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# ELUCIDATING THE DECOMPOSITION KINETICS OF XANTHATE COMPOUNDS IN MINING WATERS BY HEADSPACE GAS CHROMATROGRAPHY-MASS SPECTROMETRY

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# ELUCIDATING THE DECOMPOSITION KINETICS OF XANTHATE COMPOUNDS IN MINING WATERS BY HEADSPACE GAS CHROMATROGRAPHY-MASS SPECTROMETRY

By

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This thesis has been accepted as conforming to the required standards by: Kingsley Donkor (Ph.D.), Thesis Supervisor, Dept. Physical Sciences Jonathan Van Hamme (Ph.D.), Co-Supervisor, Dept. Biological Sciences Heidi Huttunen-Hennelly (Ph.D.), Examining Committee member, Dept. Physical Sciences Dated this 1<sup>st</sup> day of May, 2018, in Kamloops, British Columbia, Canada

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## ABSTRACT

Xanthates are a widely used class of floatation reagents used for the recovery of valuable sulphide minerals. Floatation utilizes large quantities of water that lead to rapid hydrolysis of xanthates in circuit leading to a reduction in mineral recovery and an overall decrease in mill efficiency. Currently the knowledge on xanthate degradation is sparse with only a few studies reporting kinetic parameters for xanthate degradation into carbon disulphide (CS<sub>2</sub>). A headspace GC-MS method was developed to directly measure the presence of CS<sub>2</sub> in the gas phase. Kinetic parameters were then established for potassium amyl xanthate (PAX), sodium isobutyl xanthate (SIBX), potassium isopropyl xanthate (PIPX), and sodium ethyl xanthate (SEX) based on the generation of CS<sub>2</sub>. The decomposition of all xanthate studied followed first order kinetics and the rate constants were determined using a 7650A auto sampler and a PAL3 auto sampler. The rate constants were found to be 7.05 x  $10^{-4}$ , 4.07 x  $10^{-4}$ , 5.11 x  $10^{-4}$ , and 1.48 x  $10^{-4}$  h<sup>-1</sup> for PAX, SIBX, PIPX, and SEX respectively at 25 °C using the 7650A auto sampler. For the PAL3 auto sample the rate constants were found to be  $3.71 \times 10^{-6}$ ,  $4.39 \times 10^{-6}$ ,  $1.86 \times 10^{-6}$ , and  $4.03 \times 10^{-6} h^{-1}$ for PAX, SIBX, PIPX, and SEX respectively at 30 °C. The rate constants were found to increase as the temperature was increased. These data were used to calculate the activation energies for each decomposition reaction. The activation energies were found to be 19.83, 10.80, 34.44, and 22.64 kJ/mole for PAX, SIBX, PIPX, and SEX respectively. These data show that the methods presented are viable options for further analytical studies on xanthate decomposition kinetics and for higher throughput applications in industrial settings.

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## **1. INTRODUCTION**

Alkyl dithiocarbonates, more commonly known as xanthates, are a class of widely used mineral collectors in mine ore slurry. When combined with a technique know as froth floatation, xanthates are able to selectively and efficiently concentrate sulphide minerals such as chalcopyrite (CuFeS<sub>2</sub>) (*Li*, *et al.*, 2015). This has propelled xanthates to the forefront of choice reagents for the floatation of copper and gold sulphide minerals (*Rezaei, Massinaei, and Zeraatkar Moghaddam, 2018*). Xanthate molecules, shown in *Figure 1*, all share a common dithiocarbonate group (-OCS<sub>2</sub>) and have a variable alkyl chain attached through an ester



Figure 1 General structure of a xanthate anion. The R-group will always be one of four alkyl groups: ethyl, isopropyl, isobutyl, or amyl group.

