1	mg/ml
SIBX added	1	ml
DF-400 Addition		
DF-400 dosage	15	g/t
DF-400 concentration	100%	
DF-400 added	1.5	mg
Density DF-400	0.968	g/l
DF-400 added	1.55	µl
Seawater addition		
Solids % in float	5.16%	
Seawater added	1615	ml
Total water in float	1838	ml
Desorption		
Solids % in float	5.16%	
Seawater added	1838	ml
Total water in float	1838	ml

A. B.



C. D.



E.

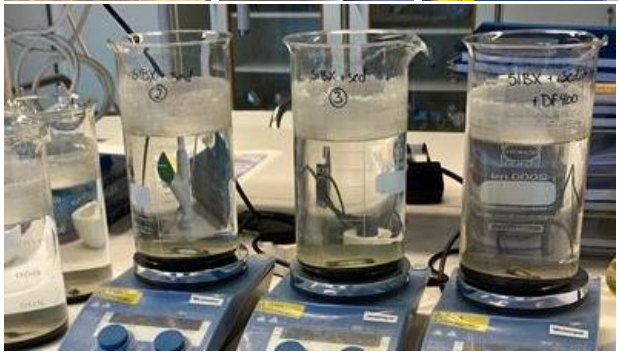


Figure 2: Experimental set-up for partitioning experiment. (A) 1:10 scale adsorption of SIBX, FF, and freshwater with stirring and bubbling at ~5.5 l/min. (B) 0.45 µM syringe-mounted PTFE filter used to filter sediment from the water phase when sampling and representative sample. (C) 1:10 scale of first seawater addition. After sedimentation, a thin layer of sediment of sediment forms atop the water column. (D) Aspiration of the water phase prior to decanting. (E) Full scale test after sedimentation.

All samples were filtered with syringe-mounted 0.45 µm PTFE filters into two 1.5 ml microcentrifuge tubes (Figure 2B). Samples were then stored at -80 °C and thawed once directly before SIBX analysis. Samples were marked with SINTEF identification numbers to anonymize them prior to analysis. Samples were de-anonymized after analysis was complete. However, due to the need to normalize samples to their corresponding calibration curve, samples could be partially identified prior to analysis.

Blanks and calibration curve standards were made alongside the samples in sample matrix containing (1) freshwater and flotation solid, (2) freshwater, flotation solid, and PPG, (3) freshwater/seawater mix and flotation solid, and (4) seawater and flotation solid. Standards were subjected to the same incubation times as their corresponding samples, albeit after removal of solids.

4 Results

4.1 Analytical chemistry

4.1.1 Optimization of mass spectrometer

Mass spectrometry was chosen to analyze SIBX due to its sensitivity and selectivity. In tandem mass spectrometry, a compound is ionized to form a precursor ion, which is then collided with an inert gas to yield product ions. The combination of precursor and product ions (mass transitions) are highly specific to each compound. To determine the precursor ion, a solution containing a high concentration of SIBX (10 µg/ml) was directly infused into the system (Figure 3), which scanned from 100 to 1000 m/z (corresponding to Da in singly-ionized compounds). When scanned in positive mode, there was little to no instrument response from the SIBX solution and no recognizable ions were found in the mass spectrum (Figure 3A-B). In negative mode, there was a strong response and an ion with an m/z of 149.0 was observed, corresponding to singly ionized SIBX (Figure 3C-D). No other recognizable ions were found, including isobutyl dixanthogen. Thus, the precursor ion m/z of 149.0 was chosen. Next, an ion fragmentation scan was performed (not shown), yielding prominent ions at 73.1, 71.1, and 77.0 (in order of decreasing magnitude). These ions correspond to cleavage of the bond between the carbon disulfide and alcohol of SIBX, as summarized in Figure 3E-F. These results represent a highly specific detection of SIBX.

