

# Flame Photometry

Flame photometry is an atomic spectroscopy technique based on the light emission phenomenon of excited atoms or clusters as they return to lower energy states. It is a very important CWA detection technique that has been successfully used for a long time. The detection of the characteristic light emission by excited sulfur and/or phosphorus atoms or clusters is used to identify CWAs. Most classic CWAs, such as the G-agents, V-agents, and sulfur mustard (HD), contain phosphorus and/or sulfur in their molecules as discussed in [Chapter 2](#). Detectors based on atomic spectroscopy technology can also be used in detecting many TICs that contain phosphorus, sulfur, arsenic, or other atoms that produce characteristic light emissions.

Flame photometric detectors (FPDs) have been in use for as long as gas chromatographic and liquid chromatographic detectors. They are arguably the most useful analytical detectors for CWA studies. Since many of the chemicals of greatest concern, such as pesticides, automobile exhaust, and petroleum products, contain sulfur or phosphorous, FPDs are widely used in research and manufacturing operations. The CWA limit of detection without the addition of a gas chromatographic column is in parts per billion to parts per million.

An FPD is commonly connected to a gas chromatographic instrument to permit separation of chemicals in the sample for qualitative and quantitative analyses by benchtop instruments. The use of a gas chromatography (GC) column provides a means for increased selectivity and possible identification through respective elution times for diverse target compounds. Standard methods using gas chromatography coupled with a flame photometric detector (GC-FPD) were developed for and adopted by the Environment Protection Agency (EPA) and other government agencies for environmental studies. Needless to say, the GC-FPD method has been one of the most useful in determining CWA concentrations.

FPD instruments for field operations have portability and fast real-time analysis. Analyzing a vapor sample with a handheld FPD does not require sample preparation, as it draws a sample directly from the surrounding air and provides a content analysis

instantly. For example, the AP2C® instrument made by Proengin is designed for direct air sampling. It can simultaneously and quickly detect both phosphorus- and sulfur-containing compounds, as the sample does not pass through a GC column. If the air contains phosphorus or sulfur, the detector responds within seconds. The AP2C is the only handheld FPD available at present.

FPD for CWA detection is considered semi-selective in the sense that it responds to all sulfur/phosphorus-containing chemicals. Without a means of compound separation, the FPD detector is not capable of distinguishing whether the detected signal derives from a CWA or another substance containing phosphorous and/or sulfur.

## 7.1 PRINCIPLE OF OPERATION

You may have observed bright yellow flames in the barbecue grill when salt or marinade drops onto the charcoals. The yellow flame emission is characteristic of sodium atoms. In contrast, when potassium salt is burned, the characteristic color emission is reddish. Each element emits a particular color when burned in an open flame. FPD is based on this principle.

An atom can be simply described as a nucleus with electrons orbiting around it. Roughly speaking, electrons revolve around the nucleus at different orbits, which reflect different atomic energy levels. The energy of an electron in a given orbit is a constant. Thus, the atom can be said to possess a certain energy level based on a certain orbit.

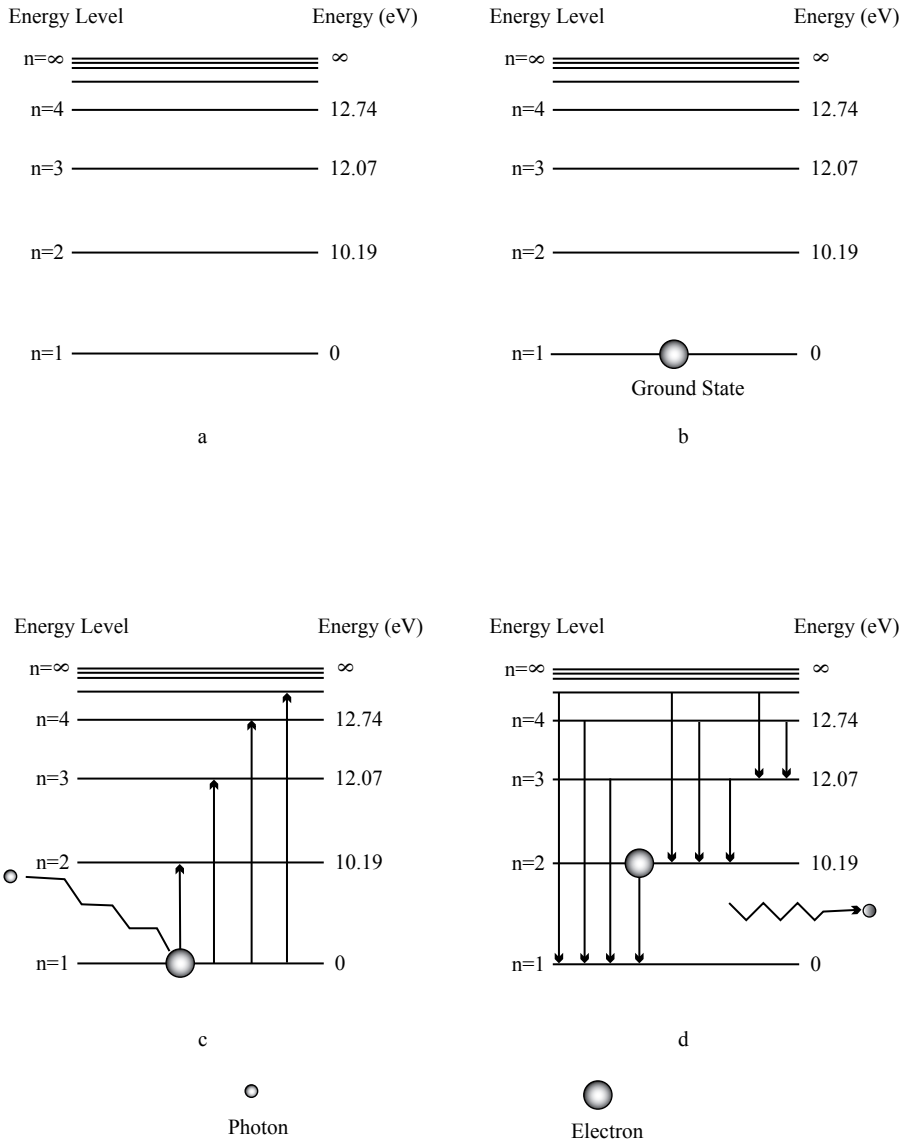
For example, hydrogen is the first element in the periodic table and each atom has only one electron. Figure 7.1a shows a few possible energy levels for a hydrogen atom. When the electron is in its lowest-energy orbit, the atom is said to be at “ground state” (Figure 7.1b), which is also the most stable. The atom will stay at this ground state as long as it is not stimulated by external energy, such as absorbing energy from a passing photon that will propel it to a higher energy, or excited, state (Figure 7.1c). At this excited state, the atom is unstable and has the tendency to return to its lower ground-state energy level whenever possible. As it returns to lower energy levels, the absorbed energy is released by emitting a photon with a certain amount of energy (Figure 7.1d). The energy associated with this release of photon is equal to the difference between an atom’s energy at an excited energy level and the ground-state energy level, which is the same as the energy absorbed initially.

