ASSESSING THE ANALYTICAL FACTORS THAT WOULD IMPROVE THE ADMISSIBILITY OF TRACE EVIDENCE IN COURT

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Abstract

The two organic pollutants that were chosen for this study are vinyl chloride (VC) and methyl ethyl ketone (MEK). These pollutants are commonly found in the environmental media such as water and leachate water. In South Africa, these organic compounds are controlled through the regulations for landfill disposal (G NR 635) under the National Environmental Management: Waste Act No 59 of 2008. MEK toxicological interactions target the liver, lungs and nervous system, and there have been several human case reports of neurological effects, from high exposure to MEK in combination with other hazardous solvents. VC is seen as even more toxic and is also carcinogenic.

When trace evidence is brought for analysis at analytical laboratories, the discussion of both customers and the laboratory analysts always centre around the quality of the data, the turnaround time of the analyses and the operational costs. In most analytical laboratories the sample preparation stage is the most time-consuming and it is also the stage where the highest probability of human error occurs. But, using the solid phase micro extraction (SPME) technique would ensure that sample preparation is quicker, reproducible and cost-effective.

After a minimum of ten sample runs per calibration point, the SPME coupled with Gas- Chromatographic (GC) method performed well as shown through the accuracy, reproducibility, working range, recoveries, uncertainty, sensitivity, selectivity and percentage of relative standard deviation (RSD). The application of this optimized method ensured the successful analyses of traces of vinyl chloride and methyl ethyl ketone pollutants in water matrix, with reduced human related errors to enhance the admissibility of the data in court.

Keywords: Admissibility, Court, Trace, Forensic Evidence, Vinyl Chloride, Methyl Ethyl Ketone, Water Organic Pollutants, SPME, GC/MS.

1. Introduction

Environmental pollution is a serious global problem that adversely affect humans that are exposed to contaminated air, soil or water.[1] In this study the two environmental pollutants of concern are vinyl chloride (VC) and methyl ethyl ketone (MEK). They are both volatile organic compounds (VOC) and contain a polar functional group.[2] In 1974 the US EPA (USA) banned vinyl chloride from aerosol hair spray propellants as well as using it in drugs and cosmetic products due to its carcinogenicity in humans and animals.[3] MEK is commonly used as a solvent in coating systems, such as varnishes, spray paints, glues, sealers, magnetic tapes, paint removers, printing inks and resins. Other sources of MEK in the environment are jet exhausts, internal combustion engines and industrial activities like gasification of coal.[4]

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[1] Agamuthu, P., Tan, Y.S., Fauziah, S.H. (2013). Bioremediation of hydrocarbon contaminated soil using selected organic wastes. Procedia Environmental Sciences 18, 694 – 702.

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Both above compounds are found on the substance priority list (SPL), updated every two years by the Agency for Toxic Substances and Disease Registry (ATSDR) in the United States.[5] Vinyl chloride and methyl ethyl ketone have a groundwater frequency ranking of 15 and 26 respectively.[6] The ranking of organic pollutants is influenced by their frequency of occurrence in all media, their toxicity and the potential for human exposure.[7] Vinyl chloride is more harmful to humans and the environment when compared to methyl ethyl ketone.

Extraction and analysis of compounds in difficult matrices are a common practice in organic environmental laboratories. Therefore, the selection of methods that have sufficient selectivity and acceptable sensitivity in accordance with the operational standards of the laboratory is crucial. This is even more challenging when working with polar compounds. VOCs that contain a polar functional group (low molecular weight ketones, alcohols, aldehydes, nitriles and ethers) are usually soluble in water and produce broad tailing GC peaks, resulting in poor quantification that are difficult to identify.[8]

VC and MEK are important pollutants as they are specified by the National Environmental Management: Waste Act 59 of 2008 (NEMWA) in South Africa. Both pollutants are compulsory to test under the national norms and standards for the assessment of waste to landfill disposal (G NR 635) and remediation of contaminated land (G NR 331) in South Africa.[9,10] These two compounds are also of global concern as it is included in the Victorian EPA and in the US EPA for drinking water.[11,12] The world health organisation also includes VC in their drinking water standards.[13] Before hazardous waste can be disposed of, both the solid (total) concentration and the leachable concentration for certain specified compounds/pollutants must be determined. This is to determine at which class landfill the hazardous waste in question can be disposed of. Vinyl chloride is a compound that also needs to be analysed during the remediation of contaminated land, part 8 of NEMWA in South Africa. Both VC and MEK are found on the substance priority list (PL) that is updated by the Agency for Toxic Substances and Disease Registry (ATSDR).[14]

All commercial laboratories are confronted with high sample volumes and fast turnaround times while working at a reduced operational cost. To achieve this, commercial methods must minimise the use of skilled labour and increase the level of automatization. A focus point is on methods that use little or no solvents as solvents are both expensive and potentially hazardous. Apart from solvents being expensive to buy, they are also expensive to dispose of, as they need to be incinerated. Therefore, the fewer solvents a laboratory uses the greener the operation and the smaller the carbon footprint becomes. Solid phase micro extraction (SPME) offers green methods

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[5] Minnich, 1993.

