Determining the Partition Coefficient of TNT in an Acetonitrile/Hexane Extraction System

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Method

Sample Preparation

One part per million (ppm) and 0.500 ppm TNT standards were prepared by diluting commercially available 1000 ppm stock TNT solution purchased from Accustandard with acetonitrile (ACN). Solutions to be extracted were prepared by mixing 1.00 ml of the TNT standard (1.00 ppm or 0.500 ppm) with 2.00 mL of hexanes (Sigma Aldrich, Certified Grade). The samples were extracted using either the shaking method or the sonication method. Once mixed, the samples were allowed to settle for 15 minutes. The top hexane layer was removed from the system by drawing off the layer with a glass pipet. A 100 uL sample of the ACN layer was withdrawn from the vial and analyzed using gas chromatography. Five samples were prepared for extractions in a set and each sample was analyzed in triplicate.

Shaking Method

The ACN/HEX mixtures were placed in 4 ml brown glass vials for extraction . The TNT-ACN/HEX system was added to each vial and hand shaken for 5 minutes. This process was completed by gripping the vial by the cap and the bottom of the vial with the thumb and index finger and then shaking vertically (Figure 1). For this method; each extraction was performed using 2 mL of hexanes and 1 mL of the TNT standard prepared in acetonitrile.

Sonification Method

A 4 ml brown glass vial was again used for each solution with extraction occurring by placing the vial in a sonicator bath (Figure 2). Sample vials were placed in a beaker fit for the sonicator bath. Vials containing water were added to the beaker to take up excess space. The beaker was filled with water to half of the height of the sample vials and placed in the sonicator bath. The samples were then sonicated for 20 minutes using a VWR model D5500A-MTH sonicator bath. For this method two extractions using 2.00 mL of hexanes were performed for a 1.00 mL standard of TNT in acetonitrile.

Instrumentation

An Agilent 6890N gas chromatograph (GC) fitted with a 6-meter (m) by 530 µm Restek TNT fused silica column and a micro electron capture detector was used to analyze the ACN layer of the TNT system. The GC was fitted with an autosampler. The method parameters can be found in Table 1.

Abstract

Residue from explosives can be transferred to surfaces when a person who has handled them has not thoroughly cleaned their hands or clothing. When collecting samples to detect for explosives, in addition to environmental contaminants collected, components from the material it was deposited on (e.g. cardboard) are also collected. To minimize interferences during chemical analysis, the explosive must be isolated from the other components. This is often done by extracting samples with an immiscible aqueous/organic solvent pair used to separate the explosive from other materials. The partition coefficient of the solvent pair determines the effectiveness of the extraction. For this study, 2,4,6-trinitrotoluene (TNT) and an acetonitrile (ACN)/hexane(HEX) extraction system was used. The extraction coefficient $K_p = [TNT]_{HEX}/[TNT]_{ACN}$ was determined using two different techniques; a manual shaking method and a sonication method. The partition coefficient for TNT in the ACN/HEX extraction system using the manual shaking method was 0.279 ± 0.012 at the 95 % confidence level. The partition coefficient for TNT in the ACN/HEX extraction system using the sonication method was determined as 0.336 ± 0.024 at the 95 % confidence level.

Figure 1. Grip used for the shaking method

Figure 2. VWR model D5500A-MTH sonicator bath

Discussion

The distribution of an analyte between two solvents is governed by the equilibrium of that species as it distributes itself between two immiscible solvents. In this study, TNT was used as the analyte and acetonitrile (ACN) and hexanes (HEX) served as the solvent system.
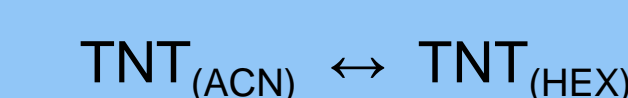
$$TNT_{(ACN)} \leftrightarrow TNT_{(HEX)}$$

The equilibrium constant for this system is

$$Kp = [TNT]_{(HEX)}/[TNT]_{(ACN)}$$

and is known as the partition coefficient. This constant describes the distribution of a solute between two immiscible solvents. To minimize interferences during chemical analysis, the explosive must be isolated from the other components, and this can easily be done via extraction. By knowing the extraction efficiency, extrapolations of the amounts of explosive deposited on the initial surface can be better estimated.

The partition coefficient of TNT in the ACN/HEX extraction system was determined for two different methods of mixing; shaking and sonication. In addition, to show the independence of the partition coefficient on concentration, two different concentrations of TNT were also employed. The resulting partition coefficients using the shaking method is shown in (Table 2). An ANOVA analysis was performed on the sets for each concentration to determine if the data could be combined. At the 95% confidence level, the ANOVA results for the 1.00 ppm TNT using the shaking method resulted in an F_{cal} value of 0.186, which was less than the $F_{critical}$. This suggested the Kp values were statistically the same, hence the individual sets could be combined. The results the 0.500 ppm TNT extraction trials were then compared using ANOVA at the 95 % confidence level and the F_{cal} value of 0.495 was also found to be less than the $F_{critical}$ value. Since F_{cal} is less than the value of $F_{critical}$ in the ANOVA, the two trials for 0.500 ppm TNT extractions using the shaking method produced the same results and were combined.

