Application Note 15
Identifying Incoming Solvents in Tank Trucks (Acetone, Phenol, Phenyl Ether)

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1. Introduction

A significant number of chemical manufacturing and chemical distribution companies have shown considerable interest in using Cyranose 320 as a quality control tool to identify chemicals in tank trucks as they come into the plant. The three chemicals used in this study were acetone, phenol and phenyl ether, which is particularly interesting as it includes samples in both liquid and solid states. As our ultimate goal is for customers to use the Cyranose 320 for "on-the-spot" identification, we designed the method to mimic as closely as possible a real life situation. Two Cyranose320 units were used in this study to discriminate and identify the three samples. This was done to show the potential reproducibility of data between units. The training set longevity was also studied.

2. Experimental

Sample preparation:
The three samples were obtained from Aldrich.
Acetone (99.5+%, phenol free, Aldrich 32377-2, lot no. TR00422MR)
Phenol (99+%, Aldrich 18545-0, lot no. 01025CU)
Phenyl Ether (99+%, Aldrich 24083-4, lot no. 04908HI).

Ten grams of phenol were placed in a 500ml clear, borosilicate glass bottle capped with a septum-lined cap. Ten milliliters of acetone and phenyl ether were placed separately in 500ml clear, borosilicate glass bottles capped with septum-lined caps. The headspaces in the three bottles were allowed to equilibrate for 3 hours, to mimic the headspace in the tank car. 40ml of headspace samples were extracted and transferred to pre-vacuumed, pre-cleaned 40ml borosilicate glass vials with Teflon/silicone septa by 10ml gastight, borosilicate glass syringes (SGE, 008960) with deflected, non-coring septum penetration needles (Popper & Sons, 7175). The 40ml vials were vacuumed using the Cyranose 320 (in "Manual Test" mode, "Pump On" and "Main Valve Closed") for 60 seconds. It is important that only new vials with new septa to be used to prevent cross contamination, and to ensure a tight vacuum condition can be held. Ten replicates were prepared for each chemical. Each vial was used only once. All samples were kept in a Lab environment at ambient conditions.

Testing Conditions:
Two Cyranose 320s' were used to test these samples. A 16-gauge needle was attached to the sampling port of the unit for sampling. The instruments were warmed up for 6 minutes before the test. The method settings are shown in Table 1. For each unit, the training set was obtained by sampling the 30 sealed vials randomly. The random order is shown in Table 2.

Data handling:
Data was recorded with the digital filter on. The sensor responses were calculated as $(R_{max}-R_{min})/R_{min}$ where R_{min} is the minimum of the resistance reading during the baseline purge and R_{max} is the maximum resistance reading during the vapor exposure. Canonical discriminant analysis (CDA), an algorithm for pattern recognition, with auto-scaling and 1-normalization was used for model-making and predictions. Identification quality for predictions was set at medium.

3. Results

The three samples clustered into three distinct regions in PCA space (Fig. 1 and Fig. 2), The model produced 100% Cross-validation with the two units showing similar Mahalonobis-distances among the samples, ranging from 16 to 33. (Fig. 3 and Fig. 4) The Canonical plots from the units are also shown in Fig. 5 and Fig. 6. The training process took about one hour for each unit and both training sets lasted at least 21 days for correct identifications of these 3 chemicals. Over a period of 21 days after the training sets were built, 93 unknown samples were tested for identifications by the two Cyranose320 units. All unknown samples were identified correctly, nearly 97% were identified with ***** ratings, while 3% were identified with *** ratings. The results are listed in Table 3.

4. Conclusion

Analysis with a Cyranose 320 created distinct patterns that allowed easy identifications of the three chemicals: acetone, phenol and phenyl ether. Sample preparations were designed for both liquid and solid samples and could be easily adapted for tank car inspection applications. From the results, we can see that the Cyranose can differentiate these three chemicals and the results are quite reproducible as shown by the results obtained from the two units used for this test. The training sets are robust and have been used to identify acetone, phenol and phenyl ether for at least 21 days.

Table 1. Method settings used in the experiments.