[6] Ibid

[7] Ibid

[8] Ibid

[9] Depart of Environmental Affairs (DEA). (2013). National Environmental Management: Waste Act, Act No 59 of 2008: National Norms and Standards for the Assessment of Waste for Landfill Disposal. Government Gazette, 578(No. 36784). Issued August 23, 2013.

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[11] Environmental Protection Agency (US-EPA). (2015). Table of Regulated Drinking Water Contaminants. Retrieved January 11, 2016, from http://www.epa.gov/your-drinking-water/table-regulated-drinking-watercontaminants#.

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[13] Esdat. (2015). Esdat Environmental Database Management Software: Selected Water Quality Standards. Retrieved January 11, 2016, from http://www.esdat.com.au/Environmental%20Standards/UK/Landfill%20Directive%20Appendix%20.

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using little or no solvents for the extraction of analytes.

Using SPME permits a high sample throughput, fast turnaround times and lower operating cost.[15] SPME allows minimal sample preparation and none or little expensive solvents to use.[16]

This study aims to improve the analysis of VC and MEK pollutants in different sample matrices while reducing errors due to human factors.

2. Experimental details

2.1 Analytical process

The analytical process consists of consecutive steps such as field sampling, handling and transporting the sample to the laboratory, laboratory sample preparation, separating, identifying and quantifying the analytes and evaluating the results.[17] Sample preparation is seen as the key component in the analytical process.[18]

2.2 SPME and GC/MS

SPME is a sample preparation method that combine extraction, concentration and sample introduction in one step while producing high sensitivity and reproducibility.[19] With a growing need to protect the environment, techniques such as SPME have been developed as they require none or small amounts of toxic solvent. The alternative traditional preparation techniques mainly involve liquid/liquid or liquid/solid extractions with toxic organic solvents, followed by a clean-up step and preconcentrating the sample.[20,21] SPME is a fast, universal, solventless, economic and sensitive method.[22] For commercial applications, SPME is used in automated samplers capable of both heating and agitating samples for optimum extraction.[23] Various conditions were optimised while the SPME is coupled with the GC/MS.

The Chromatographic separations were done on a Varian 450 GC fitted with a 1079 programmable temperature vaporisation (PVT) injector. For SPME, a straight liner with an inside diameter of 0.8mm was used. A splitless injection is used for 5 minutes followed by a 1:25 split until the run has completed. The column used is an RXi ®-5Sil MS (5 % phenyl and 95 % polydimethylsiloxane) 30 m x 0.25 mm (0.25 d_f), supplied by Restek with helium as carrier gas. The method performs the same if a VF5 30 m x 0.25 mm (0.25 μm d_f) supplied by Agilent Technologies are used. The mass spectral data was collected by a Varian 300msTQ mass spectrometer with argon as collision gas for MS/MS analysis. Automation was done using a combi-pal autosampler from CTC Analytics/Leap Technologies. The combi-pal was equipped with a heating and agitation attachment as well as a fibre bake out station, which is not essential for polar

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[15] Versfeld, L. (2004). Factors influencing the use of solid phase microextraction techniques for environmental analysis of industrial waste water. Potchefstroom University.

[16] Llompart et al., 2019.

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[22] Araniti et al., 2018.

[23] Araújo, A., Moreira, N., Lima, A. R., de Lourdes Bastos, M., Carvalho, F., Carvalho, M., & de Pinho, P. G. (2018). Analysis of extracellular metabolome by HS-SPME/GC-MS: optimization and application in a pilot study to evaluate galactosamine-induced hepatotoxicity. Toxicology Letters. doi:https://doi.org/10.1016/j.toxlet.2018.05.028.

analysis. The analysis was done using the prep ahead function of the combi-pal for faster analysis, which is preferred in a commercial lab. This means that the autosampler will start to extract the next sample while the previous sample is being separated and analysed by the GC-MS.

SPME) fibres used for the extraction of the analytes were supplied by Supelco. The fibre used was the black 75µm carboxen/PDMS, fused silica 24 Ga fibre. The fibre extracts the analytes from the aqueous medium by headspace analysis, followed by desorption in the 290 ºC injector port for five minutes and separated by the following Bruker GC program: column temperature started at 40 ºC and held for two minutes, then heated to 210 ºC at a rate of 50 ºC/minute and held for two minutes. The total GC cycle time is 7.4 minutes.

2.3 Standards and reagents

The methanol UV grade was supplied by Honeywell (Burdick & Jackson USA) and the dimethyl sulfoxide (DMSO) 99.5% was supplied by Labscan (Poland). The Goldline 32 % hydrochloric acid CP grade is supplied by ACE chemicals (Johannesburg).

The 2-butanone standard (5000 ppm) is supplied by Restek, catalogue number 30254. The standard is preserved in methanol/water (90:10). The vinyl chloride standard (2000 ppm) preserved in methanol is also from Restek, catalogue number 30089. The purity of these standards is rated at 99 % for both.