The energy of the released photon ( $E$ ) from the excited hydrogen atom from energy level 2 ( $n = 2$ ) to energy level 1 ( $n = 1$ ) (Figure 7.1d) is therefore

$$E = 10.19 - 0 = 10.19 \text{ (eV)} \quad (7.1)$$

The wavelength of the photon released from an atom depends on the energy of the photon ( $E$ ) and can be calculated with the following equation:

$$\lambda = \frac{hc}{E} \quad (7.2)$$



**Figure 7.1** Energy levels of hydrogen atom (a); ground state (b); excited state via photon (c); and release of photon by excited electron (d).

where  $\lambda$  is the wavelength in nanometers (nm,  $10^{-9}$  m);  $h$  is Planck's constant ( $h = 4.136 \times 10^{-15}$  eV·sec); and  $c$  is the velocity of light ( $3 \times 10^{17}$  nm/sec). From Equation 7.2, the relationship between the frequency ( $\nu$ ) of a photon and its energy can be calculated as

$$E = \frac{hc}{\lambda} = h \frac{c}{\lambda} = h\nu \tag{7.3}$$

**Table 7.1** Frequencies and Wavelengths of Electromagnetic Waves

Common Name of Wave	Gamma Rays	X-rays	Ultraviolet	Visible	Infrared	Microwave	Radio
Wavelength (nm)	← Shorter <0.01	0.01–1	1–400	400–700	700–10 <sup>5</sup>	10 <sup>5</sup> –10 <sup>8</sup>	Longer → >10 <sup>8</sup>
Frequency (Hz)	← Increase >3 × 10 <sup>19</sup>	3 × 10 <sup>19</sup> – 3 × 10 <sup>17</sup>	3 × 10 <sup>17</sup> – 7.5 × 10 <sup>14</sup>	7.5 × 10 <sup>14</sup> – 4.3 × 10 <sup>14</sup>	4.3 × 10 <sup>14</sup> – 3 × 10 <sup>12</sup>	3 × 10 <sup>12</sup> – 3 × 10 <sup>9</sup>	Decrease → <3 × 10 <sup>9</sup>
Energy of proton (eV)	← Higher >10 <sup>5</sup>	10 <sup>3</sup> –10 <sup>5</sup>	3–10 <sup>3</sup>	2–3	0.01–2	10 <sup>-5</sup> –0.01	Lower → <10 <sup>-5</sup>

When the hydrogen atom returns to energy level 1 (ground state) from energy level 2 (Figure 7.1d), it emits a photon of the following wavelength:

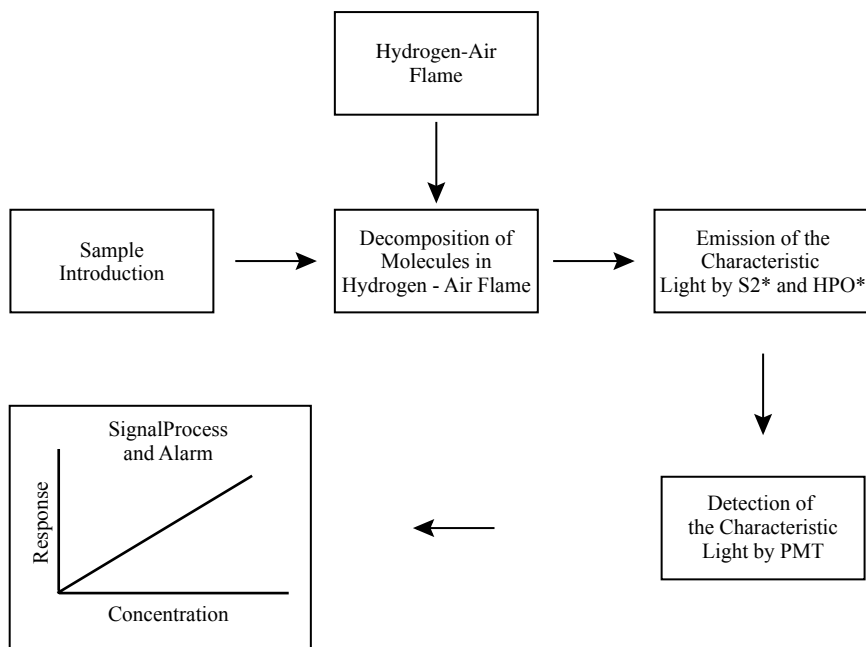
$$\lambda = \frac{hc}{E} = \frac{4.136 \times 10^{-15} (\text{eV} \cdot \text{s}) \times 3 \times 10^{17} (\text{nm} / \text{s})}{10.19 (\text{eV})} = 122 (\text{nm}) \quad (7.4)$$

Light at a wavelength of 122 nm falls in the UV range of the light spectrum (Table 7.1).