Method name	Chemicals1	
Class 1	Acetone	
Class 2	Phenol	
Class 3	Phenyl Ether (Ph_Ether)	
Class 4		
Class 5		
Class 6		
Baseline purge	20	medium
Sample draw	20	medium
Sample draw 2	0	
Snout removal	5	
1st sample gas purge	30	high
1st air intake purge	5	high
2nd sample gas purge	30	high
2nd air intake purge	0	high
Digital filtering	On	
Substrate heater	On	42°C
Training repeat count	1	
Identifying repeat count	1	
Active sensors	All sensors	
Algorithm	Canonical	
Preprocessing	Autoscaling	
Normalization	Normalization 1	
Identification Quality	Medium	

Table 2. Sampling sequence used in the training set.

Class No.	Sample	Exposure No.
1	A	1
1	A	2
3	PE	1
2	P	1
3	PE	2
1	A	3
3	PE	3
3	PE	4
3	PE	5
1	A	4
2	P	2
2	P	3
2	P	4
1	A	5
2	P	5
3	PE	6
2	P	6
2	P	7
1	A	6
1	A	7
2	P	8
1	A	8
3	PE	7
2	P	9
3	PE	8
2	P	10
1	A	9
1	A	10
3	PE	9
3	PE	10

Where A – Acetone
P – Phenol
PE – Phenol Ether

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Table 3. Identification results of the three solvents tested by the two Cyranose320 units over a period of 21 days.

Unit	Solvent	6th Day	13th Day	21st Day
Unit A	Acetone	Total of 8 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.
	Phenol	Total of 8 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.
	Phenyl Ether	Total of 8 sniffs. Seven were correctly identified with ***** ratings. One was identified correctly with *** ratings	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. Four were correctly identified with ***** ratings. One was identified correctly with *** ratings.

Unit	Solvent	6th Day	13th Day	21st Day
Unit B	Acetone	Total of 3 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.
	Phenol	Total of 3 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. Four were correctly identified with ***** ratings. One was identified correctly with *** ratings.
	Phenyl Ether	Total of 3 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.	Total of 5 sniffs. All were correctly identified with ***** ratings.

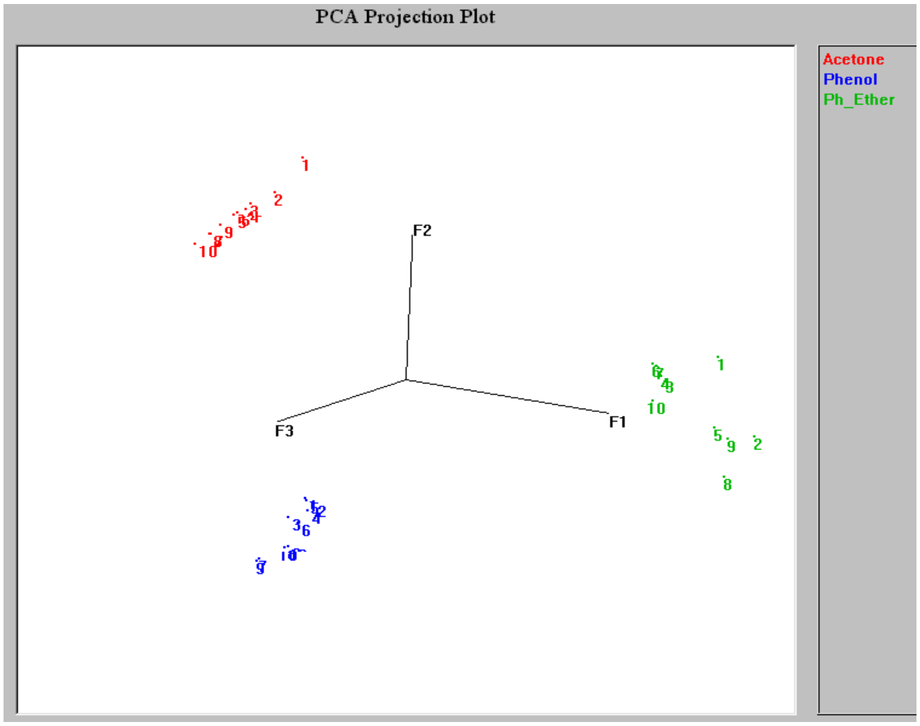

Fig. 1. The PCA plot of the training set of solvents using CDA, autoscale with 1-normalization (Unit A).

