The Detection of Date Rape Drug Residues Using X-Ray Diffraction

Emily Walsh and Virginia M. Maxwell, D.Phil.
University of New Haven - Department of Forensic Science
Henry C. Lee College of Criminal Justice and Forensic Sciences
300 Boston Post Rd. West Haven, CT 06516

Abstract

Difficulty in detection of date rape drugs in a drug facilitated sexual assault (DFSA) victim's system, more specifically their blood, hair, and urine, has been a predominant problem investigators and forensic scientists have encountered. After a matter of hours, these fast acting drugs have little chance of being detected with modern toxicological techniques due to their rapid metabolism by the body. Proving the use of these drugs can be very hard to establish due to the challenge of detection. This project utilized X-ray diffraction (XRD) in order to detect and identify date rape drugs on various materials.

The date rape drugs used for the purposes of this project were Gamma-Hydroxybutyric acid (GHB), Chloral Hydrate, Ketamine, Flunitrazepam (Rohypnol), and MDMA (Ecstasy). XRD has been implemented in many forensic laboratories due to low cost, versatility, and the non-destructive nature of analysis. The use of XRD for the purpose of detecting date rape drugs residues on clothing and in containers, such as those typically submitted as evidence, was the focus of this project.

Introduction

Date rape drugs affect the body in many different ways, often magnified when used in conjunction with alcohol. Date rape drugs are fast acting depressants which cause drowsiness, decreased anxiety, and mental impairment, taking effect within 10 to 30 minutes of consumption. The difficulty detecting these drugs stems from a property called half-life. Half-life is the period of time needed for the body to metabolize half the drug, resulting in the quantity of the drug in the body to fall to half its value. After this point the drug will continue to be metabolized and decay at an exponential rate.

The technique of X-ray diffraction is commonly used in the field of forensic science for the purpose of analyzing solid materials from minute trace amounts to large complex mixtures with several different compositions. The method has great versatility because crystalline structure is the only requirement for analysis. Materials composed of metallic, organic, and inorganic compounds can be analyzed using this technique. XRD is non-destructive to the materials being analyzed, which permits the ability of carrying out further analysis of the materials by other methods. [1,2]

The principle behind X-ray diffraction involves the crystallinity of a sample scattering x-rays. The x-rays produced by the instrument are passed through the sample and the ordered arrangement of atoms scatter the x-rays. The constructive interference created by the scattered beams moving in phase with each other ultimately produces a diffracted beam. [3] The ability to distinguish one sample from another comes from each compound having a characteristic crystal structure. This then results in a distinct and unique diffraction pattern. Diffraction patterns are influenced by both the intensity and angle of the diffracted beams gathered by the detector component of the instrument. [4] When the sample diffracts the x-rays , that are then detected by the instrument, the angle at which they were diffracted is what produces unique diffraction peak patterns.

Materials and Methods

The instrument used for this project was the Rigaku MiniFlex II Desktop X-ray Diffractometer. The software utilized for analyzing the obtained spectra was MDI Jade 9. Before every sample was run, a standard silicone test was performed to ensure the instrument was working properly.

Four fabric types: denim, white cotton, polyester, and grey cotton (90%) and polyester (10%), were cut to cover the 2 x 2 cm well on a zero background sample holder and mounted using cellophane tape. Individual spectra of the fabric samples were obtained and peak tables printed using Jade.

Pure date rape drug samples were loaded into the zero background holder with a small circular well about 2 mm in diameter using toothpicks. Spectra were obtained and analyzed using Jade.

Two mixtures of confectionary sugar and drug (Ketamine and Chloral Hydrate) were prepared to be 10% drug mixtures. After spectra of the two mixtures were obtained, peak tables were found using Jade. These peak tables were then compared to the pure drug and confectionary sugar peak tables found earlier, in order to assign the mixture peaks as being from the drug or sugar.

Pastes of the 10% drug mixtures were created using a single drop of water. The Ketamine paste was used in further testing by smearing it on the four fabric samples. These were then mounted on the zero background holder and tested with the X-ray diffractometer. Peak tables were then created using Jade and compared to find the peaks indicative of Ketamine.

Finally, a mixture of 5 mL ethanol and 0.0028 g Ketamine was prepared in a small falcon tube. A few drops of the mixture was pipetted onto a flat zero background holder. This was left out to evaporate and leave a residue behind. This was tested using XRD and peak tables were obtained and again compared to find the peaks resulting from the Ketamine.