linkage. Froth floatation begins with the grinding of raw ore into coarse particles to liberate the valuable mineral particles from the matrix. The coarse mill product is placed into a large floatation vat containing water and xanthates are added to begin the floatation process (911 *Metallurgist, 2017*). The negative sulphur atom in the xanthate will bind and reduce metal containing sulphides. The xanthate will selectively impart hydrophobicity on the mineral of interest so that it can be separated from the aqueous matrix and the other hydrophilic gangue *(Kemppinen, Aaltonen, Sihvonen, Leppinen, and Siren, 2015)* The result is a micelle like layer of xanthates with the alkyl tails facing outwards surrounding the mineral particle. An agitator then aerates the tank to create bubbles. The hydrophobic tail of the xanthate molecule will

interact with these bubbles as they are produced and float to the surface carrying the mineral with it. This process may be repeated many times with grinding between each collection to further concentrate the mineral of interest. Previous research has suggested that floatation efficiency and selectivity increase as the alkyl chain length is increased *(Taguta, O'Connor, and McFadzean, 2017)*; however, aside from the additional hydrophobicity that is imparted by the larger hydrophobic group, a consensus has not been reached on an exact mechanism.

The drawback of concentrating minerals repeatedly in large volumes of water is the catalytic nature of water on xanthates in solution (Shen, Nagaraj, Farinato, and Somasundaran, 2016). Xanthates are typically supplied to mills in a powder or pellet form (Mining World, 2017), which can then be prepared to a 5-10% solution to be used for floatation. The standard practice is to consume these solutions within three weeks due to degradation in the aqueous media. As the xanthates degrade in solution the concentration is decreased at an accelerated rate and produces multiple by-products, which can severely impact the recovery of sulphide minerals and floatation productivity on a massive scale (Kemppinen, Aaltonen, Sihvonen, Leppinen, and Siren, 2015). The most common by-product of the degradation process is carbon disulphide ( $CS_2$ ), a toxic volatile species known to accumulate in floatation mills (*Shen*, Nagaraj, Farinato, and Somasundaran, 2016). Since the degradation process is continually occurring within the floatation reactions, the generation of toxic CS<sub>2</sub> presents not only an issue with decreasing flotation efficiency, but on the health and safety of workers and the surrounding environment. It is estimated that about half of the total xanthates are consumed during the floatation reaction while the remainder is discharged into tailings waste (Li, et al., 2015). This tailings waste will continue to undergo degradation and produce toxic species, which can contaminate surrounding areas. Often the tailings water is discharged into a natural body of water without any treatment. This makes it important to understand the decomposition process of xanthates not only for industrial applications but also for waste management.

Xanthate literature has mostly focused on determination of xanthates using ultraviolet/visible (UV/Vis) spectrophotometry (Hao, Silvester, and David, 2000); however this method cannot distinguish between metal species and degradation products. The goal of these studies was to track the decrease in xanthate concentration over time in order to elucidate its decomposition behaviour. Mustafa and colleagues (2004) investigated the effects of temperature, time and pH on the stability of potassium ethyl xanthate (PEX) using a UV/Vis method. It was found that after thirteen days at a pH of 9, PEX absorbance did not decrease significantly (0.451%/day). When the pH was decreased to 7 the rate of degradation increased to 0.9024% per day, and increased even further to 2.099% as the pH was decreased to 5. Similarly, when the temperature was increased from 10 °C to 25 °C the rates of decomposition were at least tripled at each pH. By observing the appearance and disappearance of peaks when the pH was changed, two theoretical decomposition reacts were proposed (Figure 2). In acidic solution the formation of a xanthic acid intermediate  $(C_2H_5OCS_2H)$  dominated; however they did not describe how this reaction leads to an increase in the rate of decomposition. In basic solution a similar reaction occurs but instead of a xanthic acid intermediate, the dominant degradation products are ethanol and CS<sub>2</sub>. Again, the link between the different reactions and how they potentiate the differences in the rate of decomposition has not been clarified.

> (A)  $C_2H_5OCS_2K + H_2O \rightarrow C_2H_5OCS_2H + KOH$ (B)  $C_2H_5OCS_2K + H_2O \rightarrow KOH + C_2H_5OH + CS_2$

Figure 2 Decomposition reactions of potassium ethyl xanthate at acidic (A), and basic (B) pH.

A similar study presented the decomposition rates by calculating the rate constant (k) for each condition using SEX *(Zhongxi and Forsling, 1997)*. At 40 °C the rate constants all had orders of magnitude of 10<sup>-6</sup>. The order of magnitude decreased to 10<sup>-7</sup> and then 10<sup>-8</sup> as the temperature was reduced to 20 °C and 5 °C respectively. It was also found that the difference between the rate constants at pH 8.0 and 6.6 increased as the temperature was increased. This suggests that temperature may be the dominant factor driving decomposition, and at high enough temperatures pH may not significantly affect the rate compared to temperature.