The internal standard (IS) is supplied by Restek. The IS consists of three different compounds in a 2000 ppm concentration. The IS compounds are, Methyld3-tert-Butyl Ether (d3 – MTBE), 1-Bromo-4-fluorobenzene (BFB) and 1,2-Dichlorobenzene-d4. Methanol is used as the solvent for the above three compounds.

An independent verification standard is used from Restek, catalogue number 30024. It is called a TCLP VOA mix and contains the following compounds in a 2000 ppm concentration; vinyl chloride, 1,1-dichloroethene, 2-butanone (MEK), chloroform, carbon tetrachloride, 1,2-dichloroethane, benzene, trichloroethene, tetrachloroethene, chlorobenzene and 1,4-dichlorobenzene. The standard is preserved in methanol/water (90:10).

2.4 Sample extraction

Water samples were analysed directly with no external or separate sample extraction or preparations. Using the headspace analysis, the sample volume of 5 mL in a 10 mL sample vial was placed on the instrument for extraction using SPME and GC/MS analysis.

3. Results and discussion

3.1 Organic solvents

Since the two polar compounds are part of regulatory standards, their detection limits should ideally be lower than the limits of the regulatory standard. Both acetonitrile and methanol were tested for use as solvents for the extraction purpose.

Acetonitrile showed the lowest response/peak area for VC and MEK and it also interfered with the internal standard. Acetonitrile can still be used as solvent if there is no other option because the peak area is still large enough to identify a clear peak with a signal to noise ratio that is greater than 10:1. However, if acetonitrile is the only option a different internal standard should be used, or an external calibration should be used.

While methanol is not the optimum choice of solvent for the analysis of VC and MEK, it was chosen as a solvent for extraction because it produced adequate responses when compared with those produced by acetonitrile.

During VC analysis the extracted quantity of analyte decreased as the methanol concentration increases because the VC dissolves in it thus leaving less analytes in the headspace. The effect of MeOH on VC is reduced when using 1 % of MeOH rather than 10 % of MeOH. Using 10% MeOH will have a factor 10 influence on the detection limit as well. If a 10 % MeOH calibration is used together with 10 % MeOH samples the results produced are reliable and repeatable.

Figure 1 demonstrates the effect that MeOH has on VC. The upper reporting limit for VC is 600 ppb, above this, the sample will need to be diluted and therefore for concentrations above 600 ppb a water calibration can be used, because the MeOH concentration will be equal or less than 1 %.

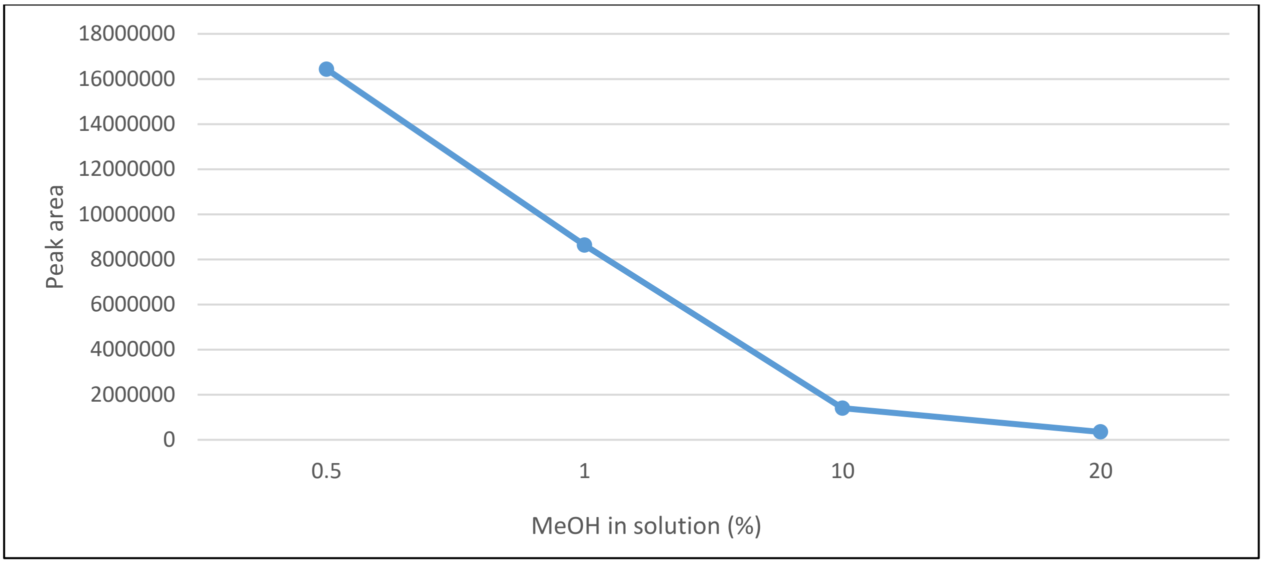

Figure 1: The effect of MeOH in solution on vinyl chloride.

