Matrix and pH Effects on the Degradation Kinetics of Xanthates in Mining Waters

William L. Primrose, Adrian M. Batista. Supervisor: Dr. Kingsley Donkor

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ABSTRACT

Determination of optimal pH conditions for a xanthate solution representative of a real matrix in an industrial setting (such as a flotation tank or a tailings pond) was researched to help ensure mill efficiency in mines. The primary method for analysis was the use of headspace GC-MS. Aqueous samples of xanthates in basic solutions without minerals were tested for degradation by testing for the generation of carbon disulfide (CS_2). Potassium isopropyl xanthate (PIPX) and potassium amyl xanthate (PAX) were primarily studied and rate constants were compared to determine optimal pH conditions for the slowest degradation of individual xanthates. The rate constant for 110.6 ppm PIPX was found to be 5.79×10^{-5} h^{-1} at pH 7.73; at the same pH, the rate constant was found to be 3.91×10^{-6} h^{-1} for 1075.2 ppm. The rate constant for PAX was found to be 5.43×10^{-5} h^{-1} at pH 9.08, 1.23×10^{-5} h^{-1} at pH 9.26, 8.12×10^{-6} h^{-1} at pH 9.34, and 4.36×10^{-5} h^{-1} at pH 9.48.

Introduction

Xanthates are a class of chemical that are consistently used in the mining industry during their mill process as a way to collect minerals from ore samples by way of floatation. They are popular due to their low cost and their efficient ability to bind to metals of interest such as copper, nickel, zinc, and iron (Shen et al., 2016). Xanthates share similarities in their dithiocarbonate groups and vary in their alkyl chains, written as $R\text{-}OCS_2^-$ (Shen et al., 2016). The negatively charged sulphur is what binds to the metals in the floatation tanks and is frothed to float it to the top for collection (Kemppinen et al., 2014). However, the process is not a simple extraction of mineral via xanthate with 100 % efficiency; one of the leading problems with xanthates in the mill processes of large mines is that they are used in aqueous conditions wherein water is a key factor in the degradation of the xanthates in solution. This degradation releases carbon disulphide which in turn renders the ability of that molecule to bind to a mineral inert without the presence of a negatively charged sulphur. Thus, a deeper understanding of xanthate kinetics in aqueous conditions is necessary to optimize mill processes.

Carbon disulphide (CS_2) is a liquid at room temperature but is highly toxic and volatile with a vapour pressure of 48.210 kPa at 25

°C (World Health Organization, 2005). As such, minimizing the generation of CS_2 not only has an economic impact through lessened use of xanthates over time, it also has a health and environmental implication if less CS_2 is produced due to its tendency to accumulate thus posing a risk to workers nearby as well as the environment surrounding a given mine (Shen et al., 2016).

Due to the high volatility of CS_2, testing for its presence is easily done in a sealed headspace vial. As such, in this project xanthate degradation was studied using headspace Gas Chromatography-Mass Spectrometry (GC-MS). The GC was used for the quantification of CS_2 generated and the MS was used for confirming the presence of CS_2 by looking for a peak at 76 m/z. Following the previous study by Batista (2018) which showed xanthate decomposition follows first order kinetics, this project's goal was to study the effects of pH on the decomposition behaviour of xanthates in aqueous solution. In particular, this research is focused on the comparison of different xanthates using the same method, something not currently found in the literature. After developing the method for detection of CS_2 under varying pH, the goal was to compare four different xanthates; two were primarily studied and the rest will be studied in future trials.

Reagents

Pure, analytical-grade CS_2 was readily available from the Thompson Rivers University (TRU) Chemistry Department and was originally purchased from Sigma-Aldrich Canada Ltd., Oakville, Ontario, Canada. New Afton Gold Mine in Kamloops, BC, Canada provided solid xanthate samples. Nearly all samples were dissolved in 18 MΩ water; where 18 MΩ water was unavailable, deionized water was used instead.

Instrumentation

All trials were isothermal and run on TRU's Agilent 7890B-GC coupled 5977A-MS using an Agilent PAL3 auto sampler with a headspace injection tool. An HP-5MS 5% phenyl methyl silox capillary column was used. For the remainder of the instrument parameters, see Table 1.

