

# CHEMICAL WARFARE AGENT MEASUREMENTS BY PID

## INTRODUCTION

Many chemical warfare agents, including nerve agents and related compounds, can be detected by PID. Table 1 lists some common agents and several of their physical properties and PID Correction Factors (CF). The CF is used by calibrating the instrument with isobutylene, and then multiplying the reading by the CF to obtain the true concentration. (See Technical Note TN-106 for full details.)

## DISCUSSION AND CONCLUSIONS

All the warfare agents listed in Table 1 can be detected with a 10.6 eV lamp, except phosgene, which requires an 11.7 eV lamp, and HCN and ClCN, which cannot be detected by PID.

VX has inherent sensitivity, but it is too heavy a compound to get to the PID sensor and thus cannot be reliably measured. The 8-hour TWAs and IDLHs are extremely low, and the PID cannot measure

nerve agents at these levels. However, it can locate sources and detect the agents at levels well below levels that are lethal in one minute (see LCy 50 in table 1). Compounds with low vapor pressures tend to respond more slowly on the PID, in some cases requiring several minutes. In the case of VX, the lethal dose is above its vapor pressure at room temperature. Therefore, the lethal one-minute dose can be attained only if the air is hot or the chemical is sprayed as an aerosol. At the maximum concentration, more than one-minute exposure is required for lethal effects.

Table 2 shows that many of the common decomposition products of aged warfare agents can also be detected by PID. These are often more volatile than the agent itself (especially for VX) and thus the products serve as a more easily detectable surrogate than the original material.

**Table 1. Properties of chemical warfare agents and simulants including detectability by PID.**

Compound	Structure	m.w.	Lamp (eV)	CF	8-h TWA (mg/m <sup>3</sup> ) (WPL)	8-h TWA (ppbv)	IDLH (ppbv)	LCt50 (ppmv-min)	Vapor press. (ppmv)
<b>Blood Agents</b>									
Arsine (SA)	AsH <sub>3</sub>	78	10.6	1.9	0.16	0.05	3,000		Gas
Hydrogen Cyanide (AC)	HCN	27	ND**	ND**	11	10,000	50,000	270	Gas
Cyanogen Chloride (CK)	ClCN	61.5	ND**	ND**	0.6 C <sub>5</sub>	300 C <sub>5</sub>			Gas
<b>Blister Agents</b>									
Lewisite (L1)	ClCH=CHAsCl <sub>2</sub>	207	10.6	~1*	0.003	0.35		140	460
Mustard (H or HD)	S(EtCl) <sub>2</sub>	159	10.6	0.6	0.0004	0.061	0.11	>230	95
N Mustard (HN-1)	N(Et)(EtCl) <sub>2</sub>	172	10.6	~1*					320
HT	60% HD & 40% T (O(EtSEtCl) <sub>2</sub> )				See HD; T part is non-volatile and poses low exposure risk				
Phosgene Oxime (CX)	HON=CCl <sub>2</sub>	114	11.7	~5*				685	15000
<b>Choking Agent</b>									
Phosgene (CG)	O=CCl <sub>2</sub>	99	11.7	8.5	0.4	100	2,000	790	Gas
<b>Nerve Agents</b>									
Sarin (GB)	O=PF(Me)(OiPr)	140	10.6	3	0.0001	0.017	17	12	3800
Soman (GD)	O=PF(Me)(OCH(Me)(tBu))	182	10.6	~3*	0.00003	0.004	6.7	9	530
Tabun (GA)	O=P(CN)(OEt)(NMe <sub>2</sub> )	162	10.6	0.8	0.0001	0.015	15	20	92
VX	O=P(Me)(OEt)(SEtN(iPr) <sub>2</sub> )	267	10.6	~0.5*	0.00001	0.00091	0.27	2.7	0.92
GF	O=PF(Me)(O-Cyclohex)	180	10.6	~3*	0.00003	0.004	6.8		79