3.2 SPME optimisation

3.2.1 Fibre selection and analyte extraction

The following fibres were tested; 75 µm carboxen/polydimethylsiloxane (PDMS), 100 µm PDMS, 65 µm PDMS/divinylbenzene (DVB) and 85 µm polyacrylate fibre. Each fibre was exposed under the exact same conditions therefore the difference in area reflects the extraction efficiency of the fibre coating.[24] Only the carboxen/PDMS fibre extracted both polar compounds, MEK and VC.

3.2.2 Sample volume

The three different volumes that were used in headspace analysis are 2.0 mL, 5.0 mL 2and 6.0 mL and their peak area responses are shown in Figure 2. 5.0 mL sample in a 10 mL vial showed adequate sensitivity and 5.0 mL sample volume is the current standard for most of the analysis already conducted in this commercial laboratory. In a commercial laboratory it is more productive to keep everything as standardised as possible.

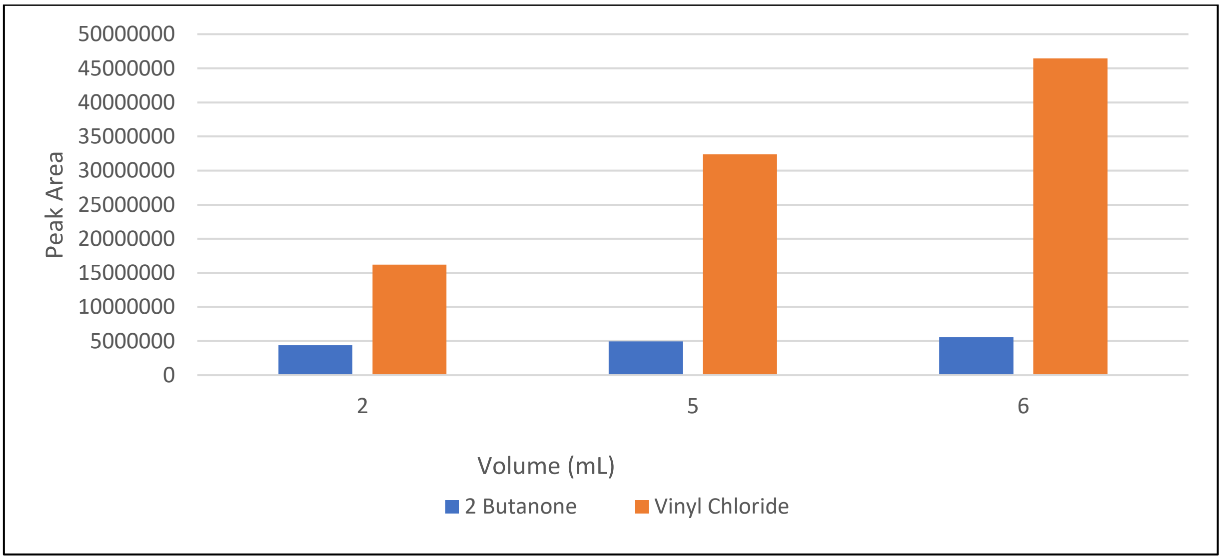

Figure 2: The effect of sample volume on the efficiency of SPME

3.2.3 Ionic strength

The ionic strength of the aqueous sample was increased after adding NaCl (salt), while the solubility of the dissolved organic analytes decreased. Figure 3 shows the effect of salt in headspace analysis using 5 mL sample in a 10 mL vial. It seems that adding large amounts of salt results in a larger peak areas, thus

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[24] Araújo et al., 2018.

a greater sensitivity. However, the peak areas from no salt also resulted in more than adequate peak areas, and thus a high sensitivity.