The number of electrons that can be excited depends on the element. An element's atomic number (listed in the periodic table) is determined by the number of protons in its nucleus, and the number of protons is equal to the number of electrons in the atom. For example, a phosphorous atom has 15 electrons, and a sulfur atom has 16 electrons. The electrons revolve around the nucleus at different orbits according to the energy each possesses when the atom is at ground state. Because more than one electron can be excited, and each of the electrons can be excited to different energy levels, when these excited electrons return to respective lower energy levels, the light they emit will be of different wavelengths, which in turn generates a light spectrum of different wavelengths. For the hydrogen atom, the light wavelengths released when its energy level falls to ground level are within the UV range, and visible light is released when its energy drops from a higher energy level to the  $n = 2$  level.

As discussed earlier, most of the CWAs contain phosphorus or sulfur. When these molecules are broken down in a hydrogen–air flame, the released phosphorus and sulfur are excited. The excited sulfur (in the form of  $\text{S}_2^*$ , and designated as  $\text{S}_2^*$ ) and phosphorous (in the form of  $\text{HPO}^*$ , and designated as  $\text{HPO}^*$ ) release light in respective characteristic wavelengths when they return to lower energy levels. FPDs identify the released characteristic wavelength of sulfur and/or phosphorous and thus determine whether a sample contains sulfur and/or phosphorous components.

Figure 7.2 is a block diagram showing the operational principle of FPDs. After the sample is introduced, the flame decomposes the molecules.  $\text{S}_2$  and  $\text{HPO}$  from molecule decomposition absorb energy and become excited in the hydrogen–air flame. The excited  $\text{S}_2^*$  and  $\text{HPO}^*$  then emit characteristic light when they return to their ground states:



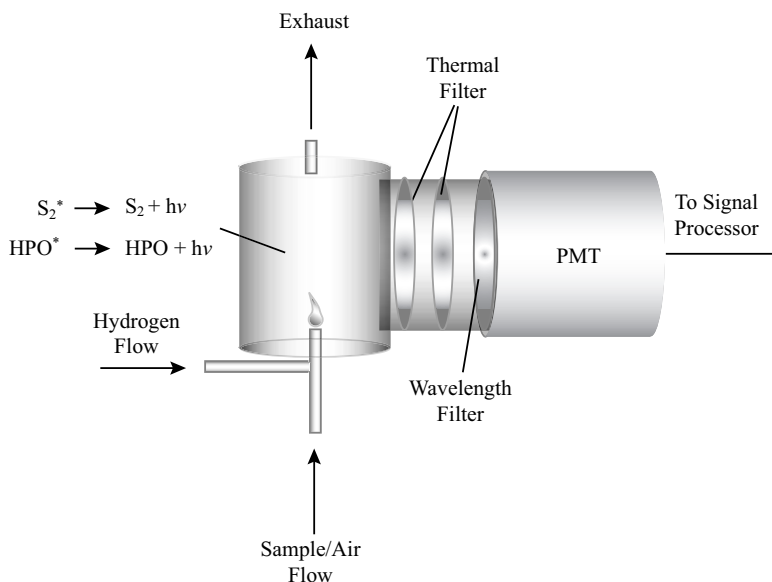
**Figure 7.2** Block diagram of FPD analysis procedure.



In Equations 7.5 and 7.6,  $h\nu$  represents the energy of the released photon. To achieve specificity, the FPD identifies the main emission wavelength of  $S_2^*$  (394 nm) and  $HPO^*$  (526 nm) with the use of filters to block photons of other wavelengths released in the burning process. The photons that pass through the light filter then strike the photomultiplier tube (PMT). The PMT monitors light intensity to produce the detection signal. The intensity of the light released is proportional to the number of  $S_2^*$  or  $HPO^*$  atoms, which is in turn related to the concentration of sulfur or phosphorous species in the sample. Thus, the greater the target chemical concentration, the greater the detection signal intensity. With the use of standard calibration curves, concentration of targeted chemicals in the sample can be correlated.

## 7.2 INSTRUMENTATION

Figure 7.3 shows a schematic diagram of a typical FPD. The detector consists of a hydrogen inlet, air inlet, sample inlet, burner, thermal filters, light filter, PMT, signal processor, and exhaust chimney. A source of hydrogen is required to produce the hydrogen-air flame for sample ionization.



**Figure 7.3** Schematic diagram of FPD.

### 7.2.1 Direct Sample Introduction and GC Interface

The direct sample type of FPD draws the sample via a pump into its combustion chamber at a controlled rate. The sample mixes with the hydrogen and burns at the tip of the burner. CWAs or TICs that contain sulfur and/or phosphorus are decomposed and generate signals. The detection occurs quickly, and is considered as real-time detection. However, without additional identification methods, the FPD cannot distinguish among the signals generated by multiple chemicals to identify the substances (i.e., CWAs versus other chemicals). The burning of other chemicals such as pesticide compounds can produce similar sulfur and/or phosphorus signals. (FPD has been used for detecting pesticide levels for a long time.) Sulfurous and phosphorous chemicals may also be found in smoke emissions during and after fires. Fortunately, gas chromatographic elution is a very powerful tool that can be combined with the FPD to enable compound identification.

