

# **Application of Gaussian Bayes classifier to differentiate chlorine-based chemical agents**

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## ABSTRACT

The Portable Isotopic Neutron Spectroscopy (PINS) is a commercialized system developed by Idaho National Laboratory (INL) to examine chemical warfare agents (CWA) non-destructively, utilizing Prompt Gamma Neutron Activation Analysis (PGNAA) techniques. The PINS system takes advantage of a high-resolution gamma-ray spectrum from a mechanically-cooled high-purity germanium (HPGe) detector. One of the difficult technical challenges is to discriminate the chlorine-based chemical agents. Especially, CN, CNB, CNS and CG have similar chemical compositions to make it hard to discriminate them with a higher confidence. Current identification algorithms for PINS systems with  $^{252}\text{Cf}$  sources have been improved and updated continuously as more field data became available, and new algorithms were studied to complement the current algorithms by adopting the Gaussian Bayes classifier. These new algorithms were intended to be applied to a subset of chlorine-based chemical agents, and their main goal is discriminate CN, CNB, CNS and CG with their ratios of the chlorine neutron inelastic 1763keV peak to the chlorine thermal neutron capture 1959keV peak, which is referred to as the “Cl i/c” or “clic” ratio in this study. The Cl i/c ratios were assumed to follow Gaussian distributions with the means and the standard deviations unique to their corresponding chemical agents. The prior probabilities of these four chemical agents were optimized with a collection of field data to achieve the best performance in terms of precision or positive predictive value (PPV). Finally, their posterior probabilities as functions of the Cl i/c ratio were implemented in the current version of PINS analysis software in order to be tested with more field data.



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## ACRONYMS

Cl i/c	Chlorine inelastic-to-capture
CG	Phosgene, choking agent
CN	Riot control/tear agent
CNB	Riot control/tear agent
CNS	Riot control/tear agent
CWA	Chemical Warfare Agents
D-D	Deuterium-Deuterium
D-T	Deuterium-Tritium
HN-3	Nitrogen mustard-3, blister agent
CK	Blood agent
HPGe	High purity germanium
INL	Idaho National Laboratory
PGNAA	Prompt Gamma Neutron Activation Analysis
PINS	Portable Isotopic Neutron Spectroscopy
PINS+	Portable Isotopic Neutron Spectroscopy identification software
PINS-CF	Portable Isotopic Neutron Spectroscopy system with a <sup>252</sup> Cf source
PINS-DT	Portable Isotopic Neutron Spectroscopy system with a D-T neutron generator
PPV	Positive Prediction Value
PS	Chloropicrin

# Application of Gaussian Bayes classifier to differentiate chlorine-based chemical agents

## 1. INTRODUCTION

CN, CNB, CNS and CG have similar chemical compositions as summarized in **Table 1** and their differences in the neutron-induced gamma-ray spectra are very subtle to distinguish one from the other [1]. Previous research efforts to improve PINS-CF algorithms also identified that discrimination of these four chemical agents are quite challenging task to achieve [2-3]. Nevertheless, chlorine inelastic-to-capture ratio (Cl i/c or “cl/c”, Cl 1763keV peak area to Cl 1959keV peak area) is considered one of the key indicators to discriminate CN, CNB, CNS and CG\*. Cl i/c ratios versus H/Cl (H 2223keV to Cl 1959keV) ratios from a collection of the accumulated PINS-CF data are plotted in **Figure 1**. It shows that Cl i/c ratio varies from 0.0 to 2.5, but their differences are not large enough so that their distributions show significant amount of overlaps. H/Cl ratio is not very sensitive enough to be a feature to discriminate these four chemical agents with a higher confidence level. However, Cl i/c ratio values form clusters for individual chemical agents although their boundaries are not drawn clearly. Therefore, Bayes’ theorem is applied to calculate each chemical agent’s likelihood when Cl i/c ratio values are known, assuming Cl i/c ratio values are described by a Gaussian distribution.

## 2. GAUSSIAN BAYES CLASSIFIER

The first assumption in this study is that measured Cl i/c ratios from one chemical agent can be described by a Gaussian distribution with the mean and the standard deviation unique to the chemical agent. There is no prior study or evidence to support this assumption yet, but a Gaussian distribution explains the behavior of Cl i/c ratio distribution relatively well, if not perfect, as shown in **Figure 2**. The second assumption is that each chemical agent has certain prior probability to be found in the field operations. For example, the simplest assumption is that each chemical agent has equal prior probability of 0.25. As shown in **Figure 1**, Cl i/c ratios of all four chemical agents are described by Gaussian distributions derived from their corresponding data, respectively. Once a Cl i/c ratio from a unknown spectrum is given, Bayes’ theorem is applied to calculate each chemical agent’s posterior probability by **Eq. (1)**.

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\* HN-3 and CK are excluded in this study since they are confirmed only when high energy nitrogen peaks are detected in addition to Cl i/c values. Also, PS (chloropicrin) is excluded due to lack of data to be used in this study.

$$\begin{aligned}
P(CX|x) &= \frac{P(x|CX)P(CX)}{P(x)} \\
&= \frac{P(x|CX)P(CX)}{P(x|CG)P(CG) + P(x|CNS)P(CNS) + P(x|CNB)P(CNB) + P(x|CN)P(CN)}
\end{aligned} \tag{1}$$

where  $x$  is Cl i/c ratio and  $CX$  is either CN, CNB, CNS or CG.  $P(CX)$  and  $P(x|CX)$  are each chemical agent's prior probability and likelihood, respectively.  $P(x|CX)$  is given by chemical agent  $CX$ 's normalized Gaussian distribution as a function of Cl i/c ratio  $x$ .  $P(x|CX)$  is the probability that the measured Cl i/c ratio is  $x$  given that the chemical agent is the  $CX$ .