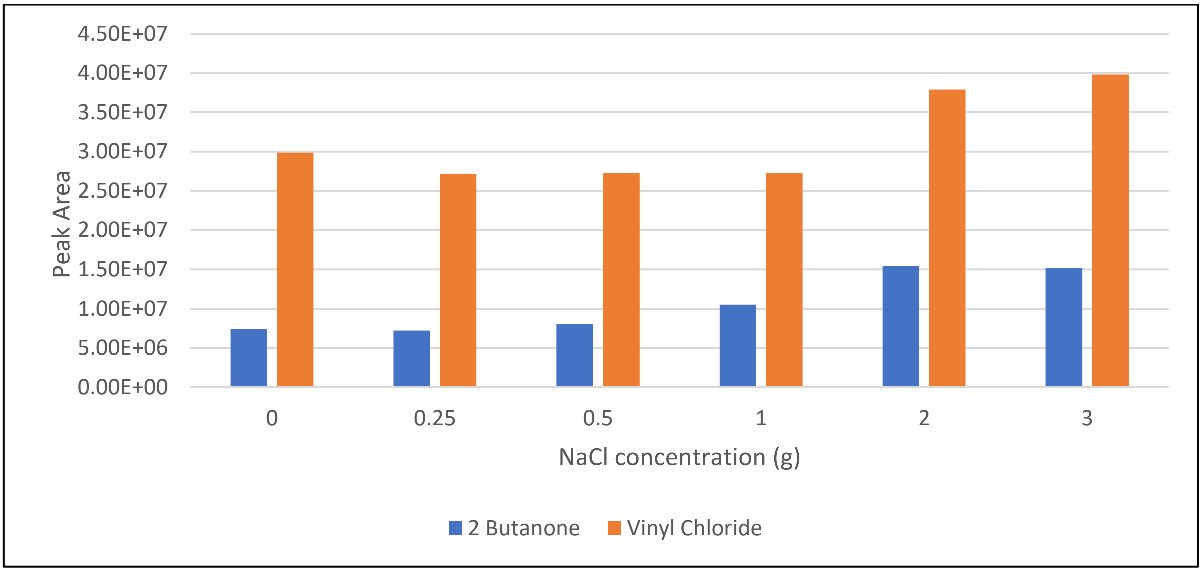

Figure 3: The effect of salt on SPME extraction efficiency of polar compounds in HS analysis.

Figure 4 shows that the peak area consistency for VC was better when no salt was used than when it was added. Therefore, more repeatable results will be achieved when no salt is used..

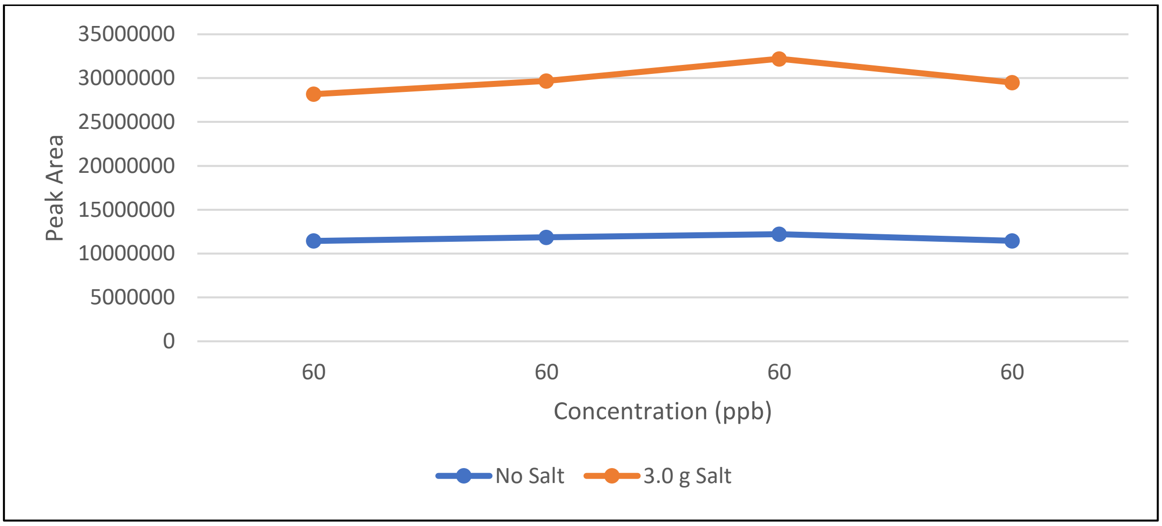

Figure 4: The influence of salt on MEK in HS analysis

3.2.4 The influence of pH

One drop of different hydrochloric acid concentrations was used during headspace analysis in 10 mL vials with changes due to variations in the ultra pure (UP)-water purifier system. As the water purifier machine is being used and the filters get saturated the pH values may change slightly depending on the pH of the UP water used. The influence of acid concentration (pH) can be seen in Figure 5.