Basically, gas chromatography separates chemicals in vapor based on each chemical's distinct distribution coefficient between the stationary and mobile phases. A column containing the stationary phase is the heart of the technique, and the carrier gas (mobile phase) is used to carry the chemicals through the column. (A complete discussion of gas chromatography is beyond the scope of this book. Numerous excellent publications on gas chromatography are available, and we have included three references in the bibliography at the end of the book.)

For the FPD, a GC column can be used to separate chemicals in the sample before they enter the mixing and combustion chamber according to their respective elution time. The combination of retention times determined by GC and the presence of sulfur and/or phosphorous signals enables the possible identification of targeted

chemicals. Identification can only be considered as possible because many substances could have similar retention times through the GC column, which in turn may yield detection peaks by the FPD. However, such combinations occur infrequently. Therefore, the frequency of false alarms is drastically reduced. The drawback of the addition of a GC in front of the FPD is that analysis time increases. Consequently, detection cannot be considered as “real time.”

## 7.2.2 Flame and Hydrogen Source

### 7.2.2.1 Hydrogen–Air Flame

A hydrogen–air mixture is ignited to produce the flame. The hydrogen–air flame, at temperatures of 2000°C to 2100°C, breaks down the incoming organic chemicals and provides the energy for exciting the electrons. This temperature is sufficient to excite  $S_2$  and HPO without ionizing them. The hydrogen–air flame is also used in the flame ionization detection technique, which is discussed in [Chapter 11](#).

### 7.2.2.2 Hydrogen Source

While benchtop instruments can use pressurized tanks as the hydrogen source, carrying pressurized hydrogen is very inconvenient in field applications, and many believe tanks in the field present a major safety hazard. Alternatively, small hydrogen alloy storage devices that contain reasonable amounts of hydrogen (in the form of a metal hydride) are available, and these can be used safely in the field.

Alloys such as Mg,  $Mg_2$ , Ni, FeTi, and  $LaNi_5$  are capable of absorbing and releasing considerable amounts of hydrogen gas in and from relatively small quantities of hydride powder. These alloys can absorb and hold large amounts of hydrogen by bonding with hydrogen to form hydrides ( $MgH_2$ ,  $Mg_2NiH_4$ ,  $FeTiH_2$ , and  $LaNi_5H_6$ ) under 1 atm. The bonded hydrogen can be released as needed. The advantage of these types of storage devices is their relatively large capacity for hydrogen absorption in small containers. The alloys can hold more hydrogen atoms than liquid hydrogen of the same volume. For instance, it has been reported that a cubic centimeter of LaNi alloy can absorb  $5.5 \times 10^{22}$  hydrogen atoms. The volume of a mole of hydrogen gas ( $6.02 \times 10^{23}$  hydrogen molecules, or  $2 \times 6.02 \times 10^{23}$  hydrogen atoms since one hydrogen molecule consists of two atoms) is 24.45 L under 1 atmospheric pressure at 25°C. Therefore, the volume of  $5.5 \times 10^{22}$  hydrogen atoms is approximately equivalent to 1 L of hydrogen gas at room temperature. For comparison purposes, 1  $cm^3$  of liquid hydrogen contains  $4.2 \times 10^{22}$  atoms, and 1  $cm^3$  of hydrogen gas contains only  $0.99 \times 10^{22}$  hydrogen atoms at barometric pressure 200. Another feature of the hydrogen alloys is the ability to absorb and release hydrogen gas for many cycles without deteriorating. The release rate of the absorbed hydrogen can be controlled by temperature or pressure regulation. The use of absorbed hydrogen has made hydrogen handling much more convenient and less hazardous than using cylinders of compressed hydrogen. The current AP2C detector uses a small cartridge of alloy-absorbed hydrogen, which contains enough hydrogen for efficient field applications.

The hydrogen enters the combustion chamber and mixes with the air sample from the air inlet to form the hydrogen–air flame. Sample air may come from the GC column if components are separated before the sample enters the detector. The flame decomposes chemicals contained in the sample. In the case of CWAs in a sample, the released and excited sulfur and/or phosphorus emit photons of a characteristic respective light spectrum for detection through the use of special light filters.

### 7.2.3 Signal Detection

The excited sulfur or phosphorus atoms emit characteristic light when they are returning to the stable ground state. This emitted light passes through two quartz windows and optical filters before reaching the PMT. Electrical signals are generated by the PMT and interpreted by a microprocessor to determine sulfur or phosphorus concentration in the sample.

#### 7.2.3.1 Thermal and Wavelength Filters

The burning of the hydrogen in the air generates a large amount of heat. If the heat is permitted to reach the PMT, undesirable background noise can render the system useless. Heat will also shorten the useful life of the photometer. Heat from a flame is usually released in the form of infrared light. To reduce the effects of heat reaching the PMT, quartz plates are used as thermal filters to block a large portion of infrared light while allowing other light spectra such as UV and visible light to pass through. The quartz filters are located in front of the optical wavelength filters. The use of two quartz filters provides more effective heat shielding.

