Raman based detection of hazardous liquids concealed in liquid consumer products

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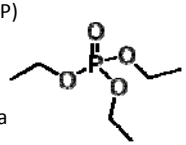
Introduction

- The objective of this work is to use vibrational spectroscopy to detect the presence of Chemical Warfare Agents in a variety of concentrations, liquids, and containers.
- Common consumer liquids mixed with a Chemical Warfare Agent Simulant were screened in a variety of containers.
- A possible application for this research would be to increase the security of public transportation centers by incorporating a liquid screener.

Reagents & Equipment

•Triethyl phosphate (TEP)



Consumer Liquids

•Tres Monjitas ® Milk
•Diet Snapple ® Iced Tea
•Heineken Lager® beer
•Malta India ®
•Pepsi Cola®
•Suave ® Shampoo
•Mystic ® Orange-Carrot Juice
•Top Care ® Mouthwash

Consumer Containers

•Green plastic bottle – Mountain Dew ®
•White plastic bottle – Tres Monjitas ® jug
•Clear plastic bottle – Pepsi ®
•Brown glass bottle – Malta India ®
•Clear glass bottle – Snapple ®
•Green glass bottle – Heineken ®

Figure 1: The liquids of human consumption used in experiments

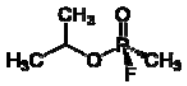
Equipment

• A Portable Raman (Raman Systems, Inc.) equipped with 785 nm Laser
•Raman Microscope (Renishaw, Inc.) equipped with 488 nm, 514, and 785 nm lasers

Methods

•Due to the toxicity of Chemical Warfare Agents (CWA), triethyl phosphate was used as a simulant for Sarin (GB) due to its similarities in structure and spectroscopic properties.

Chemical Structure of Sarin



Chemical Structure of Triethyl Phosphate

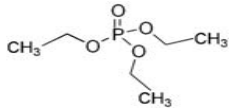


Figure 2: Both triethyl phosphate and Sarin exhibit phosphorus-oxygen double and single bonds which show up clearly in the Raman spectra.

- Raman Microscope was used to obtain the spectra of TEP in neat form.
- Solutions of concentrations of 70%, 50%, and 10% TEP and each commercial liquid were prepared
- Portable Raman was used to obtain the spectra of blanks, mixtures and pure TEP samples in each container with the initial parameters: Integration time 10 s; Frame size 3 s.

Cross Validation

- Compared known samples without TEP to the known samples containing TEP
- Used the program OPUS™ (Bruker Optics, Inc., Billerica, MA)

Discriminant Analysis

- Applied to the vectors derived from the cross validations and calibrations in order to determine the predictability rate
- Used to maximize the differences between the groups: (1) samples containing TEP; and (2) Samples with no TEP present.
- Used the program StatGraphics (StatPoint Technologies, Inc.)

Refined Parameters

- After completing the discriminant analysis, the methods were repeated with optimized spectral parameters

Table 1: Optimum parameters for acquisition of Raman spectra in each container

Container	Integration Time (s)	Frame Size (s)
clear plastic	10	3
green plastic	11	3
white plastic	78	24
clear glass	10	3
green glass	3	3
brown glass	10	8

Results

Spectral Profile of TEP

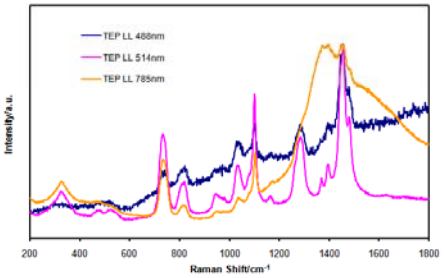


Figure 3: Raman Microscope was used to obtain the spectra of TEP excited by the three different lasers. The same bands are common to each excitation source.

Prediction Ability

- The best discriminant function was selected based on the eigenvalues obtained, the canonical correlation coefficient, the statistical significance achieved, and the percentages of cases correctly classified as calculated by StatGraphics statistical program.

Table 2: Results for discriminant analysis for the calibration of samples containing TEP and samples without TEP. 1583samples were analyzed.

Discriminant Function	*Eigenvalue*	*Relative Percentage*	*Canonical Correlation*
1	0.992188	100.00	0.70572

Table 3: Values of statistical parameters of functions derived from the PLS-DA prediction model.

Functions Derived	*Wilks Lambda*	*Chi-Squared*	*DF*	*P-Value*
1	0.501961	1082.7858	20	0.0000

Frequency Distribution Graph

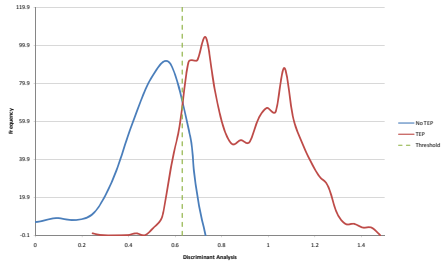


Figure 4: Relative frequency distributions of the consumer products liquids and hazardous liquids. The samples with No TEP that were correctly classified fall to the left of the threshold, while the samples containing TEP are on the right of it.

Results (cont.)

Initial Parameters		Percent Correctly Classified
	Validation	85.98%
	Calibration	88.45%
Refined Parameters		
	Validation	86.23%
	Calibration	(see below)

Table 4: Classification table found using discriminant analysis of calibration of humane and hazardous samples. 93.75% sensitivity; 6.25% missed detection; 10.43% false alarm; 89.57% specificity. This table directly corresponds to the Frequency Distribution graph. (Fig. 4)

Actual TRUE	*Group Size*	*Predicted 0*	*TRUE 1*
0	384	360	24
		(93.75%)	(6.25%)
1	1199	125	1074
		(10.43%)	(89.57%)

Percent of cases correctly classified: **90.59%**

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Acknowledgments

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