**Figure 3** shows output from the Cl i/c indicator functions defined in the current PINS-CF algorithms for CN, CNB, CNS and CG. In **Figure 4**, The posterior probabilities of the four chemical agents calculated by Bayes' theorem in **Eq. (1)** are plotted with  $P(CN) = 0.25$ ,  $P(CNB) = 0.25$ ,  $P(CNS) = 0.25$  and  $P(CG) = 0.25$ . Traditionally, PINS algorithms have adopted the indicator function as defined in **Eq. (2)** to express indicator and penalty functions.

$$ES(X, Y, Z) = \begin{cases} 0 & \text{when } X < Y \\ 0.5 - 0.5 \times \cos\left(\frac{\pi(X - Y)}{(Z - Y)}\right) & \text{when } Y \leq X < Z \\ 1 & \text{when } X \geq Z \end{cases} \tag{2}$$

It is inconvenient to use the analytical function as shown in **Eq. (1)** to use in each chemical agent's formula file. Fortunately, four chemical agents' posterior probabilities can be approximated by the ES functions whose parameter  $Y_{CX}$  and  $Z_{CX}$  values were selected to match them best. As a result, newly proposed indicator functions of Cl i/c ratio for CN, CNB, CNS and CG are expressed in the forms given by **Eq. (3)**.

$$clic = Cl\ 1763keV\ net\ peak\ area / Cl\ 1959keV\ net\ peak\ area$$

$$\begin{aligned}
pCN &= 1 - ES(clic, Y_{CN}, Z_{CN}) \\
pCNB &= Const_{CNB} * ES(clic, Y1_{CNB}, Z1_{CNB}) * (1 - ES(clic, Y2_{CNB}, Z2_{CNB})) \\
pCNS &= Const_{CNS} * ES(clic, Y1_{CNS}, Z1_{CNS}) * (1 - ES(clic, Y2_{CNS}, Z2_{CNS})) \\
pCG &= ES(clic, Y_{CG}, Z_{CG}) - Const_{CNS} * ES(clic, Y1_{CNS}, Z1_{CNS}) * (1 - ES(clic, Y2_{CNS}, Z2_{CNS}))
\end{aligned} \tag{3}$$

However, all  $Y_{CX}$  and  $Z_{CX}$  values vary whenever prior probabilities change. In order to find the best performing indicator functions, three different sets of indicator functions obtained from three different sets of prior probabilities were tested with PINS+ v6.6.0. The four default formula files of CN, CNB, CNS and CG were modified by replacing the current Cl i/c ratio indicator functions with new ones. Then,

a total of 57 spectra were analyzed to be identified by PINS+ v6.6.0 as shown in **Figure 5**. It should be noted that chemical agent PS (chloropicrin) was deactivated in PINS+ v6.6.0. The first table summarizes the analysis results by PINS+ v6.6.0 with the default formula files. The other three tables summarize the analysis results with modified formula files for different sets of prior probabilities:  $[P(CN):P(CNB):P(CNS):P(CG)] = [0.25:0.25:0.25:0.25]$ ,  $[0.1:0.2:0.3:0.4]$  and  $[0.1:0.1:0.3:0.5]$ , respectively. The set of prior probabilities of  $[0.1:0.2:0.3:0.4]$  achieved the highest precisions for all four chemical agents. Therefore, the newly proposed indicator functions are given by **Eq. (4)**.

$$\begin{aligned}
clic &= Cl\ 1763keV\ net\ peak\ area / Cl\ 1959keV\ net\ peak\ area \\
p_{CN} &= 1 - ES(clic, 0.0633, 0.2005) \\
p_{CNB} &= 0.9083 * ES(clic, 0.0644, 0.1991) * (1 - ES(clic, 0.2340, 0.5173)) \\
p_{CNS} &= 0.6400 * ES(clic, 0.2070, 0.5226) * (1 - ES(clic, 0.5393, 1.7990)) \\
p_{CG} &= ES(clic, 0.2033, 0.5258) - 0.6400 * ES(clic, 0.2070, 0.5226) * (1 - ES(clic, 0.5393, 1.7990))
\end{aligned} \tag{4}$$

The solid lines in **Figure 6** are the approximated  $P(CX|x)$  values calculated by **Eq. (4)** while the dotted lines are the analytical  $P(CX|x)$  values given by **Eq. (1)** with  $P(CN) = 0.10$ ,  $P(CNB) = 0.20$ ,  $P(CNS) = 0.30$  and  $P(CG) = 0.40$ . Finally, the newly proposed Cl i/c ratio indicator functions were tested against the 2018 blind test dataset, and the results are summarized in **Table 2** and **Table 3**. All four chemical agents were correctly identified by the highest  $P(CX|x)$  values in **Table 2**, and analysis results from PINS+ v6.6.0 with the modified formula files are summarized in **Table 3**. Again, chemical agent PS was deactivated in PINS+ v6.6.0 since identification of PS is beyond the current scope of this study.