Results

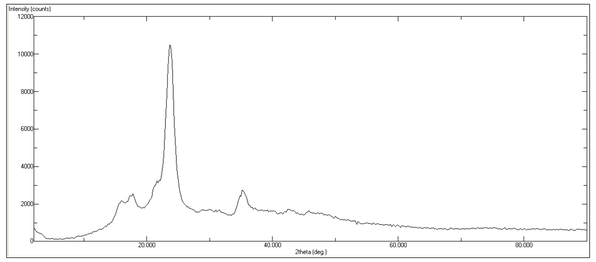


Figure 1: Spectrum of Denim Fabric. The sample was analyzed with a scan range of 2.000 – 90.00 deg at a scan speed of 5.000 deg/min.

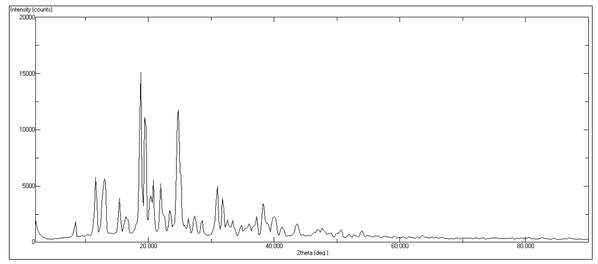


Figure 2: Spectrum of Confectionary Sugar. The sample was analyzed with a scan range of 2.000 – 90.00 deg at a scan speed of 10.000 deg/min.

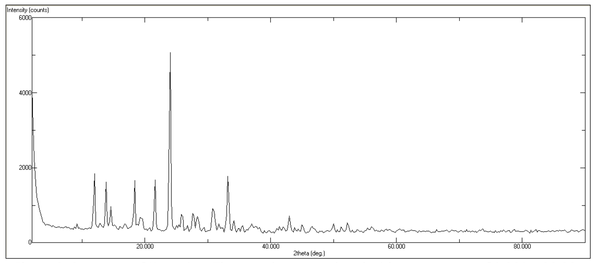


Figure 3: Spectrum of Ketamine. The sample was analyzed with a scan range of 2.000 – 90.00 deg at a scan speed of 10.000 deg/min.

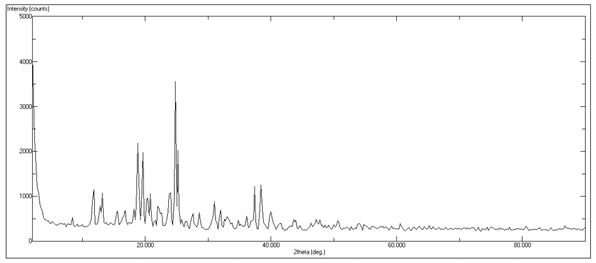


Figure 4: Spectrum of 10% Mixture of Ketamine and Confectionary sugar. The sample was analyzed with a scan range of 2.000 – 90.00 deg at a scan speed of 5.000 deg/min.

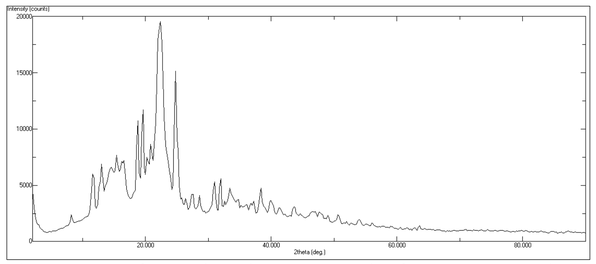
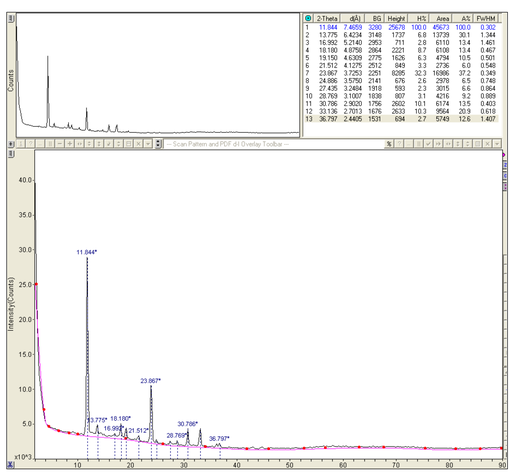


Figure 5: Spectrum of Denim Fabric with 10% Ketamine and Confectionary Sugar Paste. The sample was analyzed with a scan range of 2.000 – 90.00 deg at a scan speed of 10.000 deg/min.