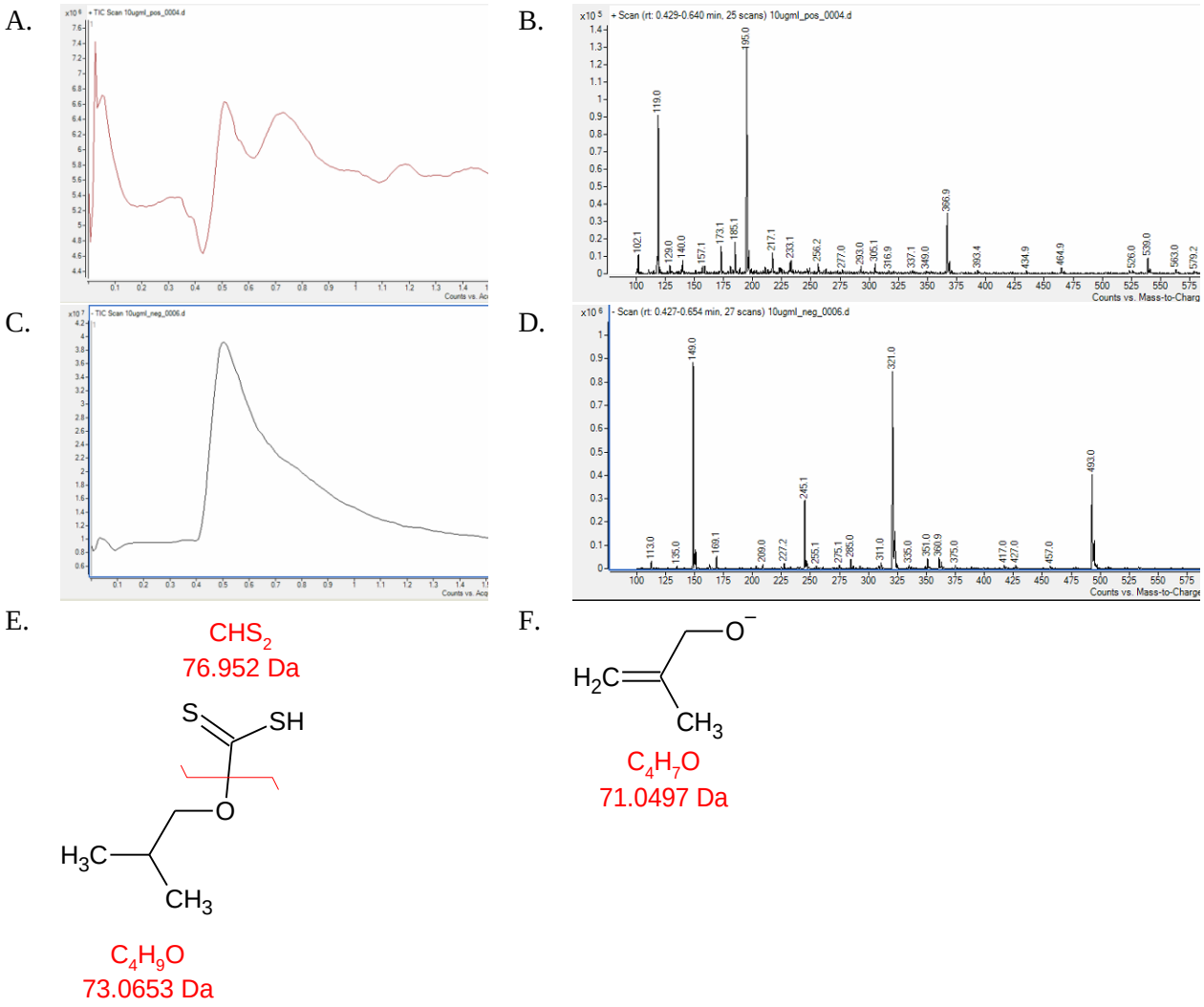


Figure 3: Mass spectrometric scan of 10 µg/ml SIBX and presumed mass transitions of SIBX fragmentation pattern in the mass spectrometer collision cell. (A) Total ion current chromatogram in positive mode shows a very small peak. (B) No recognizable ions were found in the mass spectrum of SIBX from m/z 100 to 1000 (100-575 shown). (C) Total ion current chromatogram in negative mode shows a strong signal. (D) A peak at m/z 149.0 corresponds to negatively charged SIBX ($C_5H_9OS_2^-$). (E) Cleavage of the bond between carbon disulfide and alcohol yields two ionizable compounds. (F) Upon fragmentation, the alcohol from SIBX may lose two hydrogen atoms while retaining the same net negative charge.