Table 1. Instrument and Method Parameters	
Sample Volume (mL):	0.075
Incubation Time (min):	15
Heat Agitator:	On
Incubation Temperature (°C):	30
Heat Syringe:	On
Syringe Temperature (°C):	46
Pre Injection	
Flush Time (s):	10
Sample	
Sample Vial Penetration Depth (mm):	15
Sample Vial Penetration Speed (mm/s):	50
Sample Aspirate Flow Rate (mL/min):	12
Sample Post Aspirate Delay (s):	1
Injection Signal Mode:	Plunger Up
Inlet Penetration Depth (mm):	45
Inlet Penetration Speed (mm/s):	50
Pre Inject Time Delay (s):	0.5
Injection Flow Rate (mL/min):	1
Post Inject Time Delay (s):	0.5
Flush Time (s):	60
Continuous Flush:	On
Advanced	
Agitator Speed (rpm):	250
Agitator On Time (s):	15
Agitator Off Time (s):	5

Run time for the sample was set to 5 min and the GC oven was set to 33 °C; the intent was to set a temperature close to ambient temperature to replicate mill conditions. However, cooling the oven to 25 °C proved to be difficult, so 33 °C was a choice made from instrumental limitations. The GC was run with a split ratio of 100:1 and a split flow of 100 mL/min.
The MS began its scan at 1.75 min following the 1.75 min solvent delay and scanned between BLANK and BLANK m/z.

Calibration – Preparation of CS_2

Stock solution of CS_2 was made by adding 79.4 μL of pure CS_2 to 100 mL of 18 MΩ water, forming 100 ppm solution. Then, 10 mL of the 100 ppm stock solution was diluted with 18 MΩ water in a 100 mL volumetric flask to form 10 ppm stock solution. The 10 ppm stock solution was used to generate the standards for the calibration curve as per Table 2.

Table 2. Preparation of Calibration Curve

Volume Stock added (mL)	Final Volume (mL)	Concentration (ppm)
0.5	100.0	0.05
1.0	100.0	0.10
5.0	100.0	0.50
10.0	100.0	1.00
15.0	100.0	1.50
20.0	100.0	2.00

As per the recommendation of Li et al. (2015), the standards were agitated in their - vials for 15 min prior to injection. Headspace vials with a 20 mL capacity were used for all standards and 10 mL of the stock solutions were added to the vials.

Sample Preparation

Approximately 0.0500 g of solid xanthate was added to a 500 mL volumetric flask and diluted to the mark with 18 MΩ water to prepare stock solutions of approximately 100 ppm. Stock solutions we remade after a solution was a week old and were made from 98% pure potassium isopropyl xanthate (PIPX) and 97% pure potassium amyl xanthate (PAX) Each sample vial was a 20 mL headspace vial with 10 mL of stock solution added to it. The pH level was adjusted using 0.012 M sodium hydroxide; Shen et al. used sodium hydroxide to set pH in their method and as such their method was applied here, though a buffer solution may also be a viable method of pH control for future studies. The pH level was adjusted to various levels as per Tables 3 – 6.

Results and Discussion

Calibration

The calibration curve, shown in Figure 1, shows the concentration of CS_2 in ppm of the standards and the respective peak area observed; the calibration curve showed good linearity. The limit of detection (LOD) was found to be 0.0023 ppm and the limit of quantification (LOQ) was found to be 0.023 ppm.

Minimizing Loss of CS_2

One goal of the method development was to increase the reproducibility of the trials. A concern was raised that due to its volatility, some CS_2 may have been escaping the headspace vials each time a vial cap was pierced by the heated injection syringe. Thus, trials a – f were done in the following manner: for each pH level, 8 separate vials were created under the same conditions (10 mL aliquot of xanthate sample in same pH condition) and sealed with brand new headspace caps with the intention that each cap would only be pierced once. Therefore, vial 1 would be pierced at hour 1, vial 2 at hour 2, and so on and so forth. Assuming that the rate of decomposition remains constant between trials, then the data from each vial should still follow a linear, first-order curve. Further, if it was true that the use of an individual vial was skewing the precision, then the R^2 value on the corresponding curve would be expected to increase compared to a curve from a method using only one vial being pierced every hour. However, increased reproducibility was not observed. Instead, trials a – f heralded erratic results from data point to data point and no discernable trend was found as seen in Figure 2 (Table 7).

Using a method which used a single vial per trial which is pierced multiple times over a set time interval drastically improved results and a trend was found. Over time, CS_2 evolved in a manner consistent with first order kinetics and the reproducibility was within reasonable limits ($R^2 = 0.8641 – R^2 = 0.9811$). In trials n through p, however, an instrument error resulted in the data being skewed for the first data point in each series. For trials n, o, and p, the R^2 values observed were 0.7394, 0.7383, and 0.8554, respectively. However, if the first data point in each set is discarded, the R^2 values become 0.9033, 0.8727, and 0.9518, respectively. This observation is left as an aside to show the projected correlation because the values go closer to unity, however statistical determination of which data points to remove was not completed and so the data herein is reported as recorded. Data for trials g – p are shown in Figure 3 and Table 8.