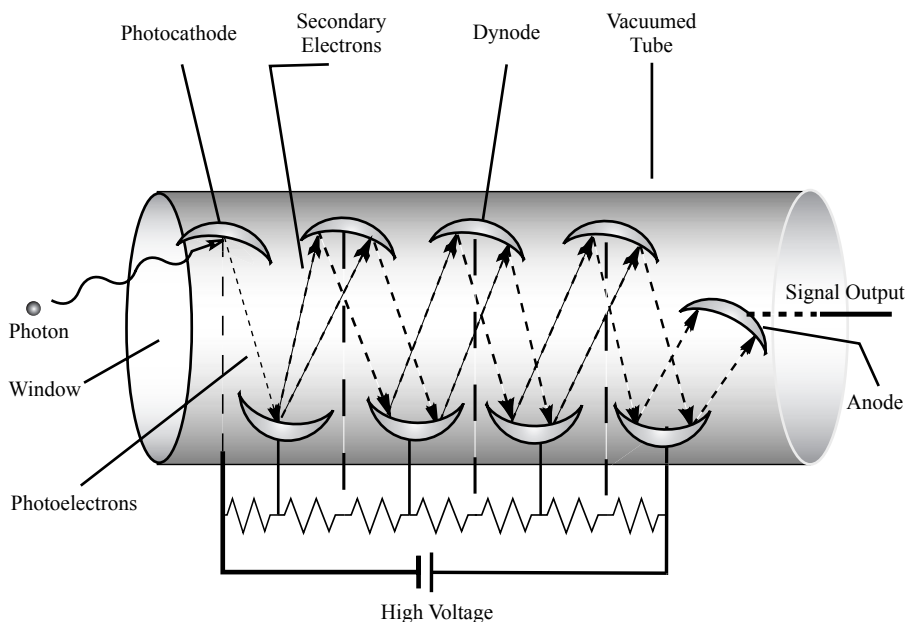
The light released by  $S_2^*$ ,  $HPO^*$ , and other substances passes through the quartz thermal filters and then reaches the wavelength filters; only light of specific wavelengths can pass through these filters. For example, a 394-nm filter is used for sulfur, and a 526-nm filter is used for phosphorous detection. A filter change is generally required to put the instrument in the correct mode for detection of a targeted chemical. More sophisticated instruments may contain a dual FPD, where one of the FPD uses the 394-nm filter for sulfur detection and the other uses the 526-nm filter for phosphorus detection. The dual FPD permits simultaneous detection of both elements, which in turn enables detection of nerve and blister agents simultaneously in CWA detection applications. However, changing filters or employing dual detectors is impractical for field applications.

Field instruments like the AP2C incorporate both sulfur and phosphorus filters within the same detector. The user switches back and forth between the two types of filters to permit measuring characteristic light emissions from both elements.

#### 7.2.3.2 PMT

After the photons emitted by sulfur or phosphorus pass through the wavelength filter, they are received by the PMT. The PMT is a vacuum tube that consists of a photocathode, several dynodes, and an anode to convert the incoming light into an





**Figure 7.4** Schematic diagram of photomultiplier tube.

electrical signal (Figure 7.4). The light strikes the photocathode, which releases electrons called photoelectrons. These electrons are accelerated through an electric field to the first dynode. They, in turn, strike the second dynode and produce the release of many more electrons, which are referred to as secondary electrons. Each of these secondary electrons is then further accelerated to the next dynode and generates still more electrons. The process is repeated through each dynode. The number of electrons generated by a single electron through the photocathode is thus increased through several dynodes and multiplied in the tube. The number of electrons received by the anode for each photoelectron could be increased by  $10^4$  to  $10^5$  depending on the photomultiplier structure. The anode receives these electrons and generates the electric signals for the microprocessor to process.

### 7.2.3.3 Chemical Identification

Since only the characteristic light wavelengths generated by  $\text{HP}^*$  or  $\text{S}_2^*$  are permitted to enter the PMT, the detection signal is considered to be an indication that the sample contains sulfur and/or phosphorous compounds. Such direct sampling results do not permit precise substance identification. As discussed previously, detection indicates only that the sample consists of substances that contain sulfur and/or phosphorus, which may or may not be targeted toxic chemicals. The AP2C is an example of this principle of detection.

When FPD is coupled with a GC column, the detected signals generated by the eluting chemicals can provide a means for compound identification. The retention time of an agent in the GC column is a function of temperature and carrier gas

pressure together with the properties of the chemical and the column. The retention time for each agent or chemical of interest is obtained by running standard samples at a defined temperature and pressure with a certain type of column. Therefore, the identification of an agent via a GC-FPD is based on two factors: retention time and presence of sulfur and/or phosphorus. This drastically reduces the false positive alarm rate. The Miniature Continuous Air Monitoring System (MINICAMS<sup>®</sup>) is an example of using the GC mode successfully together with FPD for CWA detection. In addition to the GC mode, the MINICAMS also uses sample concentration and thermal desorption to increase its sensitivity for vapor detection.

The wastes produced through the FPD processes, which include water generated by burning hydrogen in air and decomposed substances from the sample, are removed from the detector via a chimney exhaust. The toxic sample drawn into the detector is decomposed, and therefore detoxified, when it is burned in the hydrogen flame.

## 7.3 TECHNICAL SPECIFICATIONS

### 7.3.1 Selectivity

Currently, FPDs are made to detect sulfur and phosphorous compounds through specific wavelength filters, and are able to detect respective CWA compounds such as the G-agents, mustard, and certain TICs, including  $\text{PH}_3$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$ . Since other chemicals that do not contain these two elements do not emit these characteristic wavelengths, they do not interfere with detection. With the recent interest in detection of TICs, FPDs are of potential usefulness because various light filters can be installed to permit detection of other elements as well.

As discussed above, when the detector reports sulfur or phosphorus, there is no way to know if the detected substances are CWAs, TICs, or other nontargeted chemicals. Specificity can only be improved through use of a GC column, which will increase sample analysis time but permit possible compound identification and reduce false positive alarms.

### 7.3.2 Sensitivity and LOD

FPD is very sensitive for sulfur and phosphorous compound detection. The reported limit of CWA detection is at the parts-per-billion level, which is lower than the IDLH levels set for all CWAs and TICs.