4.1.2 Optimization of HPLC method

Next, HPLC separation was added to the analysis. The pKa of SIBX is estimated to be 1.14, so the negatively ionized form is most abundant in solution at pHs greater than 2. Thus, when using traditional reverse phase chromatography, an acidic modifier is necessary to retain SIBX. Indeed, good retention was observed when a C18 column was employed using ammonium formate with formic acid as the aqueous mobile phase (not shown). However, there was a reduction of sensitivity of several orders of magnitude caused by ion suppression from the acidic mobile phase. Raising the mobile phase with ammonium hydroxide resulted in loss of retention. A hydrophobic lipophilic interaction (HILIC) column was next tested with ammonium hydroxide as the modifier. Although there was very little retention on the column, the high organic content in the mobile phase enables efficient ionization and increases sensitivity. The peak using a HILIC column was well-defined (Figure 4A). UV absorbance at 301 nm in-line with the MS detector was used to further confirm the specificity of the assay (Figure 4B). The limit of quantification for the assay was determined to be 100 pg/ml (Figure 4C), and the assay was determined linear to 10 µg/ml (Figure 4D).

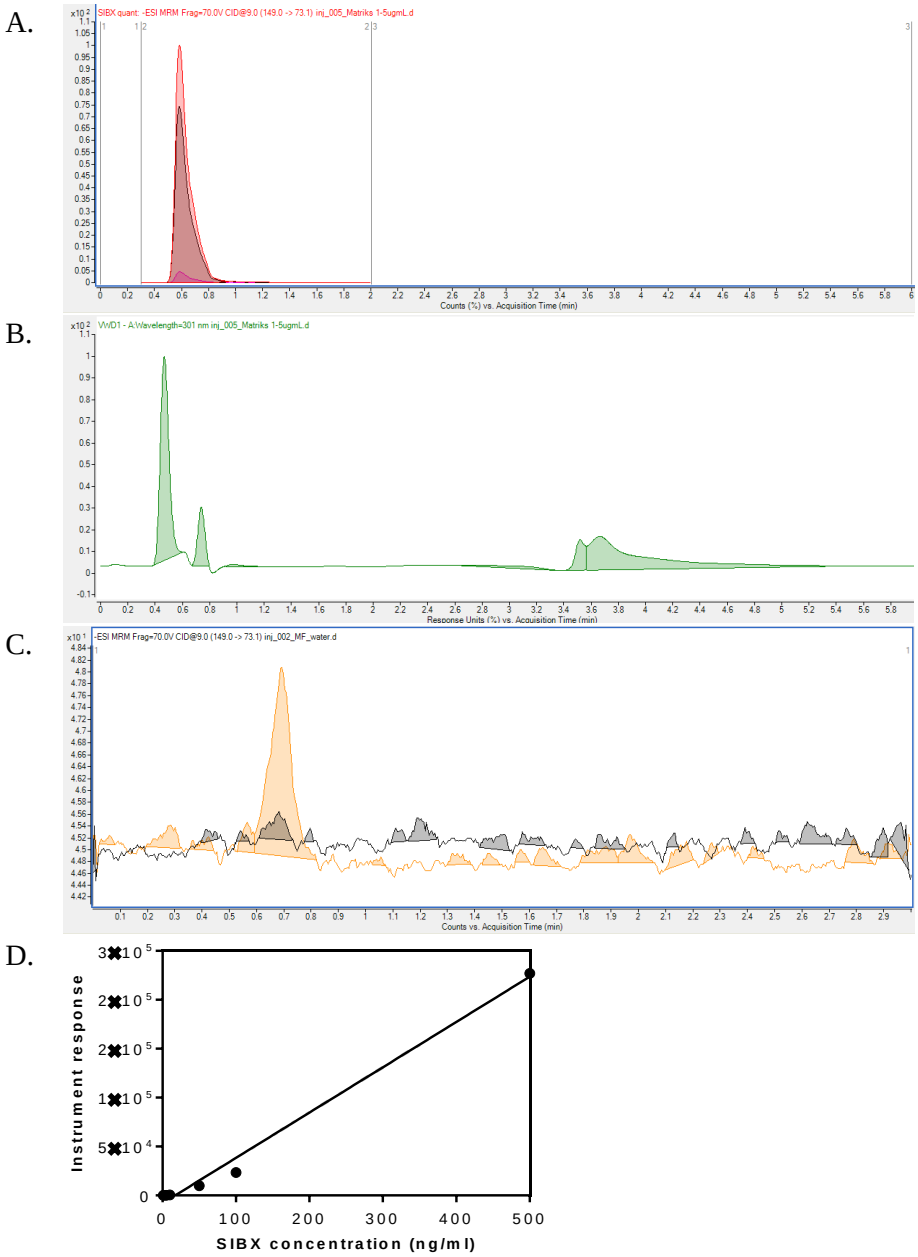


Figure 4: Overlapping SIBX peaks in LC-MS/MS and LC-UV chromatograms, and quantification limit and calibration curve for SIBX quantification by LC-MS/MS. (A) Overlapped LC-MS/MS chromatograms of all three SIBX mass transitions. (B) LC-UV chromatogram at 301 nm. Note that the UV detector is placed prior to the MS detector, so the elution time the LC-UV chromatogram is slightly earlier. (C) 100 pg/ml SIBX (orange) overlaid atop blank (black). Note the x-axis is shorter than in the above figures. (D) Calibration curve of 100 pg/ml to 500 ng/ml SIBX.