### 3. SPECIAL CONSIDERATIONS FOR PINS-DT SYSTEM

PINS-DT system utilizes 14MeV neutrons from a D-T neutron generator, and Cl i/c ratio distributions for CN, CNB, CNS and CG are expected to shift toward higher values than PINS-CF system. This is because inelastic scattering reactions are dominated while thermal neutron capture reactions are suppressed due to much higher neutron energy. A set of indicator functions similar to **Eq. (4)** were derived in order to handle PINS-DT system separately. It should be noted that Cl i/c ratio for PINS-DT system was defined differently as given by the first equation in **Eq. (5)**. Cl i/c ratios versus H/Cl (H 2223keV to Cl 1959keV) ratios from a collection of 78 PINS-DT spectra are plotted in **Figure 7**. The solid lines in **Figure 8** are the approximated  $P(CX|x)$  values calculated by **Eq. (5)** while the dotted lines are the analytical  $P(CX|x)$  values given by **Eq. (1)** with  $P(CN) = 0.10$ ,  $P(CNB) = 0.20$ ,  $P(CNS) = 0.30$  and  $P(CG) = 0.40$ .

$$clic = Cl\ 1763keV\ net\ peak\ area / (Cl\ 1951keV\ net\ peak\ area \times 2/3)$$

$$pCN = 0.2205 * (1 - ES(clic, 0.0000, 0.7780)) + 0.1847 * (1 - ES(clic, 1.5000, 3.0000))$$

$$pCNB = 0.6704 * ES(clic, -0.8578, 0.7989) * (1 - ES(clic, 1.0497, 2.3838)) \quad (5)$$

$$pCNS = 0.5837 * ES(clic, 0.5688, 2.9675) * (1 - ES(clic, 4.4877, 14.0785))$$

$$pCG = ES(clic, 0.5429, 2.8023) - 0.5837 * ES(clic, 0.5688, 2.9675) * (1 - ES(clic, 4.4877, 14.0785))$$

The newly proposed Cl i/c ratio indicator functions for PINS-DT system were tested against the 2018 blind test dataset, and the results are summarized in **Table 4** and **Table 5**. All four chemical agents were correctly identified by the highest  $P(CX|x)$  values as shown in **Table 4**. It is clear that PINS-DT system is less effective than PINS-CF system to differentiate CN from CNB due to their large overlap in Cl i/c ratios. Analysis results from PINS+ v6.6.0 with the newly proposed DT formula files are summarized in **Table 5**. Again, chemical agent PS was deactivated in PINS+ v6.6.0 since identification of PS is beyond the current scope of this study. All three CN cases were misidentified as CNB but CNS identification was improved by the newly proposed indicator functions as is clearly shown in **Table 5**.

#### 4. SUMMARY

Gaussian classification was applied to the four chlorine-based chemical agents CN, CNB, CNS and CG. Chlorine i/c ratio distribution of each chemical agent was assumed to follow Gaussian distribution, and Bayes' theorem was applied to calculate each chemical agent's posterior probability for a given Cl i/c ratio. The set of prior probabilities of  $[P(CN):P(CNB):P(CNS):P(CG)] = [0.1:0.2:0.3:0.4]$  was found to be the best performing one after performance evaluation against a collection of 57 PINS-CF spectra of the four chemical agents. New Cl i/c ratio indicator functions of these four chemical agents were proposed for PINS-CF and PINS-DT systems, respectively. PINS+ v6.6.0 was tested against CF and DT formula files with the newly proposed Cl i/c ratio indicator functions. These new indicator functions improved performance in identifying these four chemical agents compared to the current formulae. This study demonstrated that Gaussian Bayes classifier derived from Cl i/c ratio distributions could prevent CNS from being misidentified as CG effectively.

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- [3] D. Lee, Application of artificial neural network to prompt gamma neutron activation analysis for chemical warfare agents identification, Idaho National Laboratory report INL/EXT-19-55616 (2019)

Table 1. Chemical compositions of the chlorine-based chemical agents CN, CNB, CNS and CG.

Chemical agent	Chemical formula
CN (chloroacetophenone, riot control/tear agent)	$C_8H_7ClO$
CNB (CN + carbon tetrachloride + benzene)	$C_8H_7ClO + CCl_4 + C_6H_6$
CNS (CN + chloroform + chloropicrin)	$C_8H_7ClO + CHCl_3 + CCl_3NO_2$
CG (phosgene, choking agent)	$COCl_2$

Table 2. Calculated posterior probabilities of the four chemical agents at given Cl i/c ratios for PINS-CF system.