Final Results

Overall, the data shows that the rate of CS_2 evolution increases as pH is decreased and furthermore, the rate follows a linear trend. Shen et al. (2016) also showed a similar trend with sodium isobutyl xanthate (SIBX) wherein the xanthates decomposed to the greatest extent at approximately pH 2 and decomposed less and less as pH increased. Their research was primarily focused on developing a method to act as a foundation for researching these compounds further, whereas the aim of this project was to begin filling in specific gaps in the literature regarding rate constants.

The rate constant for 110.6 ppm PIPX was found to be 5.79×10^{-5} h^{-1} at pH 7.73; at the same pH, the rate constant was found to be 3.91×10^{-6} h^{-1} for 1075.2 ppm. While the rate is noticeably smaller at the higher concentration, and assuming a constant rate, is should follow that the rate constant will decrease as per the equation Rate = k[xanthate] i.e. as the xanthate concentration increases, a constant rate will cause a decrease in rate constant. As such, no major difference in rate between concentrations was observed at this level of experimentation.

The rate constants for potassium amyl xanthate (PAX) are shown in Table 8 and 9, but Table 9 shows the trend as pH level rises. The slowest rate constant appears at pH = 9.34. The rate constant begins to increase again slightly at pH 9.48 which may be a result of the alkaline conditions facilitating the appearance of dixanthogen compounds or dithiocarbonates which have been detected in more basic solutions (Shen et al., 2016). This suggests that there exists a “sweet spot” for pH level such that higher pH slows the rate of decomposition, but pH that is too high allows side reaction rates to increase, thus using up xanthates anyway. Further trials will have to be conducted over smaller pH intervals to prove this.

Conclusion

This project has shown that xanthate decomposition rate constants tend to decrease at higher pH levels which is in line with literature that suggested an increased rate of degradation in more acidic conditions. However, highly alkaline conditions may also be increasing the rate of xanthate decomposition.

The implications of this research include increase in mineral yield such that mining companies (like New Gold New Afton Mine) can further develop their industrial processes to make better use of xanthates. As well, mining companies will be able to minimize and potentially decrease environmental and health hazards posed by by-products such as carbon disulphide gas. This will help ensure that mines can create environmentally sustainable procedures and processes to keep their workers in safe conditions and their mills operating at peak efficiency.

Future Work

The next step for this project is to run more trials with additional xanthates, namely sodium isobutyl xanthate (SIBX) and sodium ethyl xanthate (SEX) for further comparison of common xanthates used in the industry. As well, calculation of figures of merit and validation of the method will be done in the next stages of the research. Additionally, trials should be done in a buffer solution as well to determine the efficiency of adjusting the pH using solely NaOH. Lastly, further trials will have to be conducted over smaller pH intervals to prove where the minimum rate constant exists for each xanthate.

Acknowledgements

I would like to thank Dr. Kingsley Donkor and Dr. Dipesh Prema for their support as well as Trent Hammer for his instrument expertise and guidance. Thank you to Dayton Shaw for helping keep the lab spaces safe and organized and thank you to TRU’s Chemistry Department for continued support. A big thank you to New Afton Gold Mine for support and providing samples, and to NSERC for providing funds to make this project possible. Finally, thank you to the TRU Research Office (UREAP) for funding my project. This has been an invaluable experience and I am grateful to all those involved for making this project a success.

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Tables and Figures

Table 1. Instrument and Method Parameters	
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Sample Aspirate Flow Rate (mL/min):	12
Sample Post Aspirate Delay (s):	1
Injection Signal Mode:	Plunger Up
Inlet Penetration Depth (mm):	45
Inlet Penetration Speed (mm/s):	50
Pre Inject Time Delay (s):	0.5
Injection Flow Rate (mL/min):	1
Post Inject Time Delay (s):	0.5
Flush Time (s):	60
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Table 2. Preparation of Calibration Curve

Volume Stock added (mL)	Final Volume (mL)	Concentration (ppm)
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1.0	100.0	0.10
5.0	100.0	0.50
10.0	100.0	1.00
15.0	100.0	1.50
20.0	100.0	2.00

Table 3. Development of PIPX standards (a - f)

Xanthate	[Xanthate] ppm	Sample label	pH	pOH	Volume 0.012 M NaOH added (L)	Volume 0.012 M NaOH (mL)	Total Volume (L)
PIPX	100.8	a	10.95	3.05	0.000800	0.8000	0.01080
		b	10.24	3.76	0.000150	0.1500	0.01030
		c	9.77	4.23	0.000050	0.0500	0.01010
PIPX	100.2	d	9.31	4.69	0.000017	0.0170	0.01002
		e	9.01	4.99	0.0000085	0.0085	0.01009
		f	8.49	5.51	0.0000025	0.0025	0.01003

Table 4. Development of PIPX standards (g - h)

Xanthate	[Xanthate] ppm	Sample label	pH	pOH	Volume 0.012 M NaOH added (L)	Volume 0.012 M NaOH (mL)	Total Volume (L)
PIPX	110.6	g	7.72	6.28	0.000022	0.0220	0.50002
PIPX	1075.2	h	7.72	6.28	0.000022	0.0220	0.50002