The inability to distinguish between the different xanthates in solution has lead to the development of alternative methods such as ion-interaction high performance liquid chromatograph (HPLC) *(Trudgett, 2005)*, and capillary electrophoresis (CE) *(Kemppinen, Aaltonen, Sihvonen, Leppinen, and Siren, 2015)*. These methods have allowed for the separation and monitoring of the individual xanthates. A novel gas chromatography method was developed by Li and colleagues (2015) for the detection of isobutyl xanthate (IBX) in surface and drinking water. The research was based on the decomposition of IBX into CS<sub>2</sub> under acidic conditions. Li argued that previous methods that aimed to prevent the decomposition of the xanthate during analysis have used pH levels that are too acidic for use with a C<sub>18</sub> column. Additionally, CE methods have suffered from high detection limits (10<sup>-6</sup> to 10<sup>-7</sup> g/ml), which are not compatible with residual xanthate concentrations typically seen in floatation and wastewater circuits (7 x  $10^{-7}$  g/ml). By detecting the evolution of volatile CS<sub>2</sub> using a headspace GC method with an electron capture detector a detection limit of 3 x  $10^{-10}$  g/ml was obtained.

The use of a stable degradation product to quantify xanthates has allowed for the development of methods where decomposition is examined by monitoring the appearance of  $CS_2$  directly. A study by Shen and colleagues (2016) used a headspace GC - mass spectrometry (GC-MS) for the detection of volatile  $CS_2$  evolved from the decomposition of SIBX. The

derived rate law from these experiments showed SIBX followed first order kinetics with respect to the generation of CS<sub>2</sub>. The work also supported previous research by noting the increase in degradation associated with increased temperatures and acidic pH. These changes were reflected by the rate constants determined under various conditions. At 25 °C, k was found to be 9.3 x 10<sup>-4</sup> h<sup>-1</sup>. This value increased to 1.7 x 10<sup>-2</sup> h<sup>-1</sup> when the temperature was increased to 50 °C, and to 1.3 x 10<sup>-1</sup> h<sup>-1</sup> at 70 °C. A maximum rate of decomposition was measured at pH 2.2, and it was noted that above pH 8, no significant change in the rate of decomposition was observed.

GC-MS is a technique that combines the separative technique of gas chromatography with the detection ability of a mass spectrometer. A general schematic for the instrument is shown in *Figure 3*. In GC, an inert gas such as helium is used as a mobile phase to carry the sample through the column (*Bacher, 2016*). The column contains a solid support coated with a high boiling point liquid polymer. Columns may be capillary based, containing a coating directly around the inner diameter of the capillary. Separation is achieved based on interactions between the stationary phase and the components of the sample. If a non-polar polymer is used, the column will retain non-polar components of the sample while the polar components will be left to flow through freely. Components are also separated based on their boiling points. Compounds with low boiling points have high vapour pressure and will spend more time in the gaseous phase than interacting with the liquid stationary phase, yielding shorter retention times than compounds with higher boiling points.



Figure 3 Schematic diagram of a gas chromatograph single quadrupole mass spectrometer (GC-MS) (Li et al., 2015).

As the components of the sample are separated and eluted at different times they are detected by the mass spectrometer. MS ionizes molecules in a vacuum as they emerge from the GC using a beam of high-energy electrons *(Clinical Mass Spectrometry, 1995).* This removes an electron from the highest occupied molecular orbital of the molecule to produce a radical with a charge of +1. The molecule may also be fragmented extensively by excess energy to produce fragments that can help elucidate structure. The charged molecules are then subject to a quadrupole mass analyzer. Four cylindrical rods are arranged parallel to one another and a radiofrequency voltage is applied to one pair of rods while an opposing DC voltage is applied to the other pair. Ions travel down the quadrupole and the voltages are adjusted so only ions of a particular mass to charge (m/z) ratio will have stable trajectories and reach the detector. The voltages are continually adjusted to detect ions with a mass range of up to 5000 m/z. The detector collects and counts the ions to produce a signal proportional to the number of ions that have impacted its surface. This yields not only a mass spectrum showing the molecular mass of

the compounds in the sample, but a chromatogram that can yield quantitative information base on parameters such as peak height or peak area, both of which are proportional to concentration.