2018 Blind test true ID	Cl i/c ratio, $x$	$P(CN/x)$	$P(CNB/x)$	$P(CNS/x)$	$P(CG/x)$
CN	0.0890	<b>0.9156</b>	0.0727	0.0000	0.0000
CN	0.1269	<b>0.5572</b>	0.4024	0.0000	0.0000
CN	0.1160	<b>0.6775</b>	0.2912	0.0000	0.0000
CNB	0.2355	0.0000	<b>0.9082</b>	0.0129	0.0117
CNB	0.2068	0.0000	<b>0.9083</b>	0.0000	0.0003
CNB	0.2269	0.0000	<b>0.9083</b>	0.0063	0.0069
CNB	0.1777	0.0666	<b>0.8528</b>	0.0000	0.0000
CNB	0.1954	0.0033	<b>0.9066</b>	0.0000	0.0000
CNS	0.8658	0.0000	0.0000	<b>0.5396</b>	0.4604
CNS	0.8006	0.0000	0.0000	<b>0.5744</b>	0.4256
CNS	0.8446	0.0000	0.0000	<b>0.5516</b>	0.4484
CNS	0.7863	0.0000	0.0000	<b>0.5812</b>	0.4188
CNS	0.8347	0.0000	0.0000	<b>0.5570</b>	0.4430
CNS	0.8569	0.0000	0.0000	<b>0.5447</b>	0.4553
CNS	0.7196	0.0000	0.0000	<b>0.6082</b>	0.3918
CG	1.4764	0.0000	0.0000	0.0981	<b>0.9019</b>
CG	1.3599	0.0000	0.0000	0.1734	<b>0.8266</b>
CG	1.6980	0.0000	0.0000	0.0101	<b>0.9899</b>
CG	1.5127	0.0000	0.0000	0.0781	<b>0.9219</b>
CG	1.4169	0.0000	0.0000	0.1346	<b>0.8654</b>
CG	1.5283	0.0000	0.0000	0.0702	<b>0.9298</b>
CG	1.8700	0.0000	0.0000	0.0000	<b>1.0000</b>

Table 3. Identifications of the 2018 blind test data by PINS+ v6.6.0 with default CF formulae (the 3<sup>rd</sup> column) and with the newly proposed PINS-CF CI i/c ratio indicator functions (the 4<sup>th</sup> column). The shaded rows are the cases correctly identified after implementing the newly proposed PINS-CF indicator functions in PINS+.

True ID	Run name	PINS+ v6.6.0 default CF formulae	PINS+ v6.6.0 w/ modified CF formulae
CG	BT18-001_P2_20Jul18_009	CG	CG
CG	BT18-006_P2_23Jul18_012	CG	CG
CG	BT18-009_P22_10Aug18_003	CG	CG
CNS	BT18-011_P2_24Jul18_003	✗ CG	✓ CNS
CG	BT18-015_P2_25Jul18_003	CG	CG
CG	BT18-018_P2_26Jul18_012	CG	CG
CNS	BT18-019_P2_26Jul18_003	CNS	CNS
CG	BT18-023_P2_27Jul18_003	CG	CG
CG	BT18-028_P2_30Jul18_006	CG	CG
CNS	BT18-032_P2_31Jul18_006	✗ CG	✓ CNS
CNB	BT18-034_P2_01Aug18_012	CNB	CNB
CNS	BT18-037_P2_02Aug18_009	✗ CG	✓ CNS
CN	BT18-051_P2_07Aug18_003	CN	CN
CNS	BT18-059_P22_09Aug18_003	CNS	CNS
CNS	BT18-064_P22_23Aug18_006	✗ CG	✓ CNS
CNB	BT18-065_P22_14Aug18_009	CNB	CNB
CNS	BT18-071_P22_15Aug18_003	CNS	CNS
CNB	BT18-073_P22_16Aug18_009	CNB	CNB
CN	BT18-075_P22_16Aug18_003	CN	CN
CNB	BT18-078_P22_17Aug18_012	CNB	CNB
CN	BT18-086_P22_21Aug18_012	CN	CN
CNB	BT18-089_P22_24Aug18_009	CNB	CNB



Table 4. Calculated posterior probabilities of the four chemical agents at given Cl i/c ratios for PINS-DT system.

2018 Blind test true ID	<sup>†</sup> Cl i/c ratio, $x$	$P(CN/x)$	$P(CNB/x)$	$P(CNS/x)$	$P(CG/x)$
CN	0.2548	0.3518	<b>0.5191</b>	0.0000	0.0000
CN	0.3452	0.3144	<b>0.6479</b>	0.0000	0.0000
CN	0.3056	0.3314	<b>0.6125</b>	0.0000	0.0000
CNB	1.4865	0.1847	<b>0.5079</b>	0.1866	0.1855
CNB	0.8249	0.1847	<b>0.6518</b>	0.0163	0.0217
CNB	1.1096	0.1847	<b>0.6511</b>	0.0702	0.0772
CNB	1.1742	0.1847	<b>0.6439</b>	0.0870	0.0936
CNB	1.1198	0.1847	<b>0.6505</b>	0.0727	0.0797
CNS	3.3150	0.0000	0.0000	<b>0.5837</b>	0.4163
CNS	3.1468	0.0000	0.0000	<b>0.5837</b>	0.4163
CNS	5.8614	0.0000	0.0000	<b>0.5546</b>	0.4454
CNS	4.3929	0.0000	0.0000	<b>0.5837</b>	0.4163
CNS	5.9153	0.0000	0.0000	<b>0.5523</b>	0.4477
CNS	3.7696	0.0000	0.0000	<b>0.5837</b>	0.4163
CNS	3.2664	0.0000	0.0000	<b>0.5837</b>	0.4163
CG	12.5541	0.0000	0.0000	0.0356	<b>0.9644</b>
CG	7.4203	0.0000	0.0000	0.4590	<b>0.5410</b>
CG	8.0366	0.0000	0.0000	0.4077	<b>0.5923</b>
CG	8.5538	0.0000	0.0000	0.3609	<b>0.6391</b>
CG	7.0379	0.0000	0.0000	0.4876	<b>0.5124</b>
CG	9.6856	0.0000	0.0000	0.2535	<b>0.7465</b>
CG	10.6235	0.0000	0.0000	0.1678	<b>0.8322</b>

