

How Accurate are Phosphine Monitoring Devices?

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Abstract

A critical component of worker safety for fumigators monitoring phosphine gas levels is an accurate monitoring device. Researchers evaluated accuracy levels of four electronic devices and a tube-type device while monitoring Oklahoma grain elevators under fumigation; particular attention was paid to accuracy levels in the dangerous range. Average accuracy of the electronic devices ranged from 60% to 100%. Although the tube-type device was technically the most accurate, in practice it may be less accurate due to operator error in reading the tubes. It is important for safety educators to fully understand the benefits and limitations of phosphine monitoring devices.

Keywords: phosphine fumigation monitors, grain storage

Introduction

The U.S. Environmental Protection Agency (EPA) mandated a review of phosphide fumigants in response to reports of human poisonings by phosphine gas inhalation (Initiation of aluminum and magnesium phosphide stakeholder process, 1998; Amendment to Reregistration Eligibility Decision for aluminum and magnesium phosphide, 2001). The review prompted new restrictions on the use of phosphine. The revised phosphine labels have incorporated several of the Risk Mitigation Measures (RMMs) proposed by EPA during the review, particularly those focused on safety of both fumigators and bystanders (Degesch America, 2004).

To help fumigators prevent injuries from phosphine use, EPA requires that workers monitor gas levels in order to determine that a safe threshold level has been reached before they enter a

structure under fumigation. If monitors indicate that gas levels are above the threshold limit value (TLV) for human safety (0.3 ppm) then workers are required to use specified personal protective equipment or wait to enter the facility until gas levels have subsided below the TLV.

Two types of phosphine gas monitoring devices are currently available, the electronic type and the tube type. Electronic monitors utilize an electrochemical sensor in which a change in current across the sensor, directly proportional to phosphine concentration, is recorded as the sensor interacts with the target gas. Tube-type devices are graduated clear glass tubes, approximately 10 x 0.5 cm, which are filled with a specialized white reactive powder that changes color along the length of the tube in direct proportion to the concentration of phosphine gas that is drawn through the tube.

In choosing a monitoring device, cost as well as functional features (e.g. ease of use, ruggedness, and accuracy) are important factors to consider. Initial purchase price of the four electronic devices tested in this study ranged from \$779 to \$1,810 while the tube-type device cost \$215. Electronic devices can be used multiple times. The tube-type device requires a single-use tube at each reading so cost increases with the number of readings. A cost analysis was performed in which initial equipment costs were amortized over a five-year use period, and annual equipment costs for each device were added to annual costs of single-use tubes for the tube-type device and annual recalibration costs for the electronic devices. Yearly cost of the tube-type device is less than that for the electronic devices if fewer than 50 readings are taken, but higher if more than 50 readings are taken. Additional details are provided in Danley (2002) and Danley et al. (2004).

Determining accuracy levels of both electronic and tube-type phosphine monitoring devices was the focus of this study; most important was the determination of whether the devices reliably detect dangerous concentrations of phosphine gas. The intent of this study is not to endorse one monitor over another but to highlight the importance of teaching fumigators about the limitations of monitors and of reinforcing proper training and use of phosphine testing equipment.

Four electronic devices and one tube-type device were selected by University researchers for a 31-day monitoring study of phosphine gas levels in Oklahoma grain elevators under fumigation. While under these typical

field conditions, the accuracy of the devices was measured in a University laboratory 16 times (approximately every other day) to determine the extent to which accuracy of each device drifted over time.

Procedures

Manufacturers of electronic monitors instruct users to periodically return the devices for calibration. In replicating normal use patterns, the electronic devices used in this study were factory-calibrated prior to study initiation.

Laboratory Readings for Electronic Monitors

During the 31-day study the devices were used in actual field conditions. Approximately every other day, or 16 times during the study, the devices were calibrated in the laboratory to determine their accuracy. Calibration was performed using an authentic quantitative standard of hydrogen phosphide gas in nitrogen and the following procedures. Three (Monitors #1, #2, and #4) of the four electronic monitors were placed in 3,778.2 ml glass jars and sealed. The devices were then placed under a laboratory hood. Ten ml of air were removed with a syringe and 10 ml of phosphine gas at 189 ppm in nitrogen were then syringed back into the jar to achieve a phosphine gas concentration of approximately 0.5 ppm. The true concentration was verified with a gas chromatograph using methods reported by Phillips et al. (1999). The study focused on accurately detecting low concentrations near the TLV for safety purposes, rather than the higher concentrations used in monitoring for fumigation effectiveness. Since monitor #3 was larger than the

glass jar, its wand, rather than the whole device, was inserted into the jar septum after the phosphine gas was syringed in.