Although literature does exist examining the decomposition of xanthates through the evolution of  $CS_2$ , no studies have been found comparing the kinetics of each of the xanthates under a common method. This study was set out with two goals in mind. First, was to develop a suitable headspace GC-MS method for the detection of  $CS_2$  in aqueous solution. Once the instrument was calibrated, the decomposition kinetics of PAX, SIBX, PIPX, and SEX were examined through the evolution of the prominent degradation product,  $CS_2$ .

#### 2. MATERIALS AND METHODS

#### 2.1 Reagents

Pure CS<sub>2</sub> solution was purchased from Sigma-Aldrich Canada Ltd., Oakville, Ontario, Canada and was of analytical grade. Xanthate standards were supplied by New Afton Gold Mine, Kamloops, British Columbia, Canada, as both dissolved solid and pure solid. All solutions were prepared using filtered 18 M $\Omega$  water. Any solutions containing dissolved xanthate was filtered through 0.45 µm nylon filter prior to use.

#### 2.2 Instrumentation

All experiments were performed using an Agilent 7890B-GC coupled 5977A-MS (Agilent Technologies, Santa Clara, CA). Half of the experiments used a 7650A (Agilent) automatic liquid sampler with a 10 – $\mu$ L headspace syringe, and the second half utilized a PAL3 (Agilent) auto sampler system equipped with a headspace tool. In both cases an HP-5MS 5% phenyl methyl silox capillary column was used (29.94 M x 250  $\mu$ M x 0.25  $\mu$ M) (Agilent Technologies, Santa Clara, CA). The temperature program used was developed from a previous method *(Shen, Cher, Cher* 

*Nagaraj, Farinato, & Somasundaran, 2016*). The temperature was held at 35 °C for 2 min before increasing the temperature by 50 °C per minute to 220 °C where it was held for an additional 1.3 min to yield a final run time of 7 min.

The optimized conditions for the 7650A auto sampler were a flow rate of 1 mL/min and a split of 20:1. The injection volume was 5  $\mu$ L a single ion monitor program was set up to observe the presence of CS<sub>2</sub> at 76.00 m/z with a gain factor of 10.00. For the PAL3 auto sampler the split was increased to 100:1 and the gain was reduced to 1 to account for the increased sensitivity of the headspace dedicated instrumentation. An injection volume of 75  $\mu$ L was used to accommodate the larger headspace needle used in the PAL3 system. The single ion monitoring was also removed in favour of an MS scan from 40 to 350 m/z.

#### 2.3 Preparation of CS<sub>2</sub> Standards

For the 7650A auto sampler 10 ppm (mg/L) samples of  $CS_2$  were prepared by diluting 0.80  $\mu$ L of pure  $CS_2$  to 100.0 mL with 18 M $\Omega$  water. Samples were then diluted further to 1 ppm before being loaded into clean and dry 2 mL glass sample vials that were capped immediately. Sample vials were shaken rapidly for 15 min in a flask shaker as suggested by Li and colleagues (2015). These samples were used to confirm detection of  $CS_2$  and to optimize detection conditions. Calibration standards were prepared using the same methodology to various concentrations. For the PAL3 auto sampler the use of 20 mL glass headspace vials allowed increased the loading volume to 10 mL. Samples were agitated at 30 °C for 15 min using the built in agitator tool prior to injection.

#### 2.4 Preparation of Xanthate Standards

All xanthate standard solutions were prepared from high purity solids. Approximately 0.0500g of solid PAX (97%), SIBX (95%), PIPX (98%), and SEX (95%) was dissolved in 18

 $M\Omega$  water to a volume of 500 mL to prepare 1000 ppm stock solutions of each. Stock solutions were stored at 4 °C in the dark to minimize aqueous degradation. Fresh stock solutions were prepared weekly. Standards were prepared by first filtering the stock solution through a 0.45  $\mu$ M nylon filter prior to dilution. 1 mL of sample was loaded into a clean glass vial for the 7650A sampler, and 10 mL was loaded for the PAL3 sampler. Samples were then shook or agitated for at least 15 min prior to injection. All 7650A samples were equilibrated under ambient conditions and a pH of about 8.50. PAL3 sample were equilibrated at varying temperatures and a pH of about 8.50.