Table 5. Development of PIPX standards (i - j)

Xanthate	[Xanthate] ppm	Sample label	pH	pOH	Volume 0.012 M NaOH added (L)	Volume 0.012 M NaOH (mL)	Total Volume (L)
PAX	103.2	i	9.48	4.52	0.000025	0.0250	0.01003
PAX	103.2	j	9.08	4.92	0.000010	0.0100	0.01001

Table 6. Development of PIPX standards (k - p) for triplicate trials

Xanthate	[Xanthate] ppm	Sample label	pH	pOH	Volume 0.012 M NaOH added (L)	Volume 0.012 M NaOH (mL)	Total Volume (L)
PAX	102.6	k	9.26	4.74	0.000015	0.0150	0.01002
		l	9.26	4.74	0.000015	0.0150	0.01002
		m	9.26	4.74	0.000015	0.0150	0.01002
PAX	102.6	n	9.34	4.66	0.000018	0.0180	0.01002
		o	9.34	4.66	0.000018	0.0180	0.01002
		p	9.34	4.66	0.000018	0.0180	0.01002

Table 7. Raw data for trials a – f

Series a				Series b				Series c			
Injection	Time (h)	Concentration (ppm)	Peak Area	Injection	Time (h)	Concentration (ppm)	Peak Area	Injection	Time (h)	Concentration (ppm)	Peak Area
1	2.65	0.0330	510077	1	2.03	0.0348	563759	1	1.00	0.0358	593947
2	3.70	0.0301	421051	2	3.08	0.0352	576239	2	2.05	0.0327	499156
3	4.75	0.0336	526675	3	4.13	0.0336	526561	3	3.10	0.0361	601537
4	5.80	0.0355	583833	4	5.18	0.0365	613296	4	4.15	0.0380	659226
5	6.85	0.0323	486876	5	6.23	0.0363	606902	5	5.20	0.0339	534699
6	7.90	0.0327	499509	6	7.28	0.0362	605391	6	6.25	0.0394	700135
7	8.95	0.0341	540455	7	8.33	0.0358	594096	7	7.30	0.0364	612135
8	10.0	0.0333	519315	8	9.38	0.0347	560915	8	8.35	0.0392	696003
Series d				Series e				Series f			
Injection	Time (h)	Concentration (ppm)	Peak Area	Injection	Time (h)	Concentration (ppm)	Peak Area	Injection	Time (h)	Concentration (ppm)	Peak Area
1	1.53	0.0537	1E+06	1	1.53	0.0265	313608	1	1.53	0.0340	540093
2	2.58	0.0213	159278	2	2.58	0.0265	313124	2	2.58	0.0261	301743
3	3.63	0.0224	190057	3	3.63	0.0246	255370	3	3.63	0.0228	203706
4	4.68	0.0266	318131	4	4.68	0.0227	199555	4	4.68	0.0298	413101
5	5.72	0.0294	400850	5	5.72	0.0267	320194	5	5.72	0.0255	285044
6	6.77	0.0296	405423	6	6.77	0.0285	375162	6	6.77	0.0300	418546
7	7.82	0.0316	465506	7	7.82	0.0294	400962	7	7.82	0.0408	741993
8	8.87	0.0292	395405	8	8.85	0.0284	370079	8	8.85	0.0746	2E+06

Table 8. Summary of Results

Series	pH level	[Xanthate] (ppm)	Xanthate Used	Rate Constant k (h^{-1})	Average k (h^{-1})
a	10.95	100.8	PIPX	-	-
b	10.24	100.8	PIPX	-	-
c	9.77	100.8	PIPX	-	-
d	9.31	100.8	PIPX	-	-
e	9.00	100.8	PIPX	-	-
f	8.48	100.2	PIPX	-	-
g	7.73	110.6	PIPX	5.79E-05	-
h	7.73	1075.2	PIPX	3.91E-06	-
i	9.48	103.2	PAX	4.36E-05	-
j	9.08	103.2	PAX	5.43E-05	-
k	9.26	102.6	PAX	1.27E-05	1.23E-05
l	9.26	102.6	PAX	8.77E-06	
m	9.26	102.6	PAX	1.56E-05	
n	9.34	102.6	PAX	1.27E-05	1.27E-05
o	9.34	102.6	PAX	1.27E-05	
p	9.34	102.6	PAX	1.27E-05	

