Taming The Beast With Good Gas Detection

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Checking a solenoid valve in a formalin line.

Formaldehyde: It's Everywhere

Formaldehyde (HCHO) is a ubiquitous compound, and has been classified as a probable human carcinogen by the US Environmental Protection Agency and the International Agency for Research on Cancer. It is also a suspected human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH).

This volatile organic compound or "VOC" is utilized in resin adhesives for pressed wood products such as particleboard, hardwood plywood, medium density fiberboard, and insulation materials. It is also used as a preservative in paints, coatings, cosmetics, and pathology applications; as the magic behind permanent press fabrics and draperies; and to impart wet-strength or other specialized properties to paper products.

Owing to its high reactivity, colorless nature, and low cost, formaldehyde is widely employed in the chemical industry as an intermediate. The most important occupational exposure occurs in any of the industries that use resin adhesives. While a smaller group, workers in health-related professions can have significant exposures, as well.

Given its status as a carcinogen, regulatory and advisory agency exposure limits for formaldehyde are quite low:

- ACGIH does not recognize an 8-hour time-weighted average (TWA) value, but publishes a "ceiling" value (that should never be exceeded) of 0.3 parts-per-million (ppm).
- The National Institute of Occupational Safety and Health (NIOSH) has set an exceedingly low TWA of 0.016 ppm and a 15-minute ceiling of 0.1 ppm.
- The Occupational Safety and Health Administration (OSHA), operating under the force of law, has established a TWA of 0.75 ppm and a ceiling of 2 ppm.

Of course, not all exposure to formaldehyde occurs in the workplace. In fact, the greatest source of atmospheric formaldehyde is from auto emissions, whether discharged directly or via the photo-oxidation of the emitted hydrocarbons. Household indoor air can be contaminated with formaldehyde by any of the resin-containing construction materials mentioned above, furniture, carpet padding, and cigarette smoke.

While reasonable minds can differ as to the validity of the modeling methods used to elevate formaldehyde to its current reputation as a carcinogen, and questions can be raised as to the wisdom of such very low exposure limits, one fact must be kept in the forefront: Formaldehyde does have proven debilitating and toxic properties, and perhaps no other dangerous chemical is as prevalent both at work and at home. It is clear, then, that exposure has to be limited, and to effect this limitation, it has to be measured.

Legacy Instrumentation Methods For The Detection Of Formaldehyde

Although environmental health agencies certainly existed before the 1970's, and various workplace studies were undertaken by academics prior to this period, this decade of disco and leisure suits also saw the proliferation of occupational monitoring for literally hundreds of substances. Serious regulatory agency activity helped drive the analytical endeavors.

Much of the early work on formaldehyde was done with detector tubes or wet chemical methods. Detector tubes, while convenient, are not accurate (± 25%). Wet chemical methods, on the other hand, can be quite accurate, but are neither convenient nor practical for regular field use. Remember that the needs of a researcher or consultant are not at all equivalent to the requirements of a busy industrial hygienist, facilities manager, or safety director.

Once baseline data was established, using wet chemistry, it was still necessary to deploy a direct-reading instrumentation method. Ideally, such an instrument would have good sensitivity, specificity, and accuracy; monitor in real time; be equipped with user-settable alarms; and provide both a meter display and analog output—to-record concentration levels. The icing on the cake would be a reasonable price tag and minimal maintenance.

Based on this new demand, instruments did appear on the market, although they were not necessarily ideal. One of the first entries was an ingenious analyzer that semi-automated the chromotropic acid wet method. Accuracy, sensitivity, and specificity were superb, but the results were not in real time. Moreover, the unit was expensive and a bit cumbersome. Yet, much good initial work was done with this instrument.

Since formaldehyde absorbs in the infrared range, the popular and versatile "miniature" infrared portable analyzers were pressed into service, but lacked sufficient sensitivity for most occupational health applications. A widely

used breath alcohol detector was proffered as an inexpensive formaldehyde instrument. The unit did provide some indication of the gas, in that formaldehyde is often supplied as formalin, an aqueous solution that typically contains 37% formaldehyde and 6-13% methanol. There were sensitivity and interferences issues with the detector, however.