4.1.3 Sample clean-up

Samples gathered contained dissolved salts from FF and salt water, both of which reduce method sensitivity and possibly damage the instrument. It was therefore necessary to introduce a sample clean-up step prior to analysis. Three solid phase extraction (SPE) column chemistries were tested: weak anion exchange (WAX), hydrophobic lipophilic balance (HLB), and standard reversed phase (C18) (Figure 5). No sample was recovered using C18 columns. Using WAX columns, 65% of SIBX was recovered from a freshwater matrix, but only 6% was recovered from samples in seawater. For HLB columns, the recoveries were 26% and 12% for freshwater and seawater, respectively. Thus, WAX columns were chosen for samples in freshwater and

HLB columns for samples in seawater. Due to sample loss, the detection limit of the assay was increased to 150 and 850 pg/ml for samples in freshwater and seawater, respectively. Note that the analysis was performed with calibration standards made in relevant sample matrix subjected to SPE.

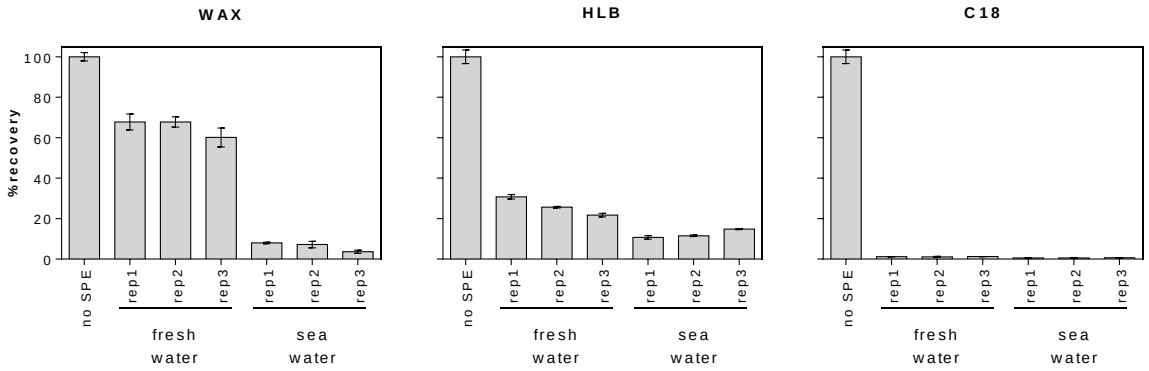


Figure 5: SPE recoveries. Error bars represent ± one standard deviation of three technical replicates.

4.1.4 SIBX stability

SIBX stability was tested in various ways. A solution of 1 µg/ml SIBX in filtered water was incubated at room temperature for 24 h in a plastic beaker, glass beaker, and glass autosampler tube (Figure 6A). No difference between samples was observed, indicating that SIBX did not bind to the container walls during that time. SIBX concentration was also measured over time in a glass beaker, showing no degradation or beaker wall adhesion (Figure 6B). Finally, SIBX was frozen at -80 °C and thawed up to five times, showing no reduction in concentration (Figure 6C).