#### **3. RESULTS AND DISCUSSION**

## 3.1 Detection and Calibration of CS<sub>2</sub>

The development of a method to detect volatile  $CS_2$  was first investigated using a 1 ppm standard solution prepared in water. This standard was chosen as it falls within the concentration range of  $CS_2$  typically observed in mining circuits. A reproducible peak was observed around 1.88 min and had an m/z of 76 (*Figure 4*), using both auto sampler systems. This peak was confirmed as the  $CS_2$  peak and a single ion-monitoring program was set to detect ions of 76 m/z for the 7650A auto sampler. No interfering peaks were noted in the chromatogram as the solvent peak comes out before 1 min, which is not detected by the mass spectrometer due to a minute long solvent delay where no ions are detected for the first minute of a run.

#### Abundance



# Figure 4 A chromatogram of a 1 ppm CS2 standard solution. Sample volume injected was 5 $\mu$ L with a split of 20:1.

Once a suitable method had been developed for the detection of CS<sub>2</sub>, a linear range was established and calibrated for. The solubility of CS<sub>2</sub> at 20 °C has been reported to be as low as 2 ppm *(World Health Organization, 2000)*, and as high as 2000 ppm *(Chemical Book, 2017)*. To be safe the highest calibration standard was chosen to be 3 ppm to see if linear range of 0.3 - 3 ppm could be established. A calibration curve was generated from these standards by plotting the area under the peak in the chromatogram against the concentration of CS<sub>2</sub> (*Figure 5*). A strong correlation between the concentration of CS<sub>2</sub> and peak area was observed (R<sup>2</sup> = 0.977). The limit of detection (LOD), or the minimum amount of analyte that can be distinguished from the absence of that analyte, and the limit of quantification (LOQ), or the minimum amount of analyte that can be detected with analytical certainty, was found using the standard deviation of the lowest concentration standard over the slope of the line by 3.3, and LOQ multiplied the same ratio by 10. These are the standard ratio multiples used for LOD and LOQ calculation in analytical studies. The LOD was found to be 0.03 ppm, and the LOQ was found to be 0.09 ppm.

These values are higher than previously reported LODs using headspace GC-MS (0.002 ppm) *(Li, et al., 2015)*; however, by increasing the number of calibration standards and replicates this LOD and LOQ can be reduced.



Figure 5 Calibration curve for CS<sub>2</sub> using the 7650A auto sampler. An injection volume of 5  $\mu$ L was used with a 20:1 split. The headspace volume was 1 ml and the temperature was 25 °C. The equation of the line and correlation coefficient are shown within the graph area.

A similar calibration protocol was carried out using the PAL3 auto sampler. Since the same instrument, column, and temperature program was used for both auto samplers the retention time of CS<sub>2</sub> was unchanged using the PAL3 system. Since the PAL3 system is equipped with a temperature-controlled agitator module and uses dedicated headspace equipment, the sensitivity of the instrument increased, and the signals were too strong to continue using the same method as before. The split ratio was increased 100:1 and the gain factor on the MS was reduced to 1. An

injection volume of 75  $\mu$ L was also used to accommodate the larger headspace needle used by the PAL3 system. Additionally, the single ion monitoring was removed from the MS, as the increased sensitivity it provided was no longer needed. A new range was established from 0.1 to 2 ppm (R<sup>2</sup> = 0.977) (*Figure 6*). The LOQ and LOD were also established for this curve using the same method as described above. The LOD was found to be 0.04 ppm and the LOQ was found to be 0.12 ppm. The lowest standard used is slightly below the LOQ, so the implications of increasing the number of repeats to reduce the LOD and LOQ will be substantial for its application in industry.



Figure 6 Calibration curve for  $CS_2$  using the PAL3 auto sampler. An injection volume of 75  $\mu$ L was used with a 100:1 split. The headspace volume was 10 ml and the temperature was 30 °C. The equation of the line and correlation coefficient are shown within the graph area.