2-Theta	d(Å)	BG	Height	H%	Area	A%	FWHM
11.844	7.4659	3295	25679	100.0	45673	100.0	0.302
13.775	6.4234	3148	1737	6.8	13739	30.1	1.344
16.992	5.2140	2963	711	2.8	6310	13.4	1.461
18.180	4.8758	2864	2221	8.7	6108	13.4	0.467
19.150	4.6309	2775	1626	6.3	4794	10.5	0.501
21.512	4.1275	2512	849	3.3	2736	6.0	0.548
23.867	3.7253	2251	8285	32.3	16906	37.2	0.349
24.886	3.5750	2141	676	2.6	2979	6.5	0.748
27.435	3.2484	1918	593	2.3	3015	6.6	0.864
28.769	3.1007	1838	807	3.1	4216	9.2	0.889
30.786	2.9020	1756	2602	10.1	6174	13.5	0.403
33.136	2.7013	1676	2633	10.3	9564	20.9	0.618
36.797	2.4405	1531	694	2.7	5749	12.6	1.407

Figure 6: Spectra and Peak Table analysis of the Ethanol and Ketamine Mixture using the MDI Jade 9 Software. This demonstrates how the software was utilized to further analyze all the samples. The peak positions, indicated above the peaks, were found by setting a background, which is the pink line. The software used threshold, intensity cutoff, and range to accurately pick and assign peak values.

Corresponding Peak Values

Denim	Confectionary Sugar	Ketamine	10% Ketamine Mixture	Denim and Paste	Ethanol and Ketamine Mixture
2-Theta	2-Theta	2-Theta	2-Theta	2-Theta	2-Theta
16.003	8.331	9.189	8.356	8.227	11.844
17.786	11.597	11.945	11.712	11.619	13.775
23.624	12.955	13.814	13.079	12.999	16.992
30.015	15.403	16.827	15.499	14.599	18.180
31.573	16.445	18.373	16.686	15.405	19.150
35.217	18.779	19.270	18.832	16.554	21.512
42.641	20.695	21.590	19.600	18.801	23.867
45.815	22.026	23.976	20.661	19.587	24.866
	23.441	25.794	23.890	22.377	27.435
	24.792	27.668	24.904	24.821	28.769
	27.386	30.873	26.517	27.463	30.786
	28.556	33.203	27.548	28.598	33.136
	30.934	35.555	28.616	31.961	36.797
	31.849	37.000	30.972	33.437	
	33.367	39.788	31.985	37.066	
	34.798	41.373	33.000	38.378	
	35.974	42.981	34.899	40.027	
	37.116	45.028	36.155	43.663	
	38.300	46.621	37.350	44.614	
	40.006	49.970	38.440	46.631	
	41.295	46.621	40.037	50.658	
	43.632	49.970	41.497	54.010	
	47.616	51.225	43.676	63.607	
	50.563	52.227	46.420		
	51.906	53.824	47.217		
	53.975	56.024	50.622		
	56.037	60.594	54.025		

Figure 7: Chart of Peak Values from the Spectra shown in Figures 1-6. The peak values highlighted in yellow correspond to the peaks that were concluded to be the detected peaks of ketamine amongst the various other components of the samples.

The pattern for cotton is shown in Figure 1, which is similar to the two other cotton samples. Fabrics analyzed with XRD give patterns of only a few (3-5) peaks, in comparison to the more complex dry sample spectra. Even though the spectra are considered quite complex, the XRD had the power to distinguish each component of the sample. Something that could change amongst same sample runs was the intensity, measured in counts, of the peaks. This occurred when the scan speed was reduced for all the samples.

Dry samples of each of the drugs tested yielded clear diffraction patterns with numerous peaks, as shown in Figures 2-5. To simulate the high sugar content of many mixed drinks, confectionary sugar was added. Additional peaks that could be attributed to the sugar were observed, but more importantly the peaks for the constituent drugs were unchanged and visible. These drug peaks are clearly showed in Figure 7. Due to the Ethanol mixture containing Ketamine, the pattern from Figure 6, through visual comparison, has similarities with the Ketamine pattern from Figure 3 . The peaks for the pattern in Figure 6 are consistent with the Ketamine peaks, which is also demonstrated by Figure 7.