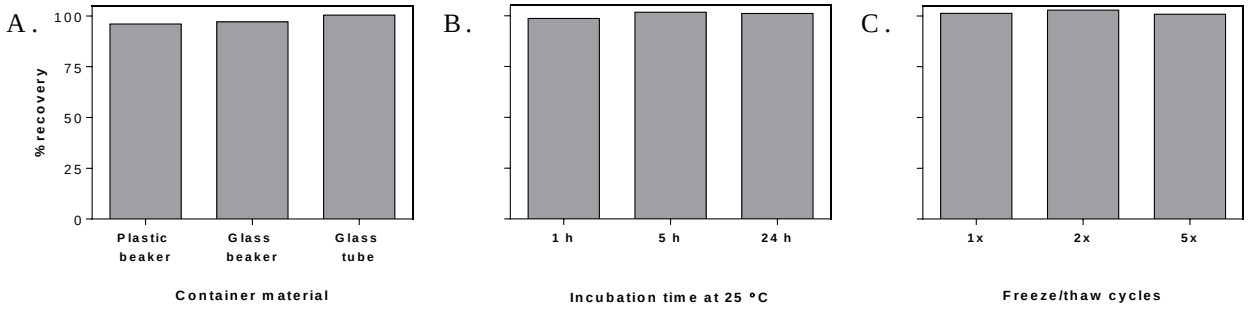


Figure 6: SIBX stability. (A) Stability of a 1 µg/ml solution of SIBX in distilled water over 24 h in different containers. (B) Stability over time of a 1 µg/ml solution of SIBX in distilled water. (C) Stability of SIBX after several freeze/thaw cycles.

4.2 Partitioning study

SIBX concentration from the aqueous phase throughout the partitioning study were measured by LC-MS/MS, and the results are presented in Table 4 and Figure 7. The SIBX concentration during the initial freshwater adsorption were high enough that they could be measured by LC-UV as well, and the values agreed with the LC-MS/MS data (not shown). Note that several values are missing from the SIBX only group. These samples were lost during processing.

The SIBX only controls showed that SIBX remains stable throughout the experiment. During the freshwater adsorption portion of the experiment, the expected SIBX concentration was 4.29 µg/ml and the measured concentration was 4.4 ± 1.0 µg/ml (± represents two standard deviations, *i.e.* 95% confidence). After seawater addition, the expected concentration was 544 ng/ml and the measured concentration was 543.6 ± 56.2 ng/ml (± two standard deviations). The variation between replicate untreated samples (22.9% and 10.3% for freshwater and seawater samples, respectively) were likely introduced during the SPE step. No SIBX was measured in the blanks. For the SIBX + FF samples, the pH was 5.5, 6.5, and 7 at t = 10 min, 24 h, and 48 h,

respectively. At t = 10, the pH was 5 for samples containing PPG, as well as SIBX- and FF-only controls. At t = 48 h, the pH was 6.5 for SIBX only controls.

Table 4: Results from SIBX partitioning study. n.s. = no signal

SINTEF-ID	Replicate	Contents	Step	Time	Non-adsorbed SIBX conc. (ng/ml)
2020-5151	1	SIBX + FF	Adsorption in freshwater	0 min	4175
2020-5152				2.5 min	3161
2020-5153				5 min	2928
2020-5154				7.5 min	2539
2020-5155				10 min	2136
2020-5156			Addition of seawater	0 h	125.3
2020-5157				20 h	30.7
2020-5158				24 h	34.3
2020-5159			Desorption in seawater	0 h	1.20
2020-5160				20 h	7.51
2020-5161				24 h	7.50
2020-5162	2	SIBX + FF	Adsorption in freshwater	0 min	4118
2020-5163				2.5 min	3661
2020-5164				5 min	2687
2020-5165				7.5 min	3488
2020-5166				10 min	3196
2020-5167			Addition of seawater	0 h	139.3
2020-5168				20 h	34.9
2020-5169				24 h	35.5
2020-5170			Desorption in seawater	0 h	1.58
2020-5171				20 h	6.97
2020-5172				24 h	5.89
2020-5173	3	SIBX + FF	Adsorption in freshwater	0 min	4230
2020-5174				2.5 min	2511
2020-5175				5 min	2578
2020-5176				7.5 min	2809
2020-5177				10 min	2071
2020-5178			Addition of seawater	0 h	132.3
2020-5179				20 h	35.2
2020-5180				24 h	39.1
2020-5181			Desorption in seawater	0 h	0.42
2020-5182				20 h	8.88
2020-5183				24 h	6.01