The direct use of CS<sub>2</sub> for calibration allows for the use of ambient conditions and native

pH values. Previous methods that indirectly calibrate for CS2 by degrading xanthates must rely

on acidic pH and high temperatures to produce a detectable amount of  $CS_2$  in an analytical timeframe (*Li, et al., 2015*). This extra sample preparation time limits industrial applicability. The current method proposed is limited to a narrower range due to the low solubility of  $CS_2$  in water; however, the window for industrial applicability still falls within this range making it more suitable to be coupled to main industrial processes.

## 3.2 Deriving the Rate Law

To establish the rate law for the decomposition of xanthates into  $CS_2$  a plot of  $CS_2$  generated against initial xanthate concentration was prepared. The curve was prepared for each of the four xanthates to be studied: PAX, SIBX, PIPX, and SEX. All the curves showed linear relationships between the initial xanthate concentration and the amount of  $CS_2$  generated (*Figure* 7). All the correlations showed  $R^2$  values greater than 0.99, except for SIBX at 0.88. The linear relationship seen confirms that the decomposition follows first order kinetics. The rate of change in the production of  $CS_2$  equals that of the change in initial xanthate concentration. The rate law can then be expressed as shown in Eq. (1):

## $Rate = k[Xanthate] \qquad (1)$

wherein rate equals the slope of the line of the curve of  $CS_2$  concentration generated during decomposition against time, k is the rate constant, and [xanthate] is the initial concentration of xanthate loaded into the sample vial.



It should be noted that this experiment was carried out only on the 7650A sampling system,

Figure 7 Plot of CS<sub>2</sub> evolved as a function of xanthate concentration at ambient temperature. Potassium amyl xanthate (PAX), sodium isobutyl xanthate (SIBX), potassium isopropyl xanthate (PIPX), and sodium ethyl xanthate (SEX) all showed linear relationships indicating first order kinetics for the decomposition.

## **3.3 Decomposition Kinetics**

A graph of CS<sub>2</sub> generated by each xanthate against reaction time was developed to study the rate constants of each xanthate. For the 7650A sampler the four xanthates all showed linear relationships with  $R^2$  values greater than 0.92 (*Figure 8*). The rate constant for the degradation reaction of each xanthate was calculated by dividing the slope of the line by the initial xanthate concentration in the sample. In all cases the concentration of xanthate used was close to 100 ppm. The rate constants at 25 °C were found to be 7.05 x 10<sup>-4</sup>, 4.07 x 10<sup>-4</sup>, 5.11 x 10<sup>-4</sup>, and 1.48 x 10<sup>-4</sup>

h<sup>-1</sup> for PAX, SIBX, PIPX, and SEX respectively (*Table 1*). These values are comparable to those found in the literature using similar methodology (*Shen, Nagaraj, Farinato, & Somasundaran, 2016*); however literature reported by Zhongxi and Forsling (1997) reported rate constants at 25



Figure 8 Plot of CS<sub>2</sub> evolved from a specific xanthate: PAX, SIBX, PIPX, or SEX, against time using the 7650A auto sampler. Samples were run at 25 °C and 5  $\mu$ L was sampled from 2 mL of headspace.

Table 1 Rate constants for PAX, SIBX, PIPX, and SEX at 25 °C determined using the 7650A auto sampler. The constant was calculated using curve of CS<sub>2</sub> generated over time.

Xanthate	k (h <sup>-1</sup> ) ± uncertainty
PAX	$7.05 \ge 10^{-4} \pm 0.89 \ge 10^{-4}$
SIBX	$4.07 \ge 10^{-4} \pm 0.28 \ge 10^{-4}$

PIPX	5.11 x $10^{-4} \pm 0.62$ x $10^{-4}$
SEX	$1.48 \ge 10^{-4} \pm 0.09 \ge 10^{-4}$