In each case, after sample addition, gas readings were taken every fifteen seconds until monitor readings of the gas level stabilized. A reading was considered stabilized after showing the same concentration for one minute without change. Accuracy was computed by first subtracting the stabilized reading from the standard (0.5 ppm), then dividing the result by 0.5 ppm, and then multiplying by 100 to give the percent error. For example, if the monitor reading was 0.4 ppm, the error factor would be 20%, resulting in an overall accuracy level of 80%. If the monitor reading was lower than 0.3 ppm (the TLV), the accuracy would be less than 60%. Accuracy rates in this range give false 'safe' readings and thus can endanger the applicator.

The length of time needed before readings stabilize, or time to stabilization, for an individual monitor was also recorded. This important measurement tells workers how long they must remain exposed to potentially high phosphine levels before they obtain a proper reading on the device. Since monitoring must be completed before workers know whether the workplace is safe to enter, workers should wear at least a self-contained respirator while monitoring inside a structure, or, monitor the atmosphere from outside the structure until determining that gas levels are at or lower than the TLV. It is important to recognize that these measurements were taken under laboratory conditions where gas level was constant; gas levels fluctuate in a field situation.

Reading Accuracy of Tube-Type Monitoring Device

The tube-type monitoring device was tested for accuracy using two techniques. The first test was of the reactive powder, in which air from a sample jar containing 0.5 ppm phosphine was drawn into the tube, similar to tests performed on the electronic monitors. The second technique tested the user's ability to accurately read this device. Although the electronic-type devices provide a digital display of the gas reading, users must read tube-type monitors by determining to what graduation on the tube the color change had progressed, much like one would read a mercury thermometer. Thus, data collectors might not read the numbers consistently.

In this study 28 Oklahoma grain elevator operators, who participated in a University-sponsored phosphine fumigation-training workshop, were instructed in the use of the devices. Each operator was then given the same set of five tubes that had been exposed to different lab-determined levels of phosphine gas (4 ml, 8 ml, and 30 ml of gas, for concentrations of 0.2, 0.4, and 1.5 ppm respectively). To maximize color contrast so that the gradations could be more easily read, the five tubes were attached to pieces of white paper. The elevator operators were asked to record their readings of the gas levels indicated in each tube. The true gas concentrations and the elevator operator readings were compared with one another to obtain measurements of operator reading accuracy.

Results

Accuracy of Electronic Monitors

Accuracy of several of the electronic monitors declined slightly during the 31-day study. By the 31st day of field testing, accuracy of the electronic monitors ranged from 71.25% to 97.63%, depending on the brand and model. Time to stabilization ranged from 0.91 minutes to 2.86 minutes, again depending on the model.

Accuracy results for Monitors #1, #2, and #4 are shown in Figure 1. Monitor #1's sensor reads from 0.0-1.0 ppm in hundredths. Its accuracy ranged from 80% to 90%. The accuracy was relatively stable throughout the study, but did not rise above 90% at any time. The 80% accuracy level resulted from 0.5 ppm phosphine levels that the device read as 0.4 ppm.

