Are Colorimetric Tubes Becoming Obsolete for HazMat/CBRN Response?

With the release of XplorIR®, which can detect and identify approximately 5,600 gases with limited interferences, are the single measurement tubes still relevant in today's response kit?

Colorimetric tubes have been used for chemical detection since 1918 when the first tube was released for the detection of carbon monoxide. The current style of tubes was first utilized in Draeger in 1937 and Kitigawa in 1946. While there have been some advances in tube design and processing, the main advances have been in the number of chemicals detected. There are now more than 250 different tube types available for the detection of approximately 500 different gases. Tubes are available from a variety of manufacturers including Draeger, Gastec, Honeywell, Kitigawa, MSA, Sensidyne, and others.

What Are Colorimetric Tubes & How Do They Work?

Colorimetric tubes are sealed tubes made of a high-quality borosilicate glass with a uniform internal diameter. The detecting reagent inside the tube is specific to the chemical or class of chemicals to be detected. The detecting reagent is adsorbed by granules of silica or alumina to create the packing that is observed within the tube. This packing changes color in the presence of the target gas.

Manufacturers select reagents for use in colorimetric tubes that are stable, have a long shelf life, have a sharp color change in the presence of the target gas, and a quick reaction time.

The advantages of using colorimetric tubes are that they are small, lightweight, do not require calibration, are easy to use, and require no power. The drawbacks include high error rates, significant cross-sensitivities, and no capability to perform continuous monitoring.

Sources of Error in Colorimetric Tubes

Colorimetric tubes deliver chemical classification and semi-quantitative results for the user. They cannot uniquely identify a threat due to the significant cross-sensitivities in pure mixtures as well as the natural presence of chemical mixtures in the environment. The semiquantitative nature of the results is due to the published error rates ranging from 10–50%, with the higher rates being at the lower concentrations. Several significant sources of error that may be in the operator's control include sample volume, environmental conditions, storage conditions, and operator interpretation.

Sample Volume

Most colorimetric tubes today are calibrated against a specific number of pump strokes where the pumps are designed to deliver approximately 100 mL of gas per stroke. These flow characteristics can vary between manufacturers therefore it is critical to use the manufacturer specified pump and tube combination.

Unfortunately, inconsistent sample pumping, degradation of pump systems, and environmental conditions all play a significant role in the total volume of gas delivered. Manufacturers have minimized the effect of variable flow rates by using various support materials and end plugs to force a consistent contact time with the reagents.

Environmental Conditions (Temperature and Humidity)

A change in the temperature of the tube and sample results in changes to sample volume, quantity of gas adsorbed, and changes in the rate of the reaction between the gas sampled and the reagent in the tube. While many tubes incorporate a dehumidifying reagent to minimize the influence of water vapor, changes in temperature can cause water droplets to condense inside the tube resulting in inaccurate vapor representation and color changes.

Storage Conditions and Shelf Life

It is important to follow the manufacturer's instructions for storing the tubes. While many tubes can be stored at room temperature, several require refrigeration to meet the stated shelf life. In most cases, the shelf life for colorimetric tubes is two years due to the natural degradation of the reagents within the tube.

Operator Interpretation

As with any color change chemistry, it is up to the operator to identify the time profile, the intensity, and the end point of the color changes. Each of these factors play a significant role in determining the perceived concentration of a threat material. Unfortunately, each of these factors can also be affected by the environmental conditions.

Chemical Cross-Sensitivities

While the chemistries used in colorimetric tubes are designed to react uniquely with a specific gas or vapor, there are many issues that arise when chemicals react similarly. For example, tubes designed to detect acetic acid with a yellow color change are generally affected by all organic acids resulting in readings that would more accurately be described as total organic acids, versus acetic acid. In addition, the same tube has been shown to turn red in the presence of mineral acids. The color change for the mineral acids is darker and can mask any changes due to the presence of organic acids.

There are many other ways that ways that chemical mixtures can affect colorimetric tube readings. They may not discolor the reagent but cause a higher or lower than expected reading. There are also some co-existing chemicals that have demonstrated the ability to reverse the color changes. An example of this is ammonia in the presence of hydrogen cyanide. While hydrogen cyanide will change the yellow substrate to a pink/red color, the presence of ammonia as a co-existing chemical can change it back to yellow, in essence, masking the presence of hydrogen cyanide.

How Many Tubes Does a Team Need?

An informal survey was conducted with several busy hazmat teams across the USA resulting in a list of the 22 most common tubes that they keep on hand (see table). Of the gases of interest, only two cannot be detected by the XplorIR as they are diatomic molecules (e.g., chlorine and fluorine).

Arsine and phosgene have limits of identification on the XplorIR that are slightly higher than IDLH (10 ppm and 3 ppm); however, the detection time using tubes was 6 min and 12 min, respectively. Therefore, a balance must be managed between time in the environment to get an answer versus faster response time with unique identification at slightly higher levels. The response time for the tubes of interest ranged from 30 seconds to 12 minutes with an average of 5 minutes. During the recon mission, time is critical.

Finally, the average cost for a box of 10 tubes is approximately $110. As each tube provides one discrete measurement, multiple tubes are required for each response. In addition, several additional tubes would be required to rule out cross-sensitivities, greatly increasing the cost per sample.