2020-5184	1	SIBX + FF + PPG	Adsorption in freshwater	0 min	4552
2020-5185				2.5 min	2899
2020-5186				5 min	2852
2020-5187				7.5 min	3712
2020-5188				10 min	3837
2020-5189			Addition of seawater	0 h	48.0
2020-5190				20 h	28.7
2020-5191				24 h	39.2
2020-5192			Desorption in seawater	0 h	0.35
2020-5193				20 h	10.76
2020-5194				24 h	5.00
2020-5195	1	FF only	Adsorption in freshwater	0 min	n.s.
2020-5196				2.5 min	n.s.
2020-5197				5 min	n.s.
2020-5198				7.5 min	n.s.
2020-5199				10 min	n.s.
2020-5200			Addition of seawater	0 h	n.s.
2020-5201				20 h	n.s.
2020-5202				24 h	n.s.
2020-5203			Desorption in seawater	0 h	n.s.
2020-5204				20 h	n.s.
2020-5205				24 h	n.s.
2020-5206	1	SIBX only	Adsorption in freshwater	0 min	3646
2020-5207				2.5 min	4214
2020-5208				5 min	4013
2020-5209				7.5 min	4542
2020-5210				10 min	4126
2020-5211			Addition of seawater	0 h	580.4
2020-5212				20 h	533.2
2020-5213				24 h	567.1
2020-5214	2	SIBX only	Adsorption in freshwater	0 min	4755
2020-5215				2.5 min	5030
2020-5216				5 min	5054
2020-5217				7.5 min	
2020-5218				10 min	
2020-5219			Addition of seawater	0 h	497.2
2020-5220				20 h	578.7
2020-5221				24 h	538.5

2020-5222	3	SIBX only	Adsorption in freshwater	0 min	
2020-5223				2.5 min	
2020-5224				5 min	
2020-5225				7.5 min	
2020-5226				10 min	
2020-5227			Addition of seawater	0 h	550.5
2020-5228				20 h	520.1
2020-5229				24 h	526.4

After 10 min of contact in freshwater, 57.5% ± 29.4% (± two standard deviations) of SIBX remained in solution. However, we observed a further reduction of aqueous SIBX (24.3% ± 2.6%; two standard deviations) shortly after seawater addition. Thus, we postulate that adsorption had not reached equilibrium at 10 min and instead stabilized after <1 h, although this was not directly observed.
Adsorption stabilized to 6.7% ± 0.92% (± two standard deviations) after 24 h. The calculation of Kd is concentration on the sediment divided by the concentration in the water. According to the OECD guideline for the testing of chemicals, the equation can be expressed as:

$$Kd = \frac{A_{eq}}{100 - A_{eq}} \times \frac{V_0}{m_{sediment}}$$

Where A_{eq} is the percentage adsorption at equilibrium, V_0 is the initial volume of the aqueous phase in contact with the sediment, and $m_{sediment}$ is the dry mass of the sediment. The calculation for the Kd is as follows:

$$Kd = \frac{93.3\%}{6.7\%} \times \frac{1838\ ml}{100\ g} = 256\ {}^{ml}/_{g}$$

Thus, 93.3% of SIBX was adsorbed after 24 h in seawater, corresponding to a Kd value of 256 l kg^{-1}. We conclude that this is the relevant value for the industrial process because SIBX will be in contact with the sediment slurry with a similar liquid/solid ratio for > 24h in the field.
The client stated that previous tests, as well as field experiments, indicate that partitioning equilibrium should occur by 10 min contact time. Regarding this discrepancy, one can speculate that the float solids received may have been oxidized during storage or that the laboratory set-up did not accurately model the conditions in the field. Ultimately, a definitive answer regarding the partitioning kinetics cannot be given without further study.