Discussion

The resulting spectra demonstrate the individualized diffraction patterns, ranging from simple to very complex, of the various samples analyzed using X-ray diffraction. Samples were analyzed at angles within the range of 2° to 90° with both the sample holder and detector moving up to 45° each. The scan speed was varied between 10.000 deg/min and 2.000 deg/min. The use of XRD for the purposes of this project was validated by the results explained best in Figure 7. The chart clearly indicates that Ketamine peaks can be detected amongst all the other components within the sample. Figure 5 demonstrates how complex XRD spectra can be. Visual comparison with the spectra from Figures 1-3 was not enough to find the peaks that represent the detection of Ketamine. Utilizing the MDI Jade 9 software, peak tables validated the outcome that Ketamine was detected in the mixtures using XRD.

The Ethanol and Ketamine mixture was prepared so that it simulated a beverage that had been "spiked" with the date rape drug. A common dosage of Ketamine, in a standard 12 fl. Oz., beverage is 200 mg. This ratio was then exercised in 5 mL ethanol by adding the calculated amount of Ketamine. After evaporation, the Ketamine was able to recrystallize in the residue left behind. The Ketamine was then successfully detected using XRD and the Jade Software, as seen in Figure 6.

Even though these successful results were concluded, it is also important to comment on the methods tried that lacked results. It was discovered that GHB would not work for the purposes of this project due to its hygroscopic property. An initial spectrum of the pure drug was unable to be obtained because the drug did not maintain its crystalline structure when exposed to the atmosphere and therefore was not able to be detected using XRD. Small amounts (traces – 0.01 g) of the drugs were consumed by testing when made into the various mixtures. Due to limited supply of Rohypnol and MDMA only initial spectra of the pure drugs were able to be obtained. No further testing was completed with those two drugs. Chloral Hydrate yielded results for the dry mixture with confectionary sugar, but when made into a paste the drug would not recrystallize. This indicated a further problem with its detection and nothing further was tested.

The spectra in Figures 1-6 are only a summation of the work completed for this project. Additional spectra and similar conclusions for other samples were also obtained. Ketamine was detected on the three other fabric samples with the paste on them through analysis with XRD and the application of peak picking and peak table comparison with the MDI Jade 9 software.

Conclusion

The technique of X-ray Diffraction was successfully employed to detect date rape drugs in pure form for this project. XRD and the MDI Jade 9 software was also utilized to detect Ketamine in various mixtures. Supplementary knowledge about date rape drugs was gained when research problems were encountered. This project was able to demonstrate and give validity to the use of XRD for the purposes of detecting date rape drugs and residues.

Future Work

Additional research will be conducted with the same methods for Rohypnol and MDMA. The use of actual alcoholic beverages will be explored by creating mixtures containing the date rape drugs and ultimately transferring these mixtures onto fabric. X-ray diffraction will continue to be utilized in order to detect the date rape drugs and any residues created.

References

[1] Kugler, Werner. "X-Ray Diffraction Analysis in the Forensic Science: The Last Resort in Many Criminal Cases." (2003). *JCPDS – International Centre for Diffraction Data*. Retrieved from http://www.icdd.com/resources/axa/vol46/v46_01.pdf

[2] Rendle, D. F. (2003). X-Ray Diffraction in Forensic Science. *The Rigaku Journal*, *19*(20), 11-22. Retrieved from http://rigaku.com/downloads/journal/Vol20.1.2003/forensic.pdf

[3] Bullen, H. "Introduction to X-ray Diffraction (XRD)." *Analytical Sciences Digital Library.* Retrieved from http://www.asdlib.org/onlineArticles/ecourseware/Bullen_XRD/LearningActivity_Diffraction_BraggsLaw.pdf

[4] Abraham, Johny T. "Application of X-Ray Diffraction Techniques in Forensic Science." *Forensic Science Communications.* (2007). 9(2). Retrieved from http://www.fbi.gov/about-us/lab/forensic-science-communications/fsc/april2007/index.htm/research/2007_04_research03.htm

Acknowledgements

Thank you to the following: the University of New Haven Summer Undergraduate Research Fellowship Program for their financial support of this project, the Henry C. Lee College of Criminal Justice and Forensic Sciences for allowing use of the instrument, and Norma Hollender-Celico for providing lab supplies and management. You were all vital to the success of this project.