<sup>†</sup> It should be noted that Cl i/c ratios in this table were calculated by the equation given in Eq. (5), which is different from the one for PINS-CF system

Table 5. Identifications of the 2018 blind test data by PINS+ v6.6.0 with default DT formulae (the 3<sup>rd</sup> column) and with the newly proposed PINS-DT CI i/c ratio indicator functions (the 4<sup>th</sup> column). The shaded rows are the cases correctly identified after implementing the newly proposed PINS-DT indicator functions in PINS+.

True ID	Run name	PINS+ v6.6.0 default DT formulae	PINS+ v6.6.0 w/ modified DT formulae
CG	BT18-001_P2_20Jul18_009	CG	CG
CG	BT18-006_P2_23Jul18_012	✖ HD	✖ HD
CG	BT18-009_P22_10Aug18_003	✖ HD	✖ HD
CNS	BT18-011_P2_24Jul18_003	✖ CG	✓ CNS
CG	BT18-015_P2_25Jul18_003	✖ CNS	✖ CNS
CG	BT18-018_P2_26Jul18_012	CG	CG
CNS	BT18-019_P2_26Jul18_003	CNS	CNS
CG	BT18-023_P2_27Jul18_003	✖ HD	✖ HD
CG	BT18-028_P2_30Jul18_006	✖ CNS	✖ Unknown
CNS	BT18-032_P2_31Jul18_006	✖ AC	✖ AC
CNB	BT18-034_P2_01Aug18_012	CNB	CNB
CNS	BT18-037_P2_02Aug18_009	✖ CG	✓ CNS
CN	BT18-051_P2_07Aug18_003	✖ HD	✖ CNB
CNS	BT18-059_P22_09Aug18_003	✖ CG	✓ CNS
CNS	BT18-064_P22_23Aug18_006	✖ HD	✖ HD
CNB	BT18-065_P22_14Aug18_009	CNB	CNB
CNS	BT18-071_P22_15Aug18_003	✖ Unknown	✖ Unknown
CNB	BT18-073_P22_16Aug18_009	CNB	CNB
CN	BT18-075_P22_16Aug18_003	✖ Unknown	✖ CNB
CNB	BT18-078_P22_17Aug18_012	CNB	CNB
CN	BT18-086_P22_21Aug18_012	✖ Unknown	✖ CNB
CNB	BT18-089_P22_24Aug18_009	CNB	CNB

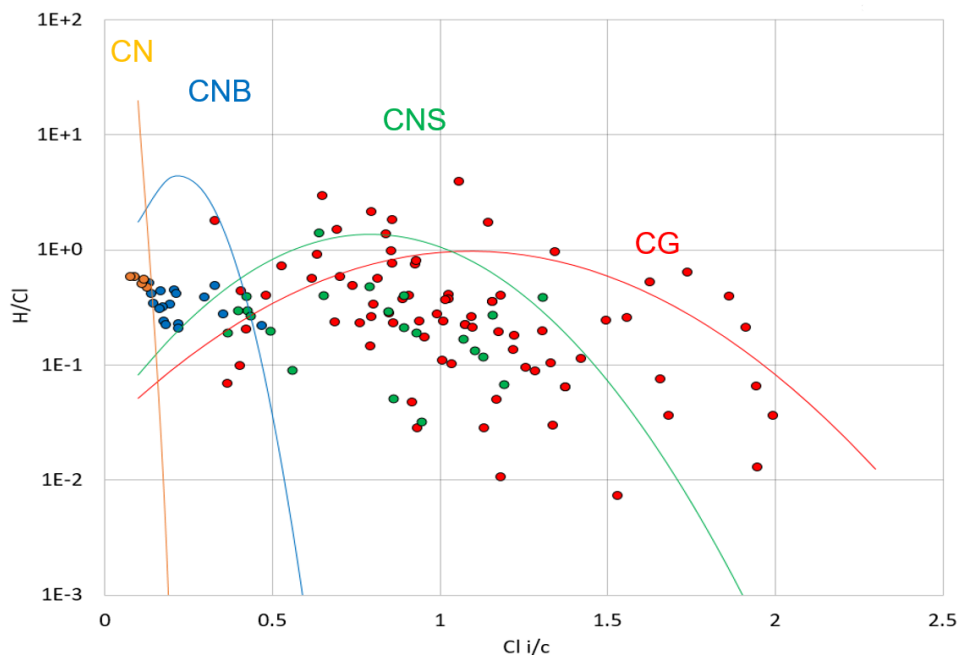


Figure 1. 2-D plot of H/Cl vs. Cl i/c ratios of CN (orange circles), CNB (blue circles), CNS (green circles) and CG (red circles) from a collection of PINS-CF data. Cl i/c ratio values of each chemical agent was fitted with a 1-D normalized Gaussian distribution. It should be noted that there is significant overlap between CNS and CG while CN and CNB are relatively well isolated.