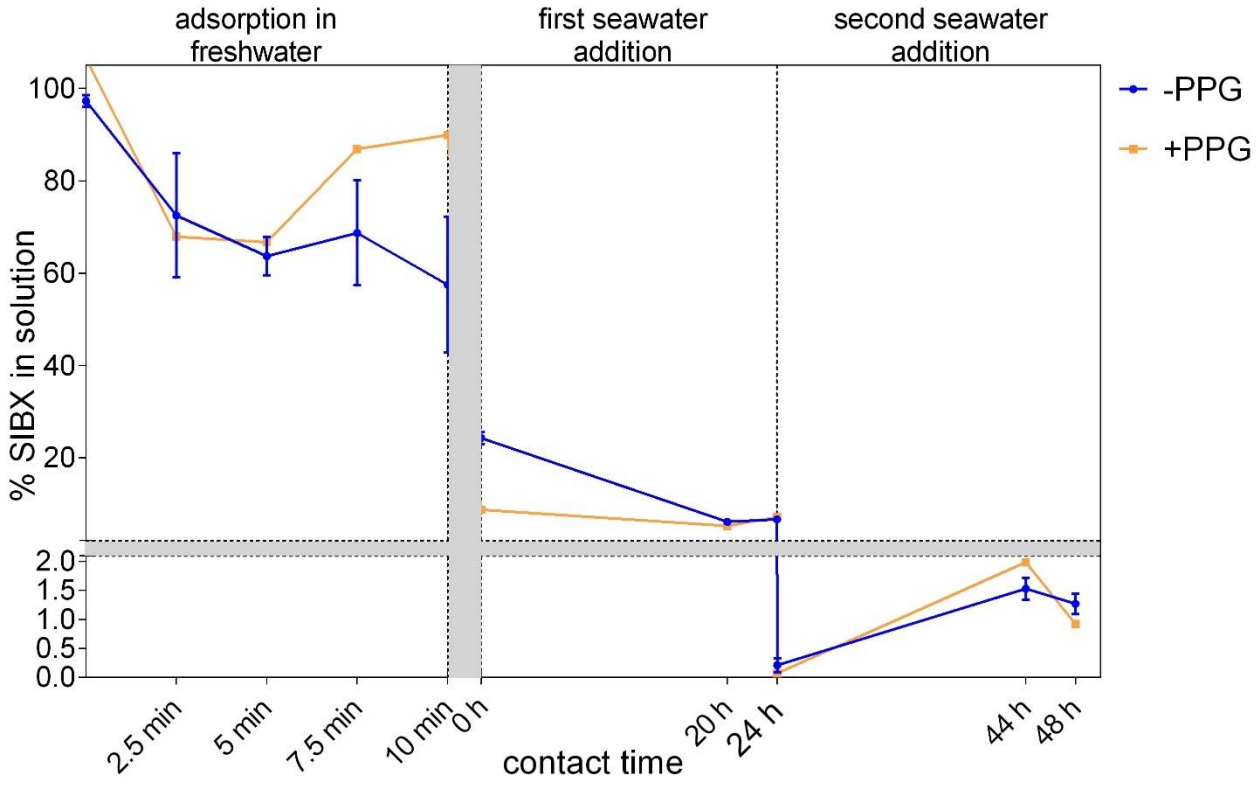


Figure 7: Results from the partitioning study. Error bars represent ± one standard deviation of three experimental replicates.

SIBX degradation during adsorption was negligible. Figure 6 shows that SIBX is stable for at least 24 h in an aqueous solution. Furthermore, SIBX concentration did not decrease over time in the SIBX only controls. It is possible that the FF could accelerate SIBX degradation; however, a full scan was run from m/z 50-320 of SIBX at t = 10 min for the adsorption test showing no degradation products (Figure 8).