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Compound	Structure	m.w.	Lamp (eV)	CF	8-h TWA (mg/m <sup>3</sup> ) (WPL)	8-h TWA (ppbv)	IDLH (ppbv)	LCt50 (ppmv-min)	Vapor press. (ppmv)
<b>Vomiting Agents</b>									
Diphenylchloroarsine (DA)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsCl	265	10.6	~0.5*					0.59
Diphenylcyanoarsine (DC)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsCN	255	10.6	~0.5*					
Diphenylaminochloroarsine (DM)	(H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> AsCl	295	10.6	~0.5*					
<b>Riot Agents</b>									
Chloroacetophenone (CN)	C <sub>6</sub> H <sub>5</sub> C(O)CH <sub>2</sub> Cl	155	10.6	~0.5*	0.32	50	2,400		7.1
<b>Stimulants</b>									
DMMP	O=P(Me)(OMe) <sub>2</sub>	124	10.6	4.3					
Triethyl phosphate	O=P(OEt) <sub>3</sub>	182	10.6	3.1					
Methyl salicylate	2-(HO)C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> Me	152	10.6	0.9					

\*Estimated value. \*\*ND = Not Detectable by PID. ⚡C = ceiling value.

**Table 2. Estimated response of warfare agent degradation products by PID.**

Agent & Products	CAS No.	IE* (eV)	CF Estimate 10.6 eV Lamp	CF Estimate 11.7 eV Lamp
<b>Lewisite(L1)</b>				
	541-25-3	?	~1	~1
2-Chlorovinyl arsenic oxide	123089-28-1	?	~1	~1
2-Chlorovinylarsonic acid	64038-44-4	?	~1	~1
Dihydroxy-2-chlorovinylarsine	85090-33-1	?	~1	~1
Sodium arsenite	11137-68-1		ND	ND
Acetylene	74-86-2	11.4	ND	2
Hydrogen chloride	7647-01-0	12.8	ND	ND
Arsenic trichloride		10.55	~10	~1
<b>Mustard (HD)</b>				
	505-60-2		0.6	~0.5
1,4-Dithiane	505-29-3	~8.5	~0.5	~0.4
1,4-Oxathiane	15980-15-1	~9	~1	~1
2-Chloroethyl vinyl sulfide	81142-02-1	~9	~1	~1
2-Chloroethyl vinyl sulfoxide	40709-82-8	~10	~1	~1
Bis-2(bis(2-hydroxyethyl)-sulfonium ethyl)		?	?	?
Bis (2-hydroxyethyl)-2-(2-chloroethylthio) ethyl sulfonium	64036-91-5	?	?	?
Divinyl sulfoxide	1115-15-7	~10	~1	~1
Hemi Mustard	693-30-1		~1	~1
Mustard sulfone	471-03-4	~10	~5	~1
Mustard sulfoxide	5819-08-9	~8.8	~1.5	~1
Thiodiglycol	111-48-8	<9	~1	~1
Dichloroethane	73-34-3	11.06	ND	0.6
1,1,2,2-Tetrachloroethane	79-34-5	11.1	ND	0.60
Tetrachloroethylene (PCE)	127-18-4	9.32	0.57	0.31
Trichloroethylene (TCE)	79-01-6	9.45	0.54	0.43
1,3-Butadiene	106-99-0	9.07	0.85	1.1
2-Butene	107-01-7	~9.6	~1	~1
Vinyl chloride	75-01-4	9.99	2	0.6

**Table 2. Estimated response of warfare agent degradation products by PID.**

Agent & Products	CAS No.	IE* (eV)	CF Estimate 10.6 eV Lamp	CF Estimate 11.7 eV Lamp
<b>Phosgene</b>	75-44-5	11.55	ND	8.5
Carbon dioxide	124-38-9	13.8	ND	ND
Hydrochloric acid	7647-01-0	12.8	ND	ND
<b>PhosgeneOxime(CX)</b>		~11.5	ND	~5
Carbon dioxide	124-387-9	13.8	ND	ND
Hydrochloric acid	7647-01-0	12.8	ND	ND
Hydroxylamine	7803-49-8	~10.0	~10	~3
<b>Sarin (DB)</b>	107-44-8	<10.6	3	~1
Diisopropyl methylphosphonate (DIMP)	1445-75-6	<10.6	~3	~1
Hydrogen fluoride	7664-39-3	16	ND	ND
Isopropanol (IPA)	67-63-0	10.12	6.0	2.7
Isopropyl fluoride	420-26-8	11.1	ND	~3
Isopropyl methylphosphonic acid (IMPA)	1832-54-8	?	?	?
Methylphosphonofluoridic acid	1511-67-7	?	?	?
Methyl phosphonic acid	993-13-3	?	?	?

\*IE = Ionization Energy, the minimum lamp energy needed to detect the compound by PID.