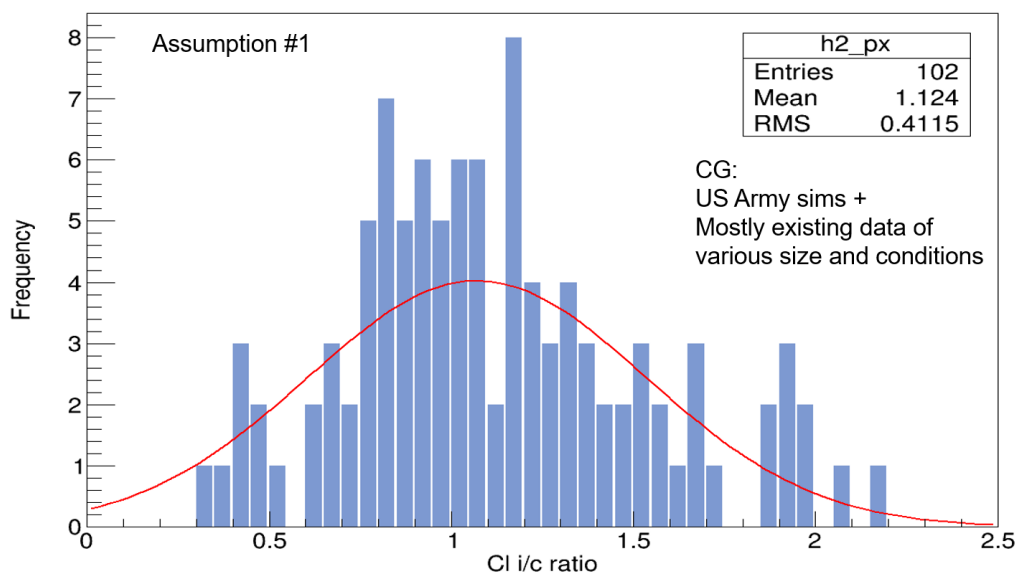


Figure 2. Cl i/c ratio values fitted with a normalized Gaussian distribution. Cl i/c ratio values are assumed to follow a Gaussian distribution (red line) in this study. More data from the field operations would be beneficial to build a larger population to reveal their true distribution in the future. The same Gaussian fittings were performed on CN, CNB and CNS data, respectively.

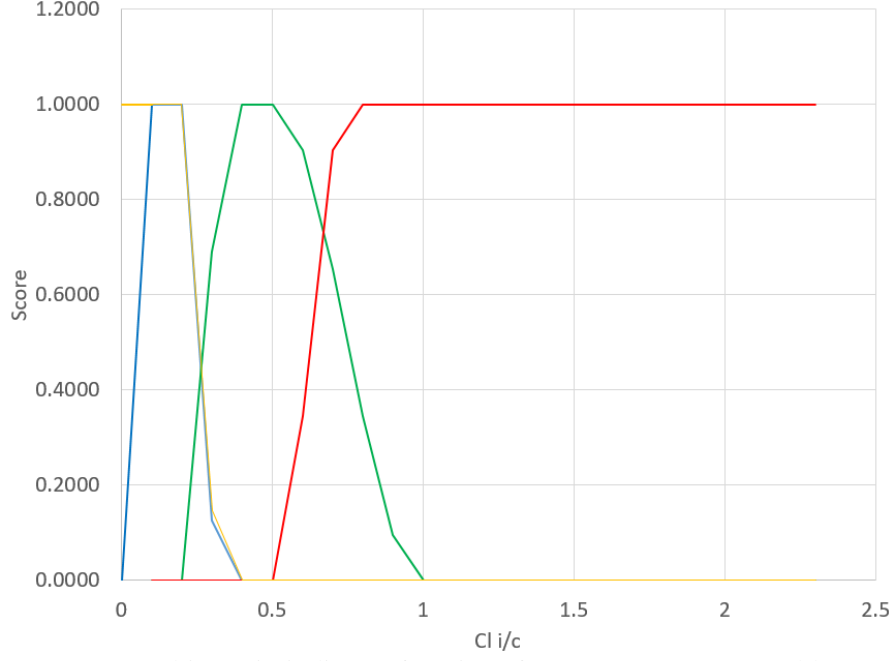


Figure 3. Current PINS-CF Cl i/c ratio indicator functions for CN (orange), CNB (blue), CNS (green) and CG (red), using the indicator function as defined in **Eq. (1)**.