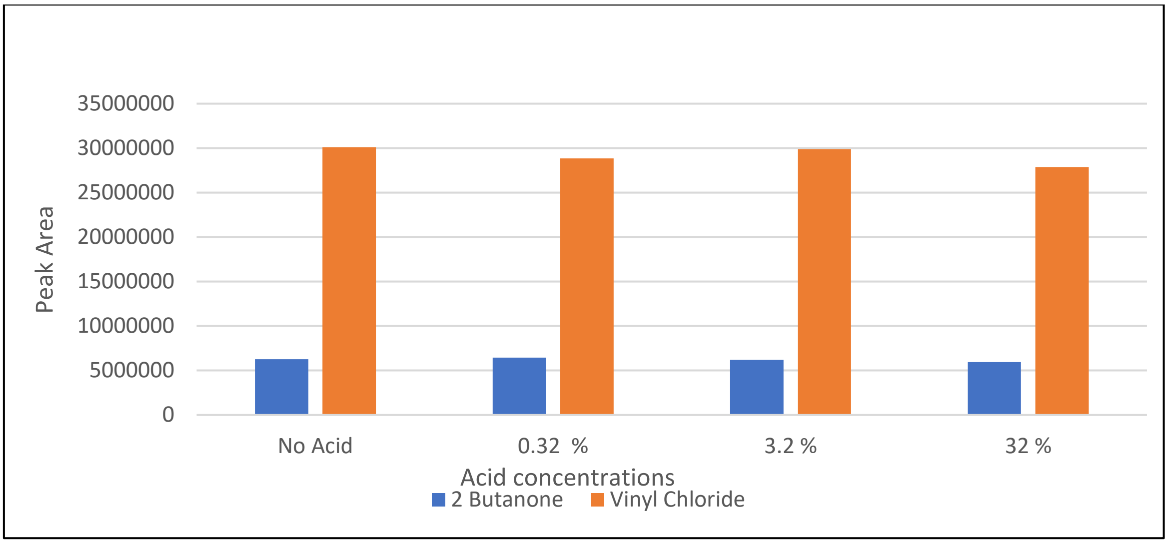

Figure 5: The effect of pH on SPME efficiency.

For this method, one drop of 3.2 % HCl per 5.0 mL sample was decided for use for all analysis. When samples are analysed matrix interference may be present, such errors were minimized by using the laboratory grade water and standards. therefore one drop of acid is used.

3.2.5 Extraction mode, extraction temperature and mode of extraction

Different agitator temperatures were used during the ten-minute extraction time and with an agitation speed of 300 rpm. Figure 6 shows the effect of extraction temperature and agitation compared to HS analysis and submerged analysis at room temperature. HS extraction were selected as the best extraction method for the polar compounds of interest.

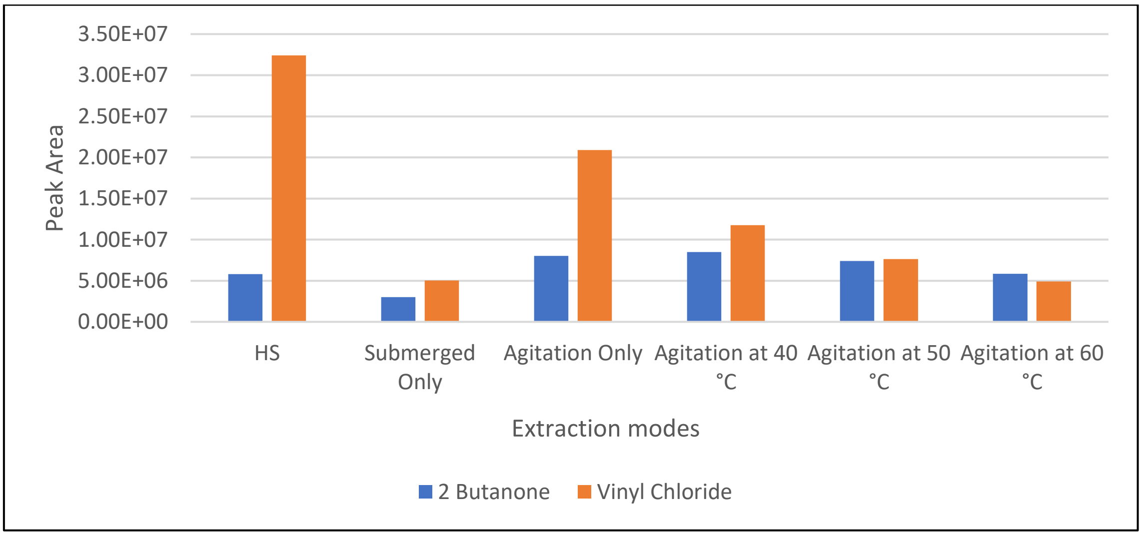

Figure 6: The effect of extraction modes and extraction temperature on the extraction efficiency of SPME.

The data from the five different injection temperatures that were tested is displayed in Figure 7. The recommended desorption temperature for the carboxen/PDMS fibre is between 250 °C and 310 °C.

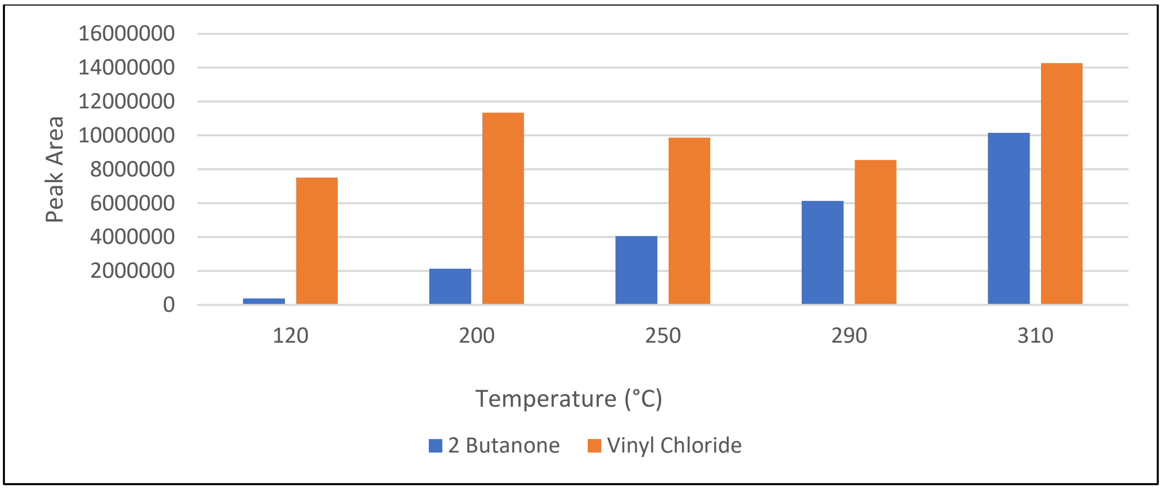

Figure 7: The effect of different injection/desorption temperatures.