A technician checks a pressurized formaldehyde line for potential leaks. Maintenance and safety personnel are trained to check joints, gauges and valves as these tend to be strong potential leak points.

Since formaldehyde, after all, is a VOC, photoionization and flame ionization detectors, commonly used for other VOCs, were tried in this application. With the help of a chromatographic column, interferences could be removed, but sensitivity, lack of real time results, and price all presented problems.

A New Electrochemical Sensor For Formaldehyde

From the very founding of Interscan, there was an interest in producing a formaldehyde sensor. However, conventional electrode and electrolyte formulations, typical to sensors for gases such as CO and H2S, proved disappointing when applied to formaldehyde. Two things had to happen that would jump-start sensor development: One was the increased interest in monitoring for this gas; the other was the tightening of applicable standards.

Both of these were to occur in the early 1980's, and energized Interscan to look into some quite unconventional sensor modalities. It should be noted that this process was helped by the introduction of more convenient calibration methodology, utilizing permeation devices based on paraformaldehyde.

The biggest application for the new instrument was occupational health survey work around manufactured wood products plants, in which urea-formaldehyde or phenol-formaldehyde resins were employed. Encouraged by the good results, and the favorable attention being paid to Interscan by the industry, the company broadened the product line to include fixed systems, as well as the portable analyzers.

Inquiries soon appeared based on nearly every industrial, health care, and even agricultural use of formaldehyde. Thankfully, many of these inquiries turned into orders, and Interscan built up a wide application portfolio for this gas. Still, the greatest market penetration involved those facilities that used the formaldehyde resins, with our old friends in the engineered board business.

As customers were using the portable units in these board plants, many of them expanded the focus of the testing. It was not much of a leap from testing the ambient air, to sniffing the air around the inventory of stacked-up board itself, which was the largest point source of the formaldehyde emissions.

The most fundamental precept in all gas detection system design is to maximize protection of people. As it would turn out, there was an important application beyond protecting the workers at the affected plants. This would be the protection of the converters, contractors, and end users of the engineered board products.

Regulations had long been in place covering the allowable formaldehyde emissions from manufactured board before the product can be shipped to the customer. It did not take very long for a group of scientists and engineers at Georgia-Pacific to realize that if the air around board could be tested, it should be possible, somehow, to utilize the Interscan sensing technology to test the board directly.

The Dynamic Microchamber

At that time, the method for testing board for formaldehyde emissions involved putting a 4 x 8 foot sheet of it into an environmentally-controlled room of designated size, and periodically monitoring the air, via wet chemical analysis, for a period of two weeks. Thus, to be rigorous, a representative sample from every production run, or at least from benchmark production runs, had to be tested. A more unwieldy arrangement could hardly be imagined, yet this testing protocol was followed at every facility that manufactured the board.

A chamber could be envisioned that would simulate the room, and pieces of board, scaled down in size could be placed into this chamber. By the same token, a mathematical model could be developed that normalized all the parameters of size, air changes, and formaldehyde concentration. Given this model, appropriate sensors could be installed in the chamber, and via computerized data acquisition, the ponderous two week process could conceivably be shortened, and the logistics made much easier. All that was needed was a formaldehyde sensor but it had to be one quick, sensitive, and accurate enough to befit this miniaturized process. As a result, a collaborative effort between Georgia-Pacific and Interscan was undertaken on GP's Dynamic Microchamber that eventually became the subject of US Patent No. 5395494, and is now standard equipment at board plants and many forest products research facilities as well. The two week testing time was reduced to just a few hours with enviable ease and consistency of results. While our sensor may be the heart of this device, it is important to acknowledge the excellent work done by Georgia-Pacific in the areas of mathematical modeling, simplification of calibration, proof of concept, and certification.

It is rare indeed for a process sensing application to grow out of an environmental measuring technology. As such, Interscan regards its work on this project to be a significant and successful associative effort with Georgia-Pacific.

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