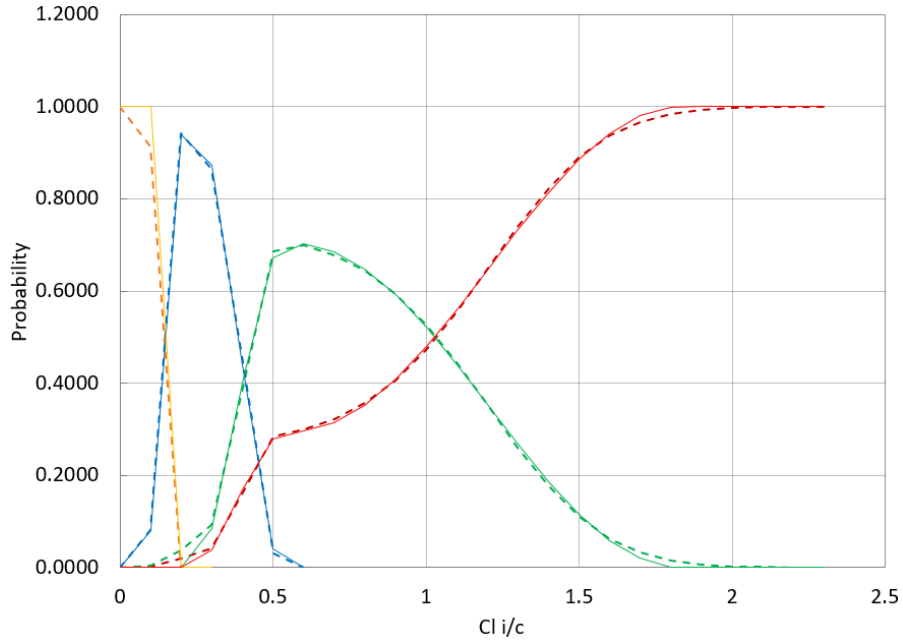


Figure 4. Newly proposed PINS-CF system's Cl i/c ratio indicator functions for CN (orange), CNB (blue), CNS (green) and CG (red) with equal prior probabilities,  $[P(CN):P(CNB):P(CNS):P(CG)] = [0.25:0.25:0.25:0.25]$ . The dotted lines are from the analytical functions while the solid lines are from the approximated ones as defined in **Eq. (3)**.

True ↓	PINS+ v660	CN	CNB	CNS	CG	etc	
	CN	3					
	CNB	3	10				
	CNS		2	4	4	1	CK
	CG		3	16	11		
	etc						
	Precision	50%	67%	20%	73%		
	P(CWA)	0.25	0.25	0.25	0.25		
		CN	CNB	CNS	CG	etc	
	CN	3					
	CNB		12	1			
	CNS			8	2	1	unknown
	CG			13	12	5	1 CK 4 Unknown
	etc						
	Precision	100%	100%	38%	86%		
	P(CWA)	0.10	0.20	0.30	0.40		
		CN	CNB	CNS	CG	etc	← Predicted
	CN	3					
	CNB		12	1			
	CNS			7	2	2	1 CK 1 Unknown
	CG			10	15	5	2 CK 3 Unknown
	etc						
	Precision	100%	100%	41%	88%		
	P(CWA)	0.10	0.10	0.30	0.50		
		CN	CNB	CNS	CG	etc	
	CN	3					
	CNB		12	1			
	CNS			4	5	2	1 CK 1 Unknown
	CG			9	16	5	2 CK 3 Unknown
	etc						
	Precision	100%	100%	31%	76%		

Figure 5. Three different sets of prior probabilities for CN, CNB, CNS and CG were tested with a collection of 57 spectra. The first table shows the results from PINS+ v6.6.0 with current PINS-CF formulae in comparison to ones with new Cl i/c ratio indicator functions. The best performing set of prior probabilities is  $[P(CN):P(CNB):P(CNS):P(CG)] = [0.10:0.20:0.30:0.40]$  with the highest precisions for all four chemical agents.

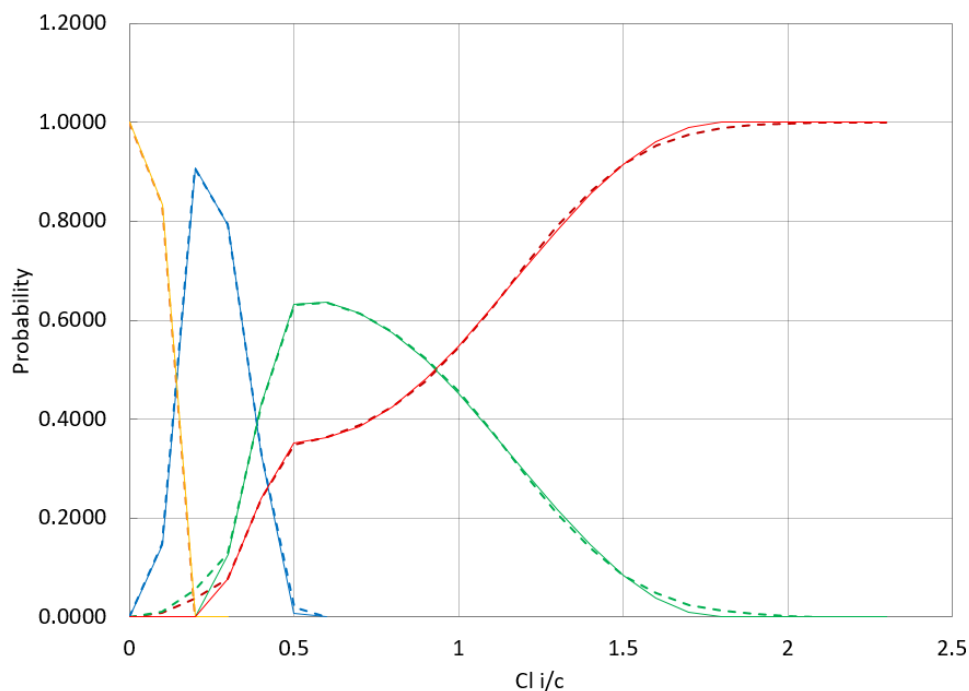


Figure 6. Newly proposed PINS-CF system's Cl i/c ratio indicator functions for CN (orange), CNB (blue), CNS (green) and CG (red) with the optimal prior probabilities,  $[P(\text{CN}):P(\text{CNB}):P(\text{CNS}):P(\text{CG})] = [0.10:0.20:0.30:0.40]$ . The dotted lines are from the analytical functions while the solid lines are from the approximated ones as defined in Eq. (4).