In this study, 290 °C was used throughout because sensitivity for both polar compounds is sufficient at this injection temperature and not working at the maximum temperature help to expand the fibre's lifetime by protecting the sorbent. The repeatability is also the best at 290 °C, as can be seen by Figure 8. Four runs were done per desorption temperature, and the most consistent results are between the four runs at 290 °C.

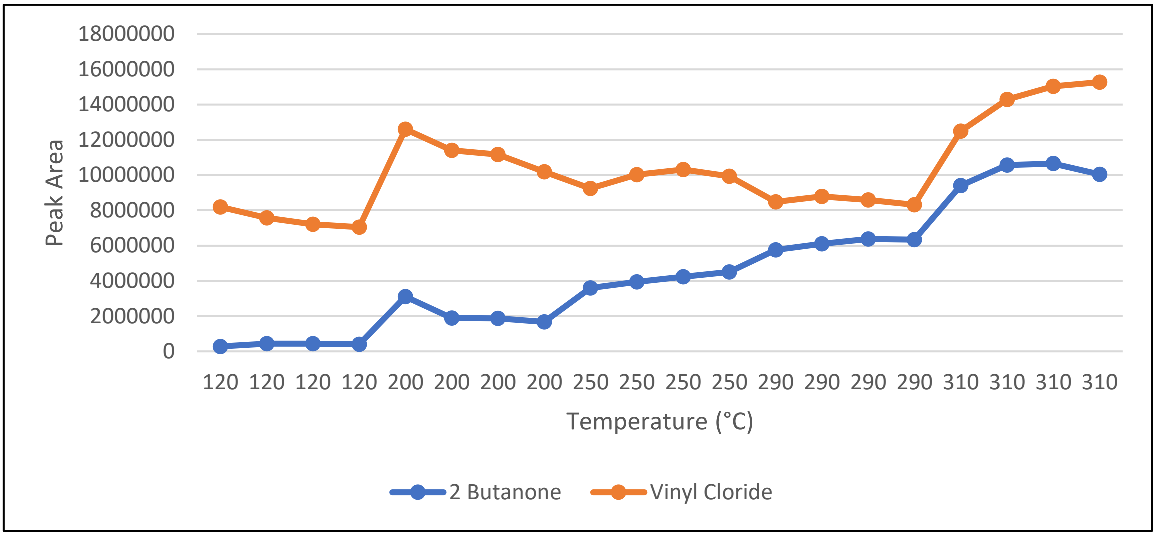

Figure 8: Repeatability of different desorption temperatures.

3.3 Method calibration and instrumental performance

In this study, an internal calibration method that uses an internal standard (IS) was applied, and it refers to a compound added to all the samples using the same concentration. The area and concentration of the IS, is used to calculate the analyte concentration. The IS are mainly used to compensate for sample/matrix interferences but can also be used to compensate for any losses during sample preparation and sample extraction. This, however, is only valuable for quantification if the IS standard is chemically similar to the analytes of interest.

When calculating a calibration curve using an internal standard, the ratio of the analyte response to that of the internal standard is used. Internal standards are also used to compensate for extractions that ended just before equilibrium was reached. The developed method uses an IS to calculate analyte concentrations.

The calibration requirement for the developed polar method must have a % RSD of equal or below 30 % and regression (r^2) of greater than 0.95. The two compounds using a four-point calibration (20, 40, 60 and 80 ppb), easily falls within the mentioned limits. The validation data indicated that the % RSD is below 9% and r^2 is greater than 0.997.

The detection for VC were tested at 0.4 ppb and MEK at 20 ppb. These detection limits are under the regulatory standards for waste assessment.

3.4 Robustness/ruggedness

The use of an internal standard makes this technique extremely rugged as the internal standard will compensate for changes in analysis conditions. In this case, the temperature fluctuations were not significant at 1.6 °C. The temperature in the laboratory is controlled by means of aircons and monitored by using USB temperature loggers. Therefore, there is usually not a large fluctuation in temperature. The temperature usually only fluctuates between 20 °C and 22.5 °C, although the limits are between 16 ° C and 32 °C. However, when different leach waters were used such as the TCLP/acetic acid, borax, wastewater, and acid rain, they give rise to different pH's and electrical conductivities. Furthermore, the verifications were prepared on different days by different analysts and ran on different times, thus under different conditions, and prove the method's ruggedness. This data indicates an analytical process that is not affected by small variations in parameters of a method and the laboratory environment. The results are displayed in Table 1, where the true value is 60 µg/L and all data were acquired on the same instrument.