Table 9. Summary of Results Sorted by Ascending pH Level

Series	pH level	[Xanthate] (ppm)	Xanthate Used	Rate Constant k (h^{-1})	Average k (h^{-1})
g	7.73	110.6	PIPX	5.79E-05	-
h	7.73	1075.2	PIPX	3.91E-06	-
f	8.48	100.2	PIPX	-	-
e	9.00	100.8	PIPX	-	-
j	9.08	103.2	PAX	5.43E-05	-
k	9.26	102.6	PAX	1.27E-05	1.23E-05
l	9.26	102.6	PAX	8.77E-06	
m	9.26	102.6	PAX	1.56E-05	
d	9.31	100.8	PIPX	-	-
n	9.34	102.6	PAX	7.80E-06	8.12E-06
o	9.34	102.6	PAX	7.80E-06	
p	9.34	102.6	PAX	8.77E-06	
i	9.48	103.2	PAX	4.36E-05	-
c	9.77	100.8	PIPX	-	-
b	10.24	100.8	PIPX	-	-
a	10.95	100.8	PIPX	-	-

Figure 1. Calibration curve for carbon disulphide observed via gas chromatography

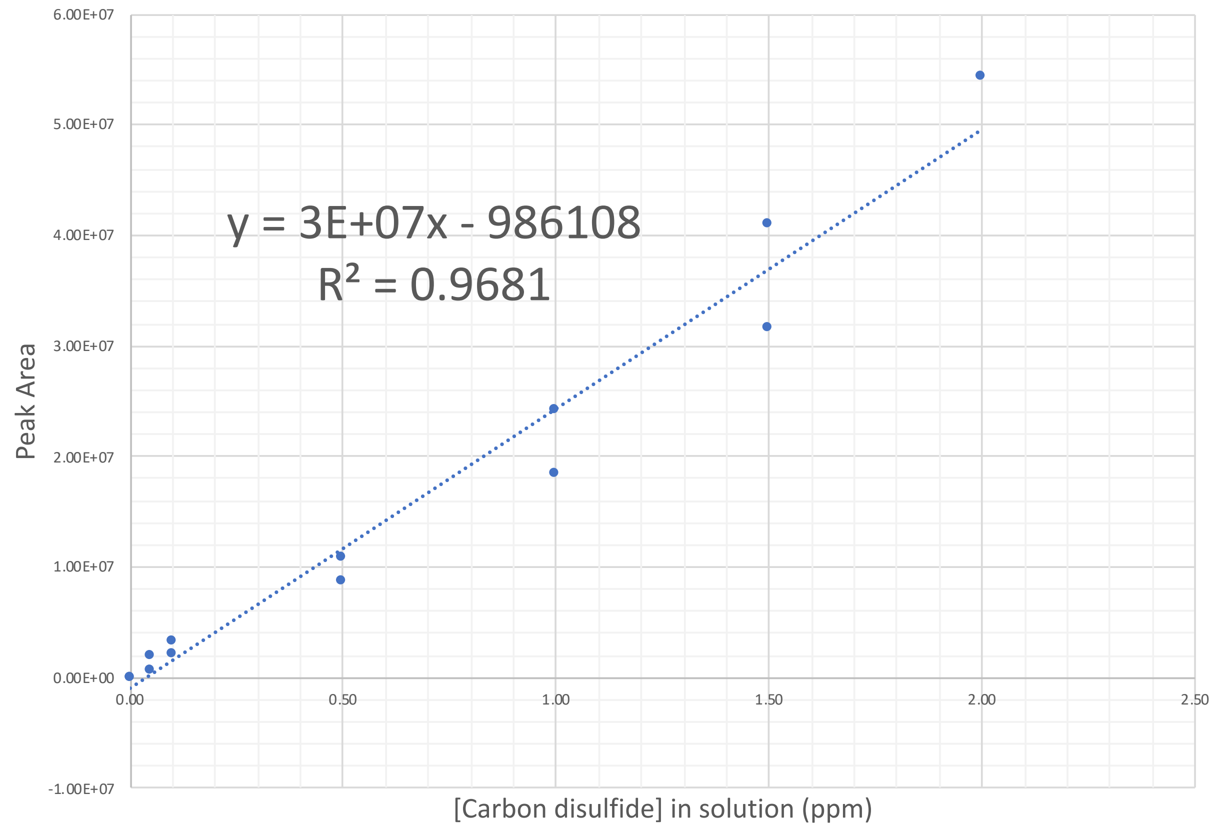
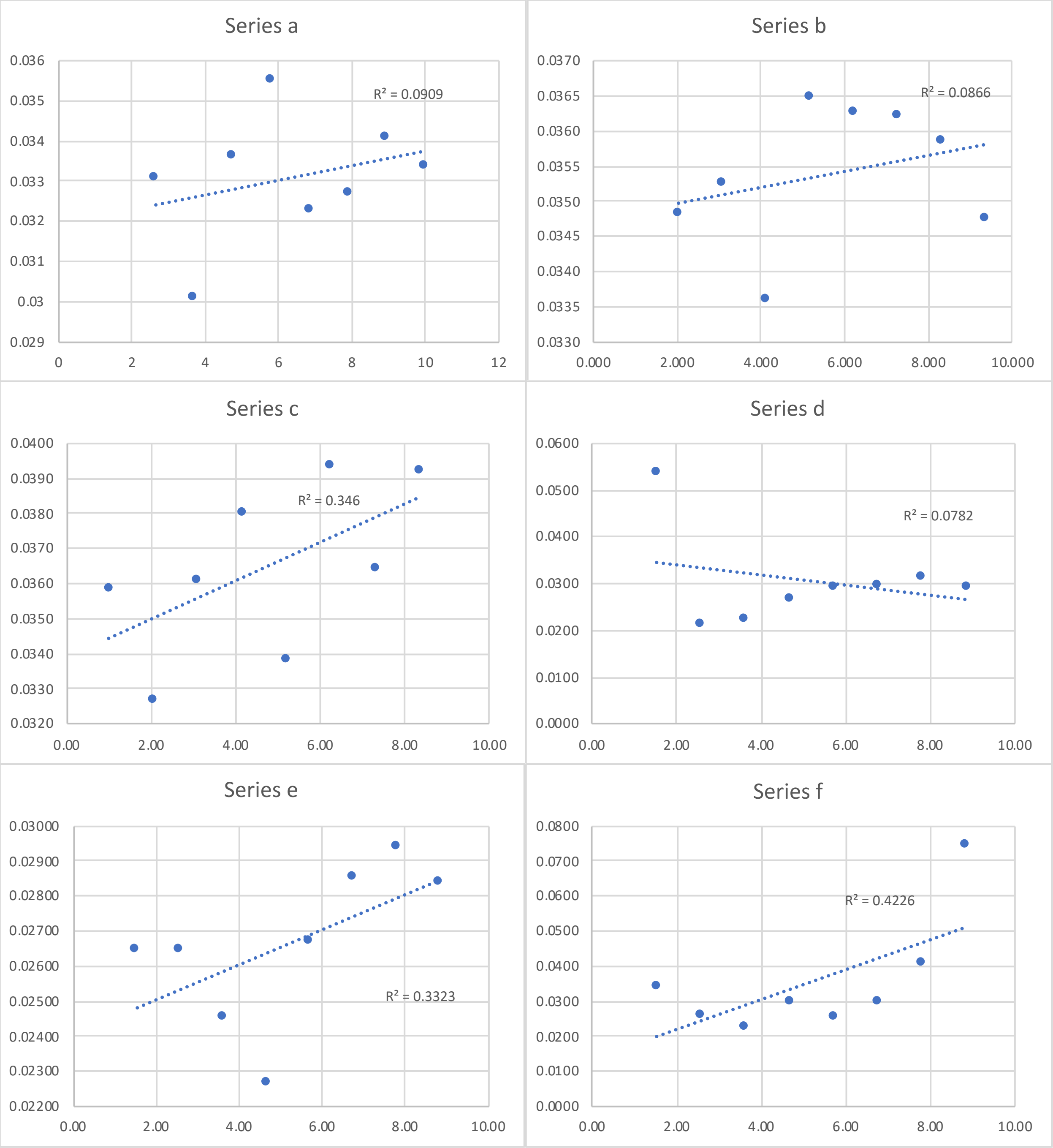