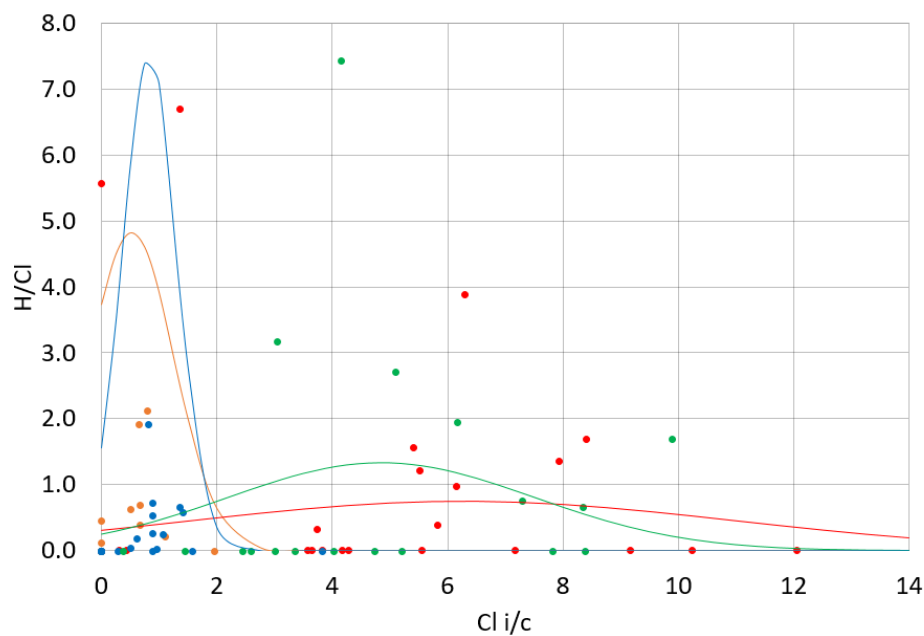


Figure 7. 2-D plot of H/Cl vs. Cl i/c ratios of CN (orange circles), CNB (blue circles), CNS (green circles) and CG (red circles) from a collection of PINS-DT data. Cl i/c ratio values of each chemical agent was fitted with a 1-D normalized Gaussian distribution. It should be noted that there is significant overlap between CNS and CG while CN and CNB are relatively well isolated.

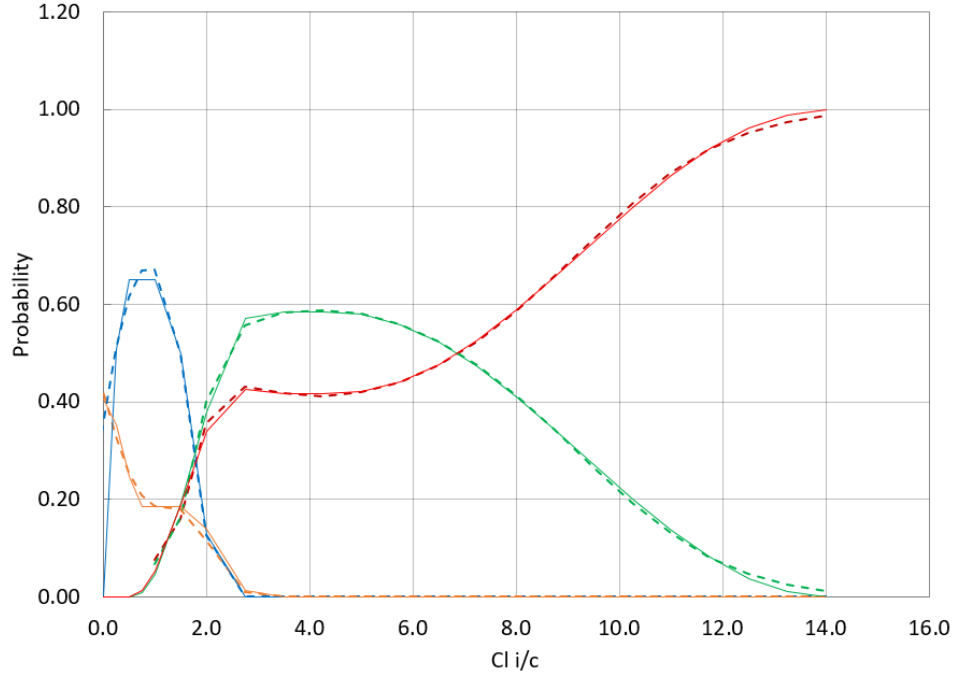


Figure 8. Newly proposed PINS-DT system's CI i/c ratio indicator functions for CN (orange), CNB (blue), CNS (green) and CG (red) with the optimal prior probabilities,  $[P(\text{CN}):P(\text{CNB}):P(\text{CNS}):P(\text{CG})] = [0.10:0.20:0.30:0.40]$ . The dotted lines are from the analytical functions while the solid lines are from the approximated ones as defined in **Eq. (5)**.