Table 1: The ruggedness of the method

Verification ID	Analyst	Temperature (° C)	pH	EC µS	Result (average ppb)
60 DW VER	A	22.0	7.01	1.67	66.7
60 AR VER	A	22.0	4.0	55	58.25
60 Borax VER	A	22.0	9.3	11420	65.75
60 TCLP	A	22.3	5.08	5290	59.15
60 Waste VER	A	22.0	12.0	2078	72.1
60VER627	B	21.6	N/A	N/A	57.0
60VER578	C	20.7	N/A	N/A	61.5
60 5mL	A	22.0	N/A	N/A	60.6

3.5 Various validation data

Tables 2 and 3 show at some of the validation data gathered for the developed method with a good method accuracy and recovery. The results with relatively low standard deviations indicate that the analyte data was reliably quantified. The uncertainties are also indicated.

Table 2: Statistical data for vinyl chloride

EXPECTED VALUE (ppb)	**0.4**	**1**	**20**	**40**	**60**	**80**	**600**	**1000**
Acceptance criteria (30%)	± 0.12	± 0.3	± 6	± 12	± 18	± 24	± 180	± 300
1	0.5	0.9	20.9	34.5	54.2	93.0	534.8	764.2
2	0.4	0.9	19.3	35.0	70.8	95.8	533.6	768.5
3	0.4	0.9	21.9	35.9	68.1	96.9	547.2	817.3
4	0.4	1	21.6	42.0	71.2	91.6	557.4	793.8
5	0.4	0.9	19.8	34.4	72.3	77.7	509.2	745.9
6	0.5	1.1	21.4	35.2	71.4	84.5	527.3	800.6
7	0.4	1	18.3	35.1	68.8	82.8	521.0	
8	0.4	1.1	20.7	39.4	67.4		508.7	
9		1	19.4	36.3	67.3			
10		1	17.6	38.0	70.2			
Average	0.43	0.98	20.09	36.58	68.17	88.90	529.90	781.72
Standard Deviation	0.046	0.08	1.45	2.48	5.21	7.28	17.14	26.58
% RSD	10.89	8.05	7.21	6.79	7.65	8.19	3.24	3.40
Accuracy (% Recovery)	106.25	98.00	100.45	91.45	113.62	111.13	88.32	78.17

Uncertainty at 95% Confidence	0.09	0.16	2.90	4.97	10.43	14.55	34.29	53.16
Expanded Uncertainty	0.12	0.23	3.93	5.25	14.44	19.61	50.09	90.21
Expanded Uncertainty (%)	29.5	23.2	19.6	13.1	24.1	24.5	8.4	9.0
Meet Criteria?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Table 3: Statistical data for methyl ethyl ketone

EXPECTED VALUE (ppb)	**20**	**40**	**60**	**80**	**600**	**1000**
Acceptance criteria (30%)	± 6	± 12	± 18	± 24	± 180	± 300
1	22.2	40.3	61.5	73.1	582.7	874.4
2	23.2	40.4	60.2	80.3	630.3	835.7
3	20.4	40.5	60.4	86.2	630.1	860.2
4	22.2	44.9	60.8	83.4	548.8	837.7
5	19.4	43.9	58.1	77.2	521.6	782.4
6	21.0	43.1	57.6	78.0		
7	22.3	44.7	57.5	79.9		
8	21.5	42.9	57.0	77.8		
9	22.2	43.2	59.6	78.8		
10	22.7	43.1	61.9			
Average	21.71	42.70	59.46	79.73	582.70	838.08
Standard Deviation	1.15	1.72	1.78	4.26	48.46	35.05
% RSD	5.29	4.04	3.00	5.35	8.32	4.18
Accuracy (% Recovery)	108.55	106.75	99.10	99.66	97.12	83.81
Uncertainty at 95% Confidence	2.3	3.4	3.6	8.5	96.9	70.1
Expanded Uncertainty	2.8	4.2	4.6	9.7	163.8	128.6
Expanded Uncertainty (%)	14.0	10.5	7.6	12.1	27.3	12.9
Meet Criteria?	Yes	Yes	Yes	Yes	Yes	Yes

4 Conclusion

The study successfully analysed vinyl chloride and methyl ethyl ketone water pollutants using SPME coupled with GC/MS. This method proved to be robust enough to use on various matrices such as water, wastewater and various leach waters (acetic acid/TCLP, borax, acid rain and distilled water). It is a low-cost method as water samples require no sample preparation or extraction and no preservation. The method also proved to have a high accuracy and precision. Other analytical performance criteria of the process were the working range, standard deviation, percentage relative standard deviation (RSD), uncertainty, recovery, sensitivity and selectivity as shown in Tables 2 and 3. The turnaround time of individual runs were completed quicker, that is in 7.4 minutes. This method was found to be effective and less prone to human related errors, thus enhancing the admissibility of the data in court.

Acknowledgement

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