# 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. There fore, 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 bedetected 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$^3$) (WPL) | 8-h TWA (ppbv) | IDLH (ppbv) | LCt50 (ppmv-min) | Vapor press. (ppmv) |
|---|---|---|---|---|---|---|---|---|---|
| *Blood Agents* | | | | | | | | | |
| Arsine (SA) | $AsH_3$ | 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$^\xi$ | 300 C$^\xi$ | | | Gas |
| *Blister Agents* | | | | | | | | | |
| Lewisite (L1) | $ClCH=CHAsCl_2$ | 207 | 10.6 | ~1* | 0.003 | 0.35 | | 140 | 460 |
| Mustard (H or HD) | $S(EtCl)_2$ | 159 | 10.6 | 0.6 | 0.0004 | 0.061 | 0.11 | >230 | 95 |
| N Mustard (HN-1) | $N(Et)(EtCl)_2$ | 172 | 10.6 | ~1* | | | | | 320 |
| HT | 60% HD & 40% T $(O(EtSEtCl)_2)$ | See HD; T part is non-volatile and poses low exposure risk | | | | | | | |
| Phosgene Oxime (CX) | $HON=CCl_2$ | 114 | 11.7 | ~5* | | | | 685 | 15000 |
| *Choking Agent* | | | | | | | | | |
| Phosgene (CG) | $O=CCl_2$ | 99 | 11.7 | 8.5 | 0.4 | 100 | 2,000 | 790 | Gas |
| *Nerve Agents* | | | | | | | | | |
| 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) | $O=P(CN)(OEt)(NMe_2)$ | 162 | 10.6 | 0.8 | 0.0001 | 0.015 | 15 | 20 | 92 |
| VX | $O=P(Me)(OEt)(SEtN(iPr)_2)$ | 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/m³) (WPL) | 8-h TWA (ppbv) | IDLH (ppbv) | LCt50 (ppmv-min) | Vapor press. (ppmv) |
|---|---|---|---|---|---|---|---|---|---|
| *Vomiting Agents* | | | | | | | | | |
| Diphenylchloroarsine (DA) | $(C_6H_5)_2AsCl$ | 265 | 10.6 | ~0.5* | | | | | 0.59 |
| Diphenylcyanoarsine (DC) | $(C_6H_5)_2AsCN$ | 255 | 10.6 | ~0.5* | | | | | |
| Diphenylaminochloroarsine (DM) | $(H_2NC_6H_4)_2AsCl$ | 295 | 10.6 | ~0.5* | | | | | |
| *Riot Agents* | | | | | | | | | |
| Chloroacetophenone (CN) | $C_6H_5C(O)CH_2Cl$ | 155 | 10.6 | ~0.5* | 0.32 | 50 | 2,400 | | 7.1 |
| *Stimulants* | | | | | | | | | |
| DMMP | $O=P(Me)(OMe)_2$ | 124 | 10.6 | 4.3 | | | | | |
| Triethyl phosphate | $O=P(OEt)_3$ | 182 | 10.6 | 3.1 | | | | | |
| Methyl salicylate | $2-(HO)C_6H_4CO_2Me$ | 152 | 10.6 | 0.9 | | | | | |

*Estimated value.    **ND = Not Detectable by PID.    ξC = 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 |
|---|---|---|---|---|
| *Lewisite(L1)* | 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 |
| *Mustard (HD)* | 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-hydroexyethyl)-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 |
|---|---|---|---|---|
| *Phosgene* | 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 |
| *PhosgeneOxime(CX)* | | ~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 |
| *Sarin (DB)* | 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.