Since the partition coefficient of a system should be the same for all concentrations in a specific range, the partition coefficients for the 1.00 ppm TNT extraction and the 0.500 ppm TNT extraction using the shaking method were compared. This comparison was completed using an ANOVA of the two concentrations performed at 95 % confidence level shown in (Table 3). Again F_{cal} was found to be less than $F_{critical}$ allowing all individual values for the shaking method to be combined. The overall K_p for shaking was determined to be 0.279 ± 0.012 at the 95 % confidence level. Hence, in effect, when TNT is extracted to remove contaminants and interferences there is approximately a 28% loss of the TNT to the organic solvent.

Due to the potential variability created by different users when performing the shaking method, an instrument based method was investigated to remove variability due to the operator. The sonication method provides consistent mixing for all users. The partition coefficient of TNT for the sonication method extraction trials are shown in (Table 4). A series of ANOVA analysis identical to the shaking method were performed to determine (1) if the individual trials could be combined and (2) if the different concentration samples could be combined. Results were similar to the shaking method and all the data statistically represented the same population and were allowed to be combined (Table 5). The K_p for the sonication method was determined to be 0.336 ± 0.024 at the 95 % confidence level. Sonication appears to be more efficient at saturating the hexane layer with the TNT, showing a 34% transfer of TNT to hexane.

While these two techniques do not produce the same value for the partition coefficient (Table 6), they do suggest that a significant amount of the analyte is transferred into the organic phase during extraction (28-34%). Hence when samples are taken for analysis, it must be remembered that the amount of TNT on the surface is likely to be significantly higher than the chemical analysis suggests.

Inspection of the data shows the shaking method to be more precise due to its lower variance. Intuitively, one would expect the instrumental technique of sonication would produce more consistent results, it is apparent that additional work is needed to perfect the method.

Inlet			Proprietary Column- Restek TNT	Oven	
Sample size	1 µL		Temperature	310 ºC	Temperature	175 ºC
Inlet Temperature	150 ºC	Nominal Pressure	1.05 psi	Detector (µECD)	
Carrier Flow Rate	4.2 mL/min	Combined Gas Flow: Helium with P5	60 ml/min	Initial Temperature	300 ºC
				Maximum Temperature	310 ºC

Table 1. GC operating parameters

Shaking	Partition Coefficient (Kp)		
	Trials	Combined Trials	Combined Concentra-tions
1 ppm (Trial 1)	0.279	0.284	0.279
1 ppm (Trial 2)	0.289		
0.5 ppm (Trial 1)	0.277	0.273	
0.5 ppm (Trial 2)	0.269		

Table 2. Partition coefficient for the shaking method

Sonication	Partition Coefficient (Kp)		
	Trial	Combined Trials	Combined Concentra-tions
1 ppm (Trial 1)	0.316	0.317	0.336
1 ppm (Trial 2)	0.317		
0.5 ppm (Trial 1)	0.344	0.354	
0.5 ppm (Trial 2)	0.365		

Table 4. Partition coefficient for the sonication method

Conclusion

The partition coefficient of TNT in an ACN/HEX extraction system was determined using the shaking method and sonication method. The partition coefficient for TNT extraction using the shaking method was 0.279 ± 0.012 at the 95 % confidence level. The partition coefficient for TNT using the sonication method was 0.336 ± 0.024 at the 95 % confidence level.

Compared Trials		F_{calc}	F_{crit}
1 ppm (Trial 1)	1 ppm (Trial 2)	0.186	5.318
0.5 ppm (Trial 1)	0.5 ppm (Trial 2)	0.495	5.318
1 ppm (Trial 1 + 2)	0.5 ppm (Trial 1 + 2)	0.915	4.414

Table 3. ANOVA results comparing trials using the shaking method at the 95 % confidence level

Compared Trials		F_{calc}	F_{crit}
1 ppm (Trial 1)	1 ppm (Trial 2)	0.006	5.318
0.5 ppm (Trial 1)	0.5 ppm (Trial 2)	0.269	5.318
1 ppm (Trial 1 + 2)	0.5 ppm (Trial 1 +2)	3.035	4.414

Table 5. ANOVA results comparing trials using the sonication method at the 95 % confidence level

T-test at 95% confidence level	Sonication	Shaking
Mean	0.336	0.279
Variance	0.003	0.001
Observations	20	20
df	19	
t_{calc}	4.289	
t_{crit}	2.093	

Table 6. T-test comparing the shaking and sonication methods

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