### 7.3.3 Response Dynamic Range

The concentration–response relationship, unlike ion mobility spectroscopy detectors, is usually linear. For phosphorus, this relationship remains linear over a large concentration range. However, since sulfur exists in the flame as  $\text{S}_2$ , the concentration–response relationship is a second-order one. Response linearity is related to the square root of sulfur concentration. The overall dynamic range for both sulfur and phosphorous are over  $10^4$  or even  $10^5$ .

### 7.3.4 Quantitative Analysis Capability

FPDs such as MINICAM use the intensity of signals generated by sulfur or phosphorous to determine target chemical concentration in the sample. They are widely used in laboratories for determining concentrations of CWAs in samples and have demonstrated excellent quantitative analysis capability. For field applications, responses are presented in a semiquantitative manner for simplicity. As an example, the AP2C detector uses five light bars to indicate detected concentration levels.

For quantitative analysis, it is important that background signals are corrected to reduce interference from background noise. This may be achieved by using two reference optical filters to monitor the light with wavelengths in the neighborhood of the light emitted by sulfur or phosphorus. These filters reveal the background intensity near the sulfur or phosphorous wavelengths that could add signals to the detector. The signals are then compensated for by the microprocessor to minimize the noise effect.

### 7.3.5 False Alarm Rate

As discussed above, FPD is made specifically selective to sulfur and phosphorus components for CWA detection purposes. Thus, other targeted and nontargeted sulfur and phosphorous components may trigger false positive alarms. False positive alarms may also be caused by interfering chemicals that emit photons at the same or similar wavelengths as those of sulfur or phosphorus.

### 7.3.6 Response Time

Detection of CWAs with FPD can be considered real time by instruments designed for direct air analysis. Air is continually being drawn through the detector and analyzed in real time. Detection time will increase if a GC column is used to separate sample chemicals, and is determined by the elution time of the targeted chemical through the column. GC column use will generally require sample pre-concentration to produce a sample size adequate for detection.

### 7.3.7 Other Specifications

FPDs are usually designed as very rugged devices, and require very little maintenance. The PMT has quite a long life, and can be changed easily when replacement is necessary. In general, because the hydrogen–air flame used in this type of detector produces very high temperatures and burns clean, very little residue in the combustion chamber is expected. However, if the detector has been used to analyze samples with high organic matter content for a long period of time, it is possible that carbon may coat the thermo filter and sensitivity will be reduced. Maintaining the proper hydrogen–air mixture is the key to produce consistent flame temperature, and thus long-term consistent analytical sensitivity.

## 7.4 PULSED FLAME PHOTOMETRY

A relatively new technique called pulsed flame photometry has been developed and commercialized for benchtop instruments. It is based on the same fundamental principles as the FPD, except that the flame is pulsed through the use of various flow patterns and flow rate control. Hydrogen combines with air sample flows into a small, pulsed-flame chamber that contains a continuously heated wire igniter. Here the combustible mixture is ignited and propagated back to the gas source and self-terminated within a few milliseconds. The sample in the ignition chamber continues to produce additional ignition for a few hundred milliseconds. This ignition-propagation-termination cycle continues in periodic pulsed fashion.

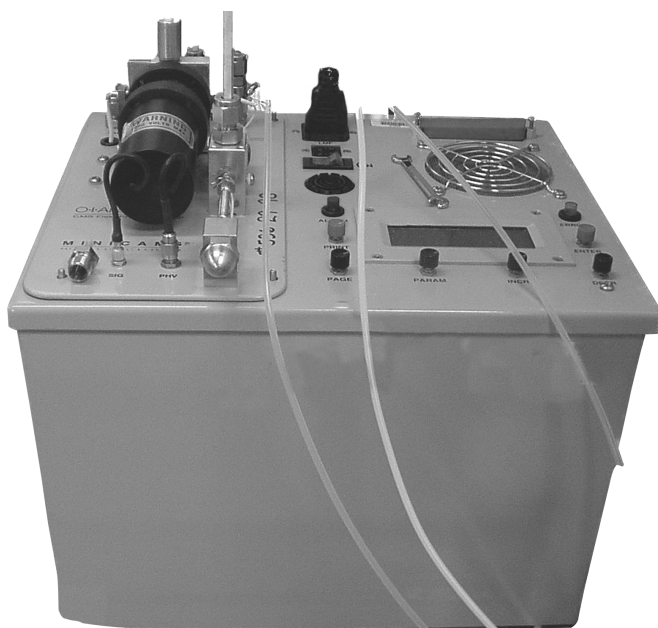
In a pulsed flame photometric detector (PFPD), the combustion of hydrocarbon molecules is fast and irreversible, and heteroatom species such as  $S_2$ , HPO, and HNO emit light after the flame is extinguished and thus under cooler temperatures. Consequently, their respective emissions can be electronically gated and separated from the hydrocarbon emission. Thus, PFPD can provide selectivity against hydrocarbon interference during detection analysis. PFPD sensitivity was reported to be superior to FPD. Moreover, N and As could be also detected. The PFPD is currently available for use in benchtop instruments, such as the MINICAMS from O. I. Analytical and other GC detector manufacturers.

The PFPD has much lower LOD and better sensitivity than FPD technology. The MDL of sulfur and phosphorous is in the  $10^{-13}$  to  $10^{-14}$  g/sec area (see Aviv Amirav et al. on [www.tau.ac.il/chemistry/amirav/pfpd.shtml](http://www.tau.ac.il/chemistry/amirav/pfpd.shtml)). In addition, the PFPD can simultaneously detect several element combinations using only one photomultiplier. Element identification can be achieved through the dual-gate-response ratio method. This detection technique is capable of identifying sulfur, phosphorous, nitrogen, arsenic, and many other elements with no interference from hydrocarbons. Thus, the PFPD would be very suitable for TIC detection.