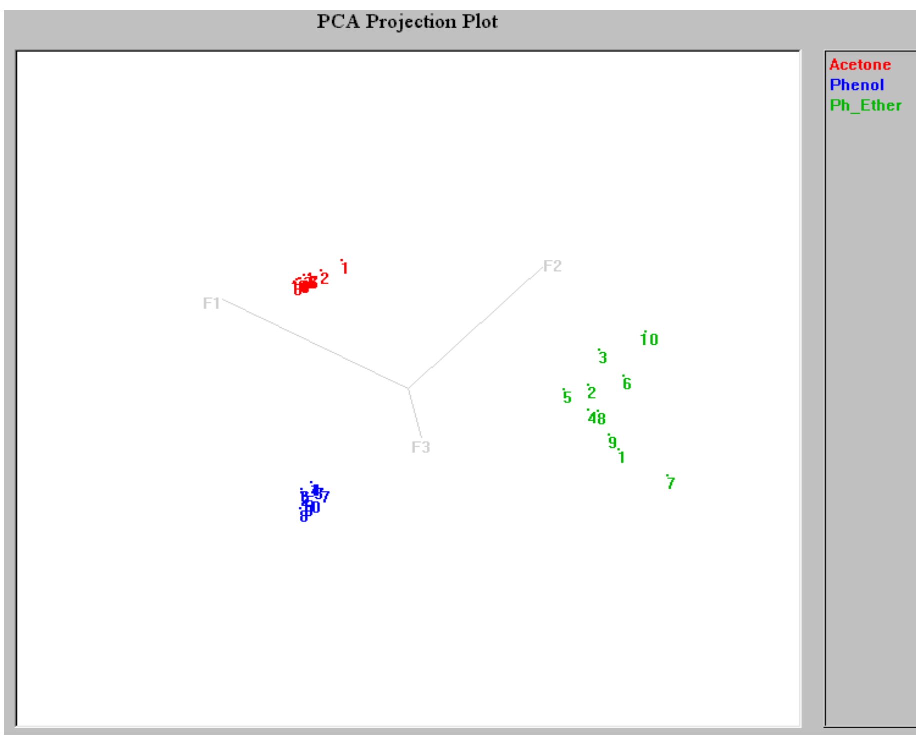

Fig. 2. The PCA plot of the training set of solvents using CDA, autoscale with 1-normalization (Unit B).

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Identified As

Trained As	Acetone	Phenol	Ph_Ether
Acetone	10	0	0
Phenol	0	10	0
Ph_Ether	0	0	10

Correct : 100.000 %
Incorrect : 0.000 %

Interclass M-Distances

	Acetone	Phenol	Ph_Ether
Acetone		32.021	16.453
Phenol			30.790
Ph_Ether			

Fig. 3. The internal cross validation of the training set of acetone, phenol and phenyl ether using CDA, autoscale, with 1-normalization (Unit A).

Identified As

Trained As	Acetone	Phenol	Ph_Ether
Acetone	10	0	0
Phenol	0	10	0
Ph_Ether	0	0	10

Correct : 100.000 %
Incorrect : 0.000 %

Interclass M-Distances

	Acetone	Phenol	Ph_Ether
Acetone		33.907	17.290
Phenol			30.425
Ph_Ether			

Fig. 4. The internal cross validation of the training set of acetone, phenol and phenyl ether using CDA, autoscale, with 1-normalization (Unit B).