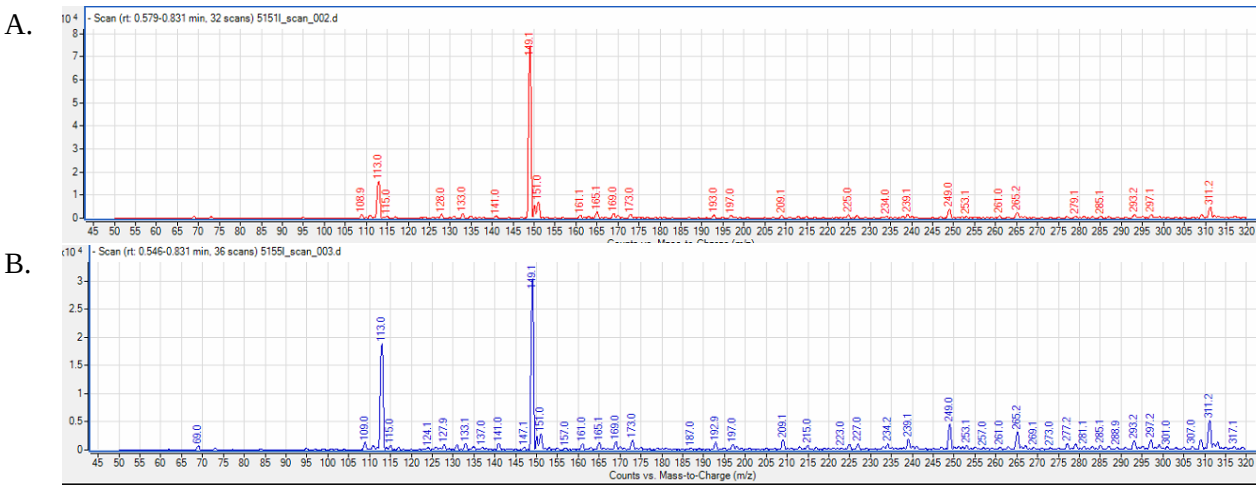


Figure 8: Mass spectrum of aqueous SIBX after 10 min (B.) shows no detectable degradation products compared to t = 0 (A.). Note that the peak at m/z 113 corresponds to a common background ion from trifluoroacetic acid.

All water was removed from the sediment after the first seawater addition and fresh seawater was added to the sediment, whereupon SIBX concentration was measured to be 0.21% ± 0.23% (± two standard deviations) of the total unadsorbed SIBX. This is likely residual aqueous SIBX that was not fully removed but may also be SIBX that has begun to desorb. After 24 h in seawater, 1.27% ± 0.35% (± two standard deviations) of SIBX is desorbed back into the water phase.
The samples containing PPG exhibited an increase in SIBX concentration dissolved in freshwater after 7.5 min during the adsorption study but were otherwise similar to those without PPG. Only one reaction was performed with PPG, so it is possible that the two unexpectedly high values represent the large variation in the samples. The SPE step is particularly susceptible to large variation and human error. Future experiments should include another xanthate *e.g.* sodium isopropyl xanthate to be spiked in prior to SPE and serve as an internal standard. Without more testing, no definitive conclusion can be made regarding the effect of PPG on the partitioning of SIBX, but the data from the seawater additions indicate that it does not alter the partitioning. This would be in line with the literature, which indicates that the use of a PPG frother does not alter the adsorption of xanthate (*7*).

4.3 Quality assurance

Laboratory blank samples were extracted with each sample set and the levels of contamination were checked against sample concentrations. Limits of detection are reported with the data set. Extractions and LC-MS/MS analysis were executed according to SINTEF internal standard operating procedures by trained personnel. Manual integration of peaks, transfer of raw data from laboratory journals, and spreadsheet formulas and calculations has been verified by an internal 'quality assuror'.

5 References

1. C. E. Rostad, C. J. Schmitt, J. G. Schumacher, T. J. Leiker, An Exploratory Investigation of Polar Organic Compounds in Waters from a Lead-Zinc Mine and Mill Complex. *Water Air Soil Poll* **217**, 431-443 (2011).
2. Y. Xu, J. P. Lay, F. Korte, Fate and effects of xanthates in laboratory freshwater systems. *Bulletin of Environmental Contamination and Toxicology* **41**, 683-689 (1988).
3. Y. Shen, Columbia University, New York (2016).
4. C. S. Zhou, A. Bahr, G. Schwedt, Studies on the Hplc Determination of Xanthates Via Copper(I) Xanthates and Dixanthogens. *Fresen Z Anal Chem* **334**, 527-533 (1989).
5. G. C. Molina, C. H. Cayo, M. A. S. Rodrigues, A. M. Bernardes, Sodium isopropyl xanthate degradation by advanced oxidation processes. *Miner Eng* **45**, 88-93 (2013).
6. C. S. Zhou, A. Bahr, G. Schwedt, Separation and Determination of Xanthates in Mixtures as Dixanthogens by Normal-Phase Hplc on a Diol-Phase. *Fresen J Anal Chem* **338**, 908-911 (1990).
7. D. Pienaar, T. Jordaan, B. McFadzean, C. T. O'Connor, The synergistic interaction between dithiophosphate collectors and frothers at the air-water and sulphide mineral interface. *Miner Eng* **138**, 125-132 (2019).

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