A similar methodology was repeated using the PAL3 sampler; however, the addition of the incubated agitator allows for the determination of k at varying temperatures. Another adaption involved sampling from a single vial over time rather than from multiple vials due to the capacity of the incubator. The rate constants for each xanthate at varying temperatures are shown in *Table 2*. An important feature to note is that all the values are smaller than those calculated using the 7650A auto sampler (*Table 1*). At 30 °C the rate constants were  $3.71 \times 10^{-6}$ ,  $4.39 \times 10^{-6}$ ,  $1.86 \times 10^{-6}$ , and  $4.03 \times 10^{-6} h^{-1}$  for PAX, SIBX, PIPX, and SEX respectively at 30 °C. These values did not increase significantly when the temperature was increased to 50 °C for PAX but did increase slightly for SIBX, PIPIX, and SEX. At 80 °C all the rate constants except for SIBX increased by an order of magnitude. These results are comparable to those published by Zhongxi and Forsling (1997) which reported rate constants to the order of  $10^{-6}$  for ethyl xanthates at 40 °C using UV/Vis spectrophotometry.

Xanthate	Temperature (°C)	k (h <sup>-1</sup> ) ± uncertainty
	30	$3.71 \ge 10^{-6} \pm 0.56 \ge 10^{-6}$
PAX	50	$4.26 \ge 10^{-6} \pm 0.23 \ge 10^{-6}$
	80	$1.10 \text{ x } 10^{-5} \pm 0.19 \text{ x} 10^{-5}$
	30	$4.39 \ge 10^{-6} \pm 0.60 \ge 10^{-6}$
SIBX	50	$7.09 \ge 10^{-6} \pm 0.59 \ge 10^{-6}$
	80	$8.19 \ge 10^{-6} \pm 1.13 \ge 10^{-6}$
	30	$1.86 \ge 10^{-6} \pm 0.27 \ge 10^{-6}$
PIPX	50	$5.59 \ge 10^{-6} \pm 0.59 \ge 10^{-6}$
	80	$1.31 \ge 10^{-5} \pm 0.34 \ge 10^{-5}$
	30	$4.03 \text{ x } 10^{-6} \pm 0.19 \text{ x } 10^{-6}$
SEX	50	$5.46 \ge 10^{-6} \pm 0.56 \ge 10^{-6}$
	80	$1.41 \ge 10^{-5} \pm 0.08 \ge 10^{-5}$

Table 2 Rate constants for PAX, SIBX, PIPX, and SEX determined using the PAL3 auto sampler. The constant was calculated using curve of CS<sub>2</sub> generated over time.

Comparing the two methods, it appears that the 7650A auto sampler system appears superior for the determination of the decomposition kinetics of xanthates; however, a few considerations must be taken into account. Firstly, the 7650A method utilizes a different analysis method where no vial is sampled from more than once. 8 samples are prepared into 8 separate vials and each is analyzed once to generate the curve. The PAL3 system uses an incubator that has the capacity for 6 vials. The method was modified to not only accompany the restrictions of the incubator, but also to automate the method further for studies at higher temperatures. Rather than separating each xanthate into a number of different vials, one vial was utilized for each

xanthate and was repeatedly sampled over time. This allowed for a much higher throughput of samples and a level of automation that would be applicable to an industrial setting. The consequence of this is that the septum of the sample vial is punctured multiple times which can create leaks where volatile  $CS_2$  can escape. This might explain why the slopes generated from the PAL3 curves are reduced, over the time course of the study some of the  $CS_2$  was likely escaping, which would artificially reduce values for the slope of the line.

There may be a few reasons the results presented here differentiate from those in the literature. In terms of developing a higher throughput method for use in industry all solutions were prepared without pH adjustment. It was noted that the innate pH of xanthate solutions are all around pH 8.5 and degradation is not severely impacted until the pH drops below 6 *(Kemppinen, Aaltonen, Sihvonen, Leppinen, & Siren, 2015)*. Values reported by Shen and colleagues (2016) used a pH of 6.8 for analysis while Zhongxi and Forsling (1997) used a pH of 8 and 6.6 and reported similar values for both. The methods used here all differ from Zhongxi and Forsling's (1997) study as the decrease in xanthate concentration was monitored rather than the evolution of CS<sub>2</sub>. The method also utilized UV/Vis spectrophotometry and bands could not be assigned unambiguously to xanthates and their related compounds giving larger uncertainties in quantification compared to headspace GC-MS methods that measure CS<sub>2</sub> directly. Both of the comparative studies also only analyzed a single xanthate (SIBX or ethyl xanthate) so no comparison can be made for both PAX and PIPX.