Figure 2. Concentration of CS_2 evolved (ppm) over time (h) for series a – f and their reproducibility values



Series a

Series b

Series c

Series d

Series e

Series f

Figure 3. Concentration of CS_2 evolved (ppm) over time (h) for series g – p and their reproducibility values

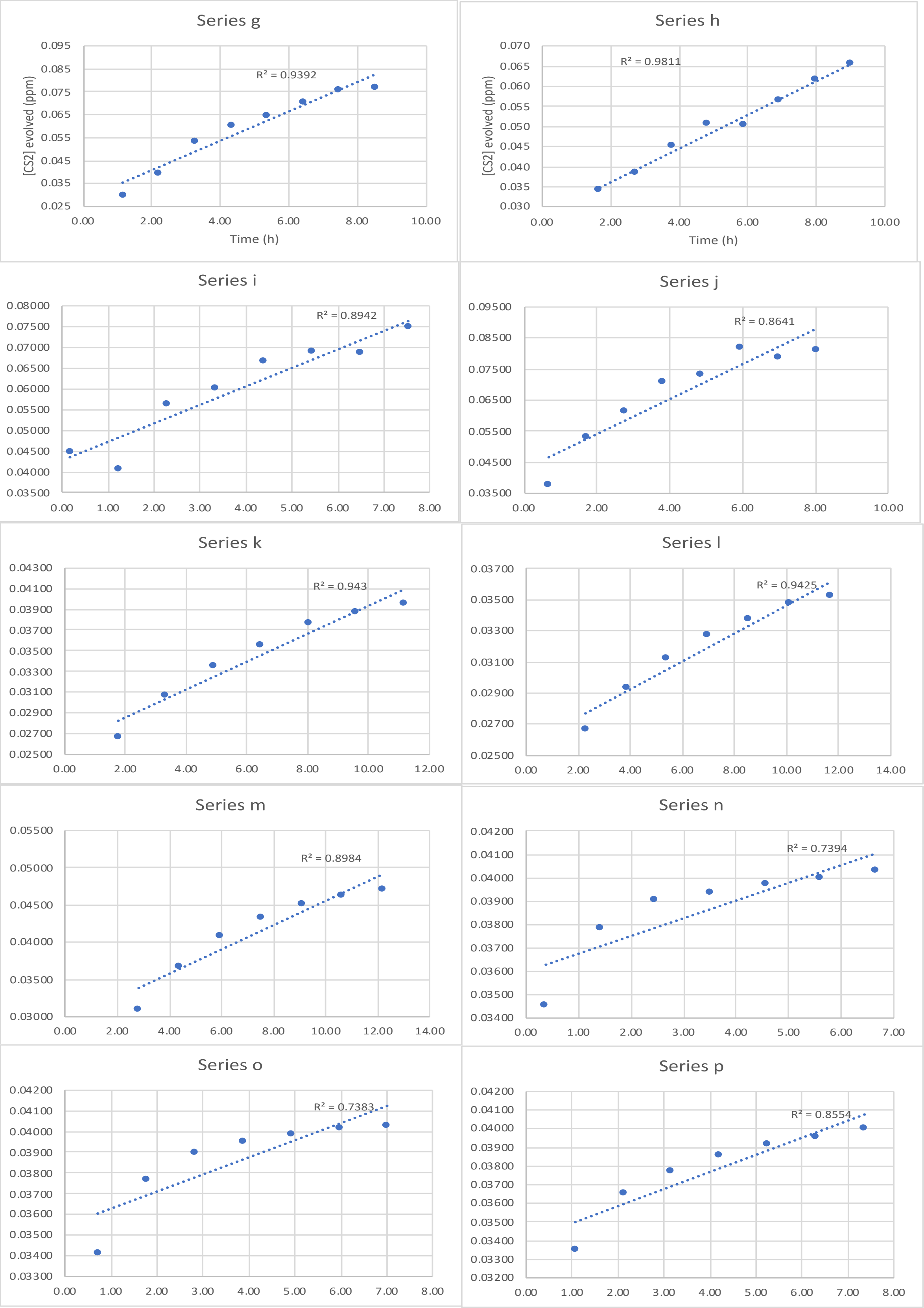


Figure 4. Chromatogram for Series g sample at 5 hours (pH 7.73, 110.6 ppm PIPX)

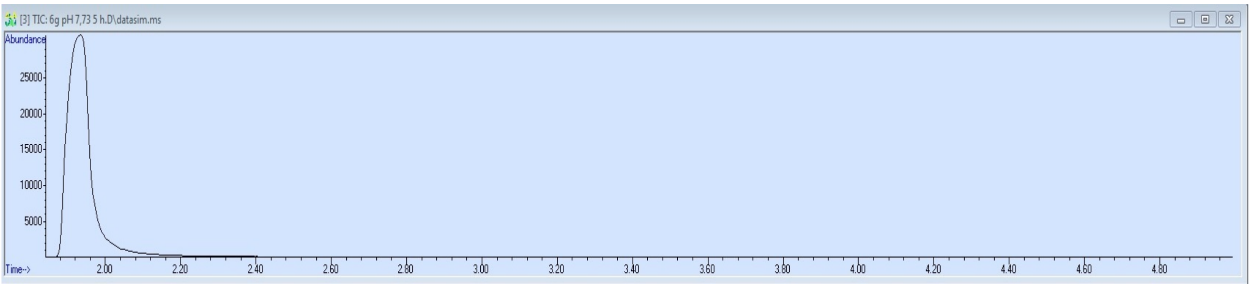


Figure 5. Chromatogram for Series n sample at 6 hours (pH 9.34, 102.6 ppm PAX)