22 Most Common Colorimetric Tubes

Tubes	PEL	IDLH	XPlorIR Limit of Identification	Colorimetric Tubes LOD	Colorimetric Detection Times	Colorimetric Cross-Sensitivities
Acetic acid	10 ppm	50 ppm	20 ppm	5 – 80 ppm	30 sec	Organic acids also turn yellow. Mineral acids indicated by red discolorations.
Alcohol (methanol)	200 ppm	6000 ppm	54 ppm	20 – 5000 ppm	6 min	Alcohols, ethers, and xylene
Ammonia	50 ppm	300 ppm	21 ppm	5 – 600 ppm	60 sec	Organic amines
Arsine	0.05 ppm	3 ppm	10 ppm	0.05 – 3 ppm	6 min	Phosphine and antimony hydride.
Carbon dioxide	5000 ppm	40000 ppm	N/A*	0.5 – 10% vol	30 sec	Sulfur dioxide
Carbon monoxide	50 ppm	1200 ppm	50 ppm	10 – 3000 ppm	4 min	Benzene and chloroform
Chlorine	0.5 ppm	10 ppm	Diatomic molecule	0.2 – 30 ppm	3 min	Bromine, chlorine dioxide, and nitrogen dioxide
Chloroform	10 ppm	500 ppm	10 ppm	2 – 10 ppm	9 min	Chlorinated hydrocarbons
Cyanide (HCN)	10 ppm	50 ppm	10 ppm	1.8 – 13.5 ppm	2.5 min	Acid gases. Cannot measure HCN in presence of phosphine. Carbon dioxide can react with cyanide in air through hydrolysis.
Ethylene oxide	1 ppm	800 ppm	25 ppm	1 – 15 ppm	8 min	Styrene, vinyl acetate, and acetaldehyde
Fluorine	0.1 ppm	25 ppm	Diatomic molecule	0.1 – 2 ppm	5 min	Nitrogen dioxide, chlorine, and chlorine dioxide
Formaldehyde	0.75 ppm	20 ppm	10 ppm	0.2 – 5 ppm	3 min	Styrene, vinyl acetate, acetaldehyde, acrolein, diesel fuel, and furfuryl alcohol.
Formic acid	5 ppm	30 ppm	18 ppm	1 – 15 ppm	3 min	Organic acids also turn yellow. Mineral acids indicated by red discolorations.
Hydrochloric acid	2 ppm	50 ppm	50 ppm	0.2 – 20 ppm	2 min	Acid gases and chlorine (changes to grey)
Hydrocyanic acid	10 ppm	50 ppm	10 ppm	0.5 – 100 ppm	2.5 min	Cannot measure HCN in presence of phosphine. Hydrogen sulfide discolors pre-layer to dark brown. Ammonia can cause indicating layer to return to yellow.
Hydrogen fluoride	0.5 ppm	30 ppm	25 ppm	0.5 – 90 ppm	2 min	Mineral acids. Presence of alkaline gases (e.g., ammonia) interfere with quantitation.
Methyl bromide	1 ppm	250 ppm	196 ppm	0.1 – 50 ppm	8 min	Ethylene dibromide, vinyl chloride, and dichloroethylene. Methyl bromide cannot be measured in the presence of perchloroethylene or trichloroethylene.
Nitric acid	2 ppm	25 ppm	10 ppm	1 – 50 ppm	4 min	Nitrogen oxide and other mineral acids. Chlorine discolors the indicating layer grey.
Phosgene	0.1 ppm	2 ppm	3 ppm	0.02 – 1 ppm 0.02 – 0.6 ppm	12 min	Chlorine and hydrochloric acid. At higher concentrations, chlorine, hydrochloric acid, and phosgene (over 30 ppm) will bleach the indicating layer.
Phosphine	0.3 ppm	50 ppm	16 ppm	0.1 – 3 ppm	8 min	Arsine, sulfur dioxide, hydrochloric acid, and hydrocyanic acid can increase reading while ammonia can decrease reading.
Sulfur dioxide	5 ppm	100 ppm	13 ppm	0.1 – 3 ppm 0.5 – 5 ppm 1 – 25 ppm	20 min 6 min 3 min	Acid gases Hydrogen sulfide and nitrogen dioxide Hydrogen sulfide and nitrogen dioxide
Sulfuryl fluoride	5 ppm	200 ppm	3 ppm	1 – 5 ppm	3 min	Fluorinated hydrocarbons. Ammonia and other basic gases can shorten or prevent color change. Require oxygen to perform properly. Tubes get HOT; avoid areas subject to explosion hazards.

🟧 *< PEL* ▨ *PEL < LOI < IDLH* 🟨 *> IDLH* 🟪 *No Detect*

**CO_2 is commonly found in the atmosphere at 400ppm or higher. CO_2 is continuously measured and quantified on the XplorIR so users can observe changes in CO_2 on scene*

XplorIR and the Future of Gas Detection

With the release of the next generation gas phase FTIR, the need for individual colorimetric tubes has drastically been reduced to just the diatomic gases. The XplorIR fills this need by continuously monitoring and identifying over 5,600 different gas phase chemicals in seconds. It is lightweight and handheld, allowing for positive gas identification with no sample preparation or pre-concentration. The XplorIR provides unique identification at toxicologically relevant levels (workplace exposure limits and immediately dangerous to life and health levels). The XplorIR is the only system commercially available which can provide continuous monitoring at operationally relevant concentrations while also uniquely identifying the threat.

In addition to the benefits of unique identification and continuous monitoring at operationally relevant levels, the XplorIR treats all gas samples as mixtures, as pure chemicals are rarely encountered in the field. This is incredibly important as this is exactly how we have alleviated the traditional issues with gas phase infrared – namely the presence of carbon dioxide and water vapor. By treating all samples as mixtures, these ever-present materials are automatically accounted for using a dynamic background adjustment without any user intervention. Using advanced statistical methods, the system can identify up to 6 components in a mixture. With a large library and very few cross sensitivities, the XplorIR is able to detect and identify gases at levels which are operationally relevant for toxicological objectives