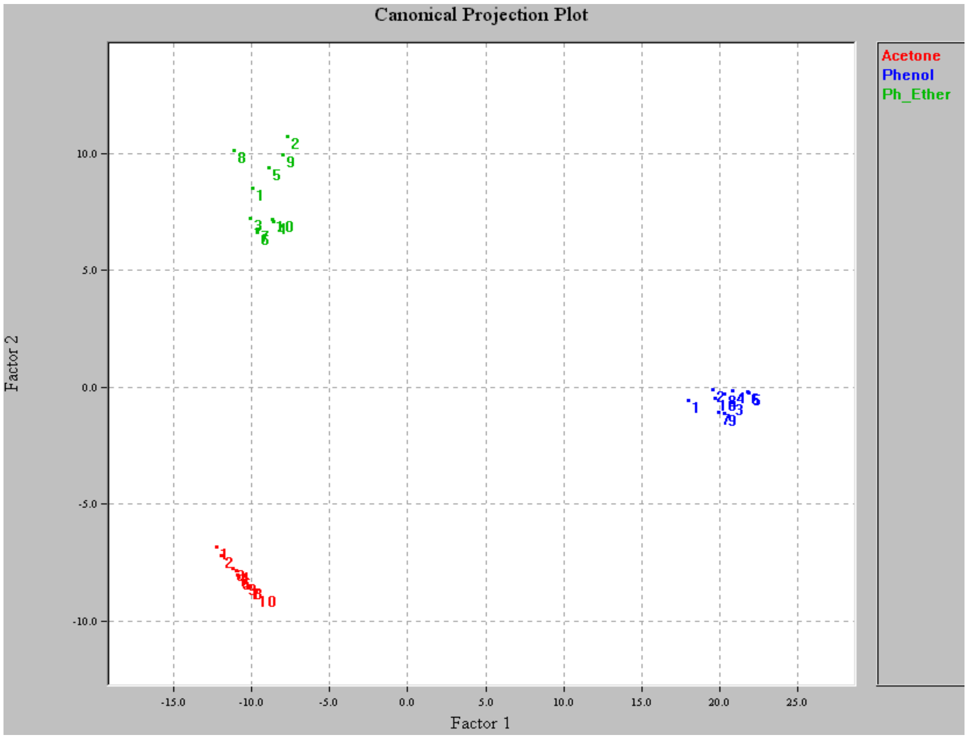

Fig. 5. The CDA plot of the training set of solvents using CDA, autoscale with 1-normalization (Unit A).

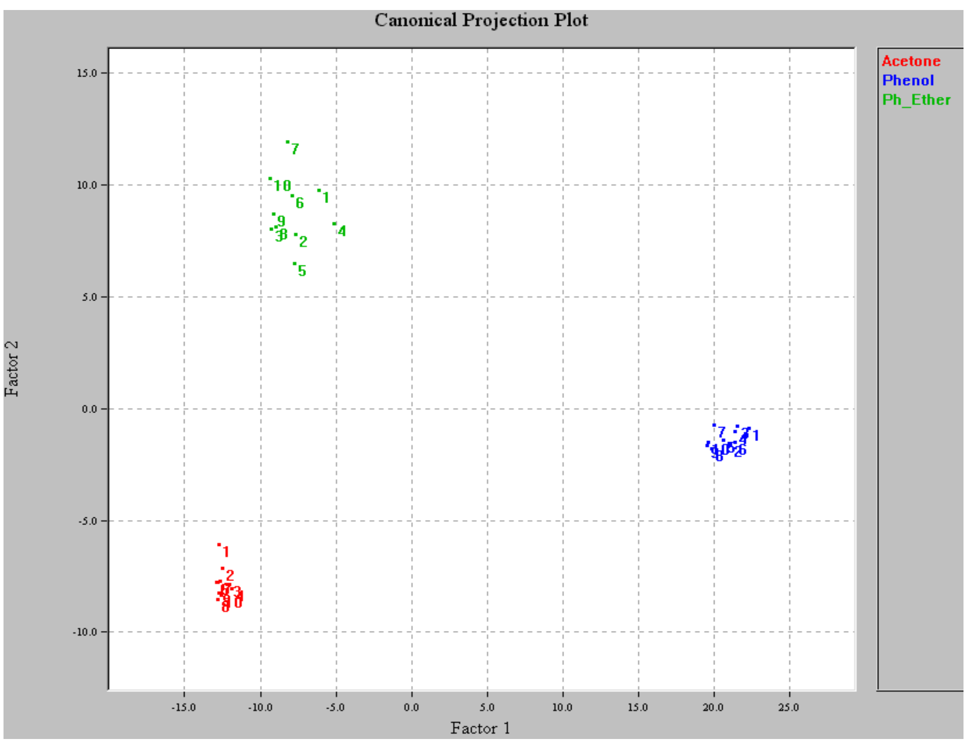

Fig. 6. The CDA plot of the training set of solvents using CDA, autoscale with 1-normalization (Unit A).