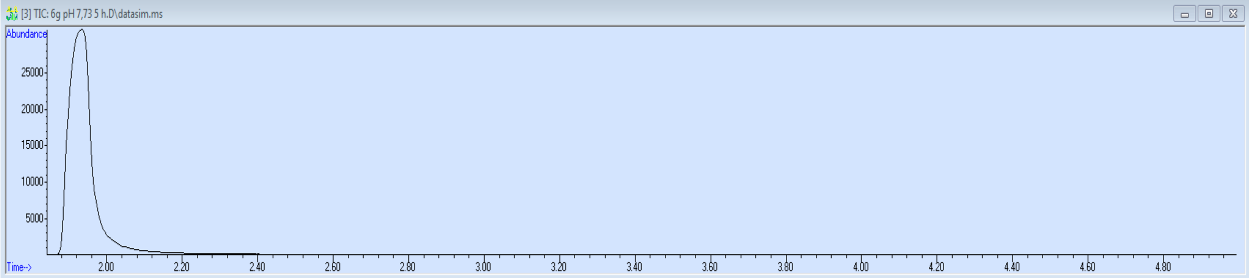


Figure 6. Chromatogram for CS_2 standard 6 (1.50 ppm)

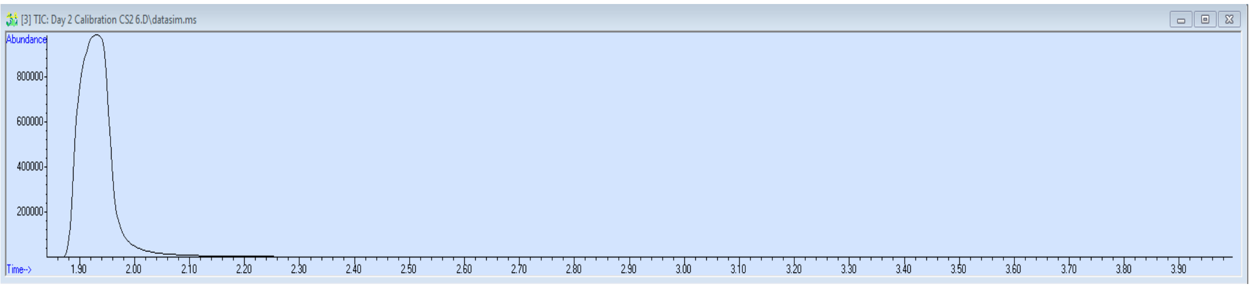


Figure 7. Mass spectrum for Series g sample at 5 hours (pH 7.73, 110.6 ppm PIPX)

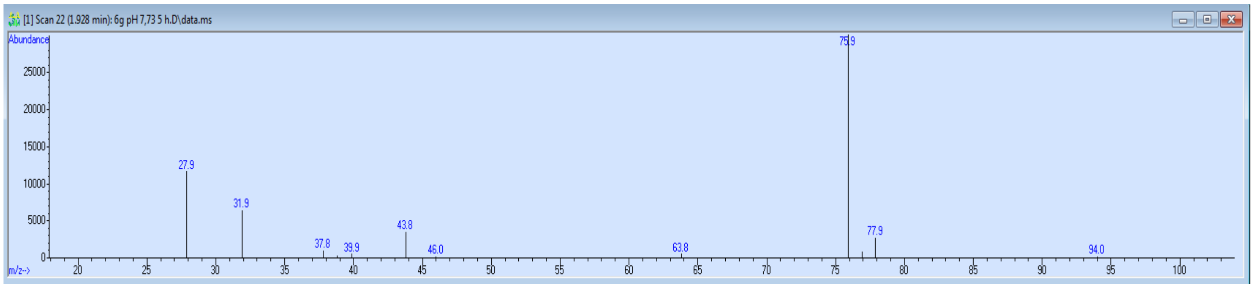


Figure 8. Mass spectrum for Series n sample at 6 hours (pH 9.34, 102.6 ppm PAX)

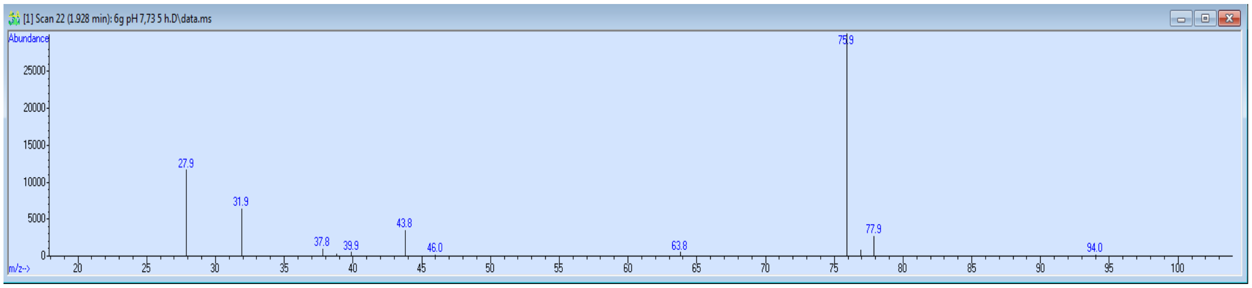


Figure 9. Mass spectrum for CS_2 standard 6 (1.50 ppm)