The author has proposed to develop and commercialize the handheld Fast GC-PFPD model combines sample concentration, thermal desorption, GC separation together with highly selective PFPD detection. This device promises high sensitivity, selectivity, and specific CWA and TIC detection. Unfortunately, as of this writing, it was not commercially available. The Fast GC-PFPD operates in a fashion similar to the benchtop MINICAMS equipped with the PFPD detector. It differs from the MINICAMS in that it does not require various gas cylinders, but rather a metal hydride cartridge. Analysis time would be 35 sec for a full-cycle analysis. It can also be operated under the “sniff” mode. The LOD for the Fast GC-PFPD is expected to be  $0.003 \mu\text{g}/\text{m}^3$  organophosphorus and  $0.2 \mu\text{g}/\text{m}^3$  organosulfur.

## 7.5 APPLICATIONS

The MINICAMS-FPD (Figure 7.5) is a prime example of how the technology has impacted on studies of CWAs. MINICAMS is the analytical instrument of choice in CWA laboratories. Given that the FPDs detect both sulfur and phosphorus effectively, the MINICAMS-FPD covers nearly all commonly tested chemical agents.



**Figure 7.5** MINICAMS Detector. Photo courtesy of K. Y. Ong.

MINICAMS-FPD has also been placed at various sites where toxic chemical exposure may occur to serve not only as an analytical tool but also as a continuous safety monitoring device. The usefulness of this device has been repeatedly demonstrated in monitoring the potential escape of CWA vapor from engineering controls in a workplace. It can detect CWA vapors at sub-AEL concentrations.

GC manufacturers such as Tracor and PerkinElmer have developed FPDs. The detector is located behind a GC column to identify elution peaks after separation take place as the sample migrates through the column. Proper installation of optical filters permits the FPD to detect various target compounds. For CWAs, filters for phosphorus or sulfur detection are used for nerve agents and HD detection, respectively. Some users deploy two separate detectors, one installed with the phosphorus detection filter while the other uses the sulfur detection filter to achieve simultaneous detection of nerve agents and HD should the sample contain either or both.

Tracor has developed a CWA detector, the HyFED<sup>®</sup>, which draws an air sample directly into the FPD for analysis. The instrument requires connection to compressed hydrogen and air cylinders to provide the hydrogen flame for sample ionization. The instrument provides the means to sample continuously and analyze an airstream in real-time fashion. This detector has proven useful in monitoring vapor concentrations generated in laboratories. Because the targeted sample is known in laboratory conditions, there is no need to use a GC column for sample separation. Therefore, detection is direct and output instantaneous. Relative response signals can be correlated to provide a quantitative determination.

The French company Proengin Inc. (78210 Saint Cyr L'Ecole) developed the AP2C detector, a handheld device capable of simultaneously detecting nerve and blister



**Figure 7.6** AP2C Detector. Photo courtesy of K. Y. Ong.

agents (Figure 7.6). According to the manufacturer's operating instructions manual, the operational temperature performance ranges from  $-32^{\circ}\text{C}$  to  $55^{\circ}\text{C}$ . The instrument weighs approximately 2 kg, including the 7.3-V battery pack and hydrogen storage cartridge that provides hydrogen for approximately 12 hours of operation when fully charged. Start-up time is less than 2 min at temperatures above  $0^{\circ}\text{C}$ , and up to 15 minutes at temperatures below  $0^{\circ}\text{C}$ . Heat is applied to the hydrogen cartridge to maintain effective hydrogen production at cold temperatures. The UC-AP2C<sup>®</sup> model includes the vapor monitor (AP2C) and the liquid or solid substance sampler (S4PE<sup>®</sup>). During normal vapor operation, sample air is drawn into the AP2C unit through the changeable "vapor-sampling" nozzle at a sampling rate of approximately 80 l/hr (1.33 l/min). The heat from the flame decontaminates the internal surfaces, which allows fast recovery times.

The instrument is sensitive and can quickly detect CW agents. It utilizes a turning wheel of light filters to alternatively sense lights emitted from phosphorus and sulfur as a sample is burned. The internal light filters are alternated automatically without the need of manually changing the detection mode. Therefore, the device is capable of detecting nerve and blister agents simultaneously. When target substances are detected, it indicates the detection of phosphorus (i.e., nerve agent) or sulfur (HD). Because VX molecules consist of both sulfur and phosphorus atoms, its characteristic flame emission includes both the sulfurous and the phosphorous characteristics. When VX is detected, both the phosphorus and sulfur light indications on the AP2C panel will show. Because of lesser sensitivity toward sulfur detection than phosphorus detection, lower concentrations of VX may trigger only the phosphorus detection response.

The detected sample concentration is reported through the use of five rows of LED bars corresponding to relative concentration of  $\text{HPO}_2$  and  $\text{S}_2$ . More bars lit indicate a higher detected concentration. The operator's manual states that the hazard threshold for unprotected humans is reached as soon as the first red indicator light flashes on.

The AP2C also has the capability to detect liquid surface contamination using the S4PE accessory. The AP2C has been tested under the Domestic Preparedness program. Interested readers can access the full report on the Homeland Defense website.

## 7.6 CONCLUSION

In summary, the flame photometric technique is based on the wavelength (or frequency) of light emissions produced as a substance is burned when it passes

through a hydrogen–air flame. This technique uses the hydrogen–air flame as its energy source to decompose the sample and excite sulfur and phosphorous atoms. The energy loss produces photons that emit light when the excited sulfur or phosphorous atoms return to their ground state. The PMT multiplies the photoelectrons and produces signals. Since sulfur and/or phosphorous is commonly found in CWAs and some TICs, FPD is therefore capable of detecting CWAs and some TICs. It is also capable of detecting several other elements using various light filters. The microprocessor converts the signal that can be related to sample concentration. Both handheld and benchtop instruments are available.