## 3.4 Thermodynamic Studies

Using the data generated from the PAL3 auto sampler the thermodynamic properties of each xanthate were also investigated. A plot of Ln (k) against the reciprocal of temperature was generated according to the Arrhenius equation. The activation energy (E<sub>a</sub>) for the degradation of

each xanthate into  $CS_2$  was found by multiplying the slope of the graph ( $E_a/R$ ) by the ideal gas constant R (8.314 j mol<sup>-1</sup>). The activation energies were found to be 19.83, 10.80, 34.44, and 22.64 kj/mole for PAX, SIBX, PIPX, and SEX respectively. Only literature values for the activation energy of O-ethyl S-methyl xanthate could be found in the literature (Adejoro, Esan, Adeboye, & Adeleke, 2017). The researchers reported an Ea of 166.200 kj/mol for the Smethylated ethyl xanthate. The values reported in this research are significantly lower which is likely due to the chemical difference between the species. The methylated sulphur reduces the overall polarity of the xanthate making it less susceptible to degradation reactions in water. This would increase the activation energy so that more energy is needed to initiate the degradation of the methylated compound. Additionally, Adejoro and colleagues (2017) utilized an in silico quantum mechanics methodology to investigate thermodynamics rather than a direct method. This work has shown that the PAL3 method may be suitable for investigating the thermodynamic properties of the xanthates in tandem with their kinetic properties. This was a pilot study that focused on simple data manipulation. Further work needs to be done to expand the Arrhenius curve to produce results with analytical applicability.



Figure 9. Arrhenius plot of ln(k) against the reciprocal of temperature. Temperature used were 30 °C, 50 °C, and 80 °C. All k values were calculated from data generated using the PAL3 auto sampler.

Table	3	Activation	energy	of PAX,	SIBX,	PIPX,	and	SEX	determined	using	the	Arrhenius
	e	quation an	d the rat	te constan	ts calci	ulates u	sing	the P.	AL3 auto sa	mpler.		

E <sub>a</sub> (kj/mole)
19.83
10.80
34.44
22.64

## 4. CONCLUSIONS

Headspace GC-MS was shown to be a suitable technique for studying the decomposition kinetics of xanthates in aqueous matrices at ambient and elevated temperatures. Conditions were optimized for the GC-MS using both a 7650A and PAL3 auto sampler system. Both systems were successfully calibrated for the detection of volatile CS<sub>2</sub> and xanthates were confirmed to follow first order decomposition into CS<sub>2</sub>. Rate constants were successfully calculated at 25, 30, 50, and 80 °C; however, the two sampling systems did not produce comparable results to one another but did reflect values presented in the literature for both headspace GC-MS methods, and UV/Vis spectrophotometric methods. This work has developed methods for both non-headspace specific (7650A) and headspace dedicated (PAL3) instrumentation. The methods automation and potential for high throughput make it ideal for use in an industrial setting where sample turnover is fast and sample prep should be minimized. This work also provides foundations for analytical studies into the degradation kinetics of xanthates in solution and decomposition thermodynamics.

## **5. FUTURE WORK**

Future work for this research should focus on increasing the analytical certainty of the values. Increasing the repeats of each sample and using fresh headspace vials and lids for each analysis will likely accomplish this. Since xanthate degradation is heavily pH dependant future studies should also explore how k changes in response to changes in pH. Additional thermodynamic studies can also be carried out to further elucidate the thermodynamics of the degradation reaction. Finally, since the floatation tank is a concoction of chemical activity, it may be beneficial to monitor for any potential destabilizing or stabilizing cosolutes in solution that may affect xanthate degradation. As more research is conducted a catalogue of the decomposition behaviour of each xanthate can be developed to allow for mining operations to adjust current floatation protocol to correct for any xanthate degradation that may be affecting mineral recovery in circuit.

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## 7. APPENDIX

## 7.1 Chromatograms of Xanthate Standards

750 ppm PAX



750 ppm SIBX

Abundance



25

# 750 ppm PIPX





Abundance



# 7.2 Mass Spectra of Xanthate Degradation Process

PAX



SIBX



PIPX



SEX



29