The desirable features of the flame photometer are sensitivity, stability, and relatively large linear dynamic range. FPDs also require very little maintenance, and are ready to use in a very short time. An FPD's response to phosphorous is a first-order relationship, while its response to sulfur components is second order because sulfur is detected as  $S_2$ . Analysis by an FPD without a GC column is considered real-time detection. Unfortunately, without GC involvement, the detector cannot provide possible compound identification due to its generic nature. The addition of GC capability permits identification of sample components that contain targeted elements, and reduces the false alarm rate.

## 7.7 FACT SHEETS ON SELECTED PHOTOMETRY-BASED DETECTORS

### Detector Name

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AP2C Vapor Detector

### Manufacturer/Distributor and Contact Information

Proengin Inc.  
405 N.E. 8th Street  
Fort Lauderdale, FL 33304  
Tel: 954-760-9990

### Technique Description

A handheld device using flame photometric spectroscopy, this detector is operable under field environments. It is designed for detection of selected TICs and nerve and blister agents at or below JSOR or IDLH levels through the use of chopping light filters to modulate light emission signals.

### Chemical Detection Capability and Performance

This device does not have inlet filter. Real-time detection response occurs in seconds. Start-up time is less than 2 min except in very cold temperature conditions. Use of a metalhydride hydrogen cartridge is required for operation.

### Other Features

LED bars are used for visual alarm indicators. Audio and remote alarms are also available, as is interface for network connection. Multicompound detection capability is based on elemental content of the substance (P or S). A surface probe (SP4) is available to sample surface contamination by vaporizing the collected substance through heating for detection by the AP2C unit, which permits detection of persistent compounds. Hydrogen flame breaks up toxic compounds into harmless elements.

### Domestic Preparedness Program Report

Domestic Preparedness Program: Testing of Detectors Against Chemical Warfare Agents — Summary Report UC P2C Portable Chemical Contamination Control Monitor Collective Unit, May 2001 (<http://hld.sbcom.army.mil/ip/reports.htm#detectors>)

### Detector Name

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Chemical Weapons Agent Detection & Confirmation System

### Manufacturer/Distributor and Contact Information

Agilent Technologies  
2850 Centerville Road  
Wilmington, DE 19808  
Tel: 800-227-9770

### Technique Description

A semiportable or stationary thermal desorption/gas chromatographic type of instrument, this device is operable in field environments in a mobile laboratory unit. It is designed for identification of a long list of TICs and nerve and blister agents down to or below AEL levels through the use of different modules equipped with various signal detectors.

### Chemical Detection Capability and Performance

The signal detectors that identify the various compounds are FPD and MSD. Because it is a sample-concentrating device using thermal desorption and GC separation/detection, process times are in minutes, according to the desired detection level, rather than in seconds. Therefore, it is not suitable for gross-level detection.

### Other Features

Interface for network connections. Additional compound detection can be programmed. Device can be networked. Multicompound detection capability according to the specific signal detector used. This device is a proven technology capable of monitoring to sub-AEL concentrations in the air.

### Detector Name

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MINICAMS Model FM-3001 (Miniature Continuous Air Monitoring System)



### **Manufacturer/Distributor and Contact Information**

CMS Field Products  
O.I. Analytical  
2148 Pelham Parkway, Bldg. 400  
Pelham, AL 35124  
Tel: 205-733-6900

### **Technique Description**

A semiportable or stationary thermal desorption/gas chromatographic type of instrument with flame photometric detector, this device is operable in field environments. It is designed for the detection of a long list of TICs and nerve and blister agents down to or below AEL levels through the use of different modules equipped with various signal detectors.

### **Chemical Detection Capability and Performance**

Requires multiple signal detectors to achieve detection of various compounds. Because it is a sample-concentrating device using thermal desorption and GC separation/detection, alarm times are in minutes, according to the desired detection level, rather than seconds. Therefore, it is not suitable for gross-level detection.

### **Other Features**

Audio and visual alarm indicators. Interface for network connections. Additional compound detection can be programmed. Multicompound detection capability according to specific signal detector used. The MINICAMS is a proven technology capable of monitoring to sub-AEL chemical-agent concentration in the air.

### **Detector Name**

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TIMs Detector for Toxic Industrial Materials Detector

### **Manufacturer/Distributor and Contact Information**

Proengin Inc.  
405 N.E. 8th Street  
Fort Lauderdale, FL 33304  
Tel: 954-760-9990

### **Technique Description**

Similar to the AP2C detector, this handheld device uses flame photometric spectroscopy detection. It is operable in field environments, designed for detection of TICs or TIMs at or below IDLH levels through the use of chopping light filters to modulate light emission signal detection. The unit is desensitized from the AP2C specially designed for TIC detection which does not require such high sensitivity.

### **Chemical Detection Capability and Performance**

Sensitivity is expected to meet/exceed current IDLH requirements. Device does not have an inlet filter. Real-time detection response occurs in seconds. Start-up time is less than 2 min except in very cold temperatures. Use of hydrogen cartridge required for operation.

### **Other Features**

Visual indicator of alarm through LED bars. Audio and remote alarms are also available. Interface for connecting to computer networks is available. Multicomponent detection capability according to elemental content of substance. A surface probe (SP4) is available to sample surface contamination by vaporizing the collected substance through heating for detection by the AP2C unit, which permits detection of persistent compounds. Hydrogen flame breaks up toxic compounds into harmless elements.