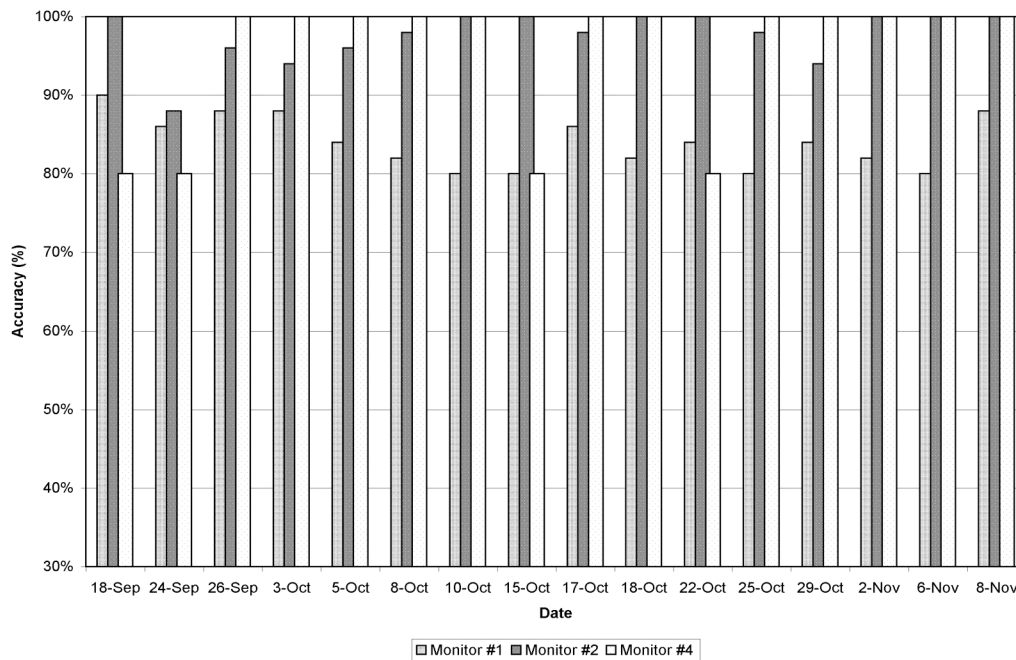


Figure 1. Accuracy of Monitors #1, #2 and #4 during 31-day study.

Monitor #2's sensor reads from 0.00-20.00 ppm in hundredths. Its accuracy ranged from 88% to 100%, and remained both high and relatively stable throughout the study. The 88% accuracy level resulted from 0.5 ppm phosphine levels that the device read as 0.44 ppm.

Monitor #4's sensor reads from 0.0-20.0 ppm in tenths. Accuracy ranged from 80% to 100%, and was relatively stable over the course of the study. The 80% accuracy level resulted from 0.5 ppm

phosphine levels that the device read as either 0.4 ppm or 0.6 ppm. Because the monitor only reads in tenths, no accuracy levels could be measured between 80% and 100%.

Monitor #3 (Figure 2) uses either of two sensors. The low-range sensor reads from 0.0-2,000 ppb, or 0.00-2.00 ppm, in hundredths. Accuracy ranged from 70% to 100%, decreasing over the course of the study. The 70% accuracy level resulted from 0.5 ppm phosphine levels that the device read as 0.35 ppm.

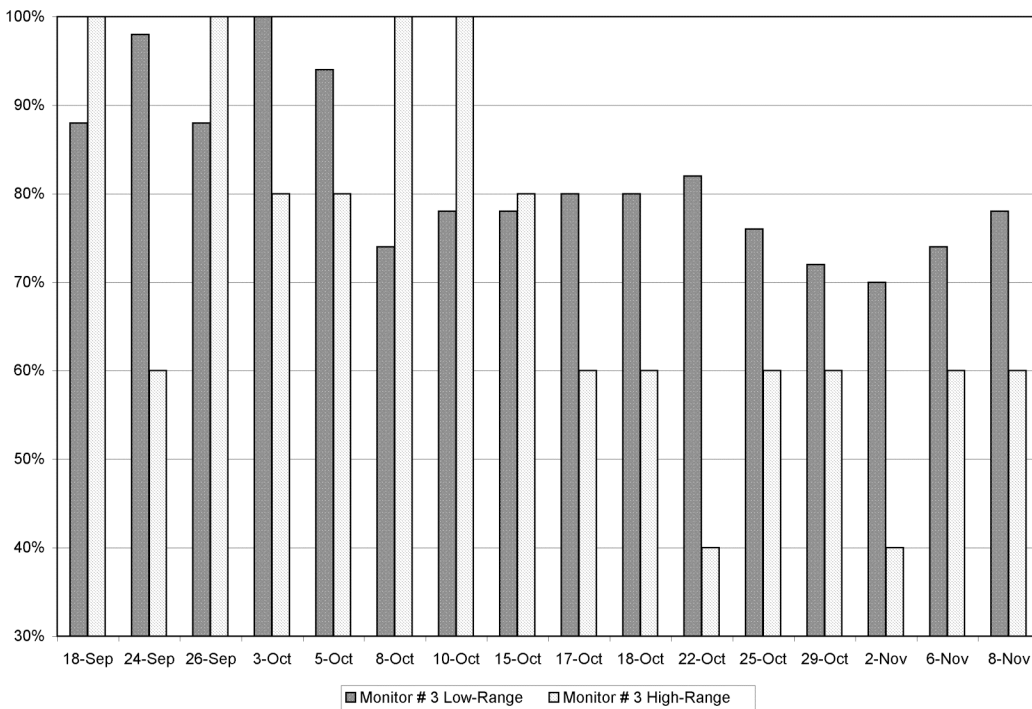


Figure 2. Accuracy of Monitor #3 (Low- and High-Range) during 31-day study.

Monitor #3's high-range sensor reads from 0.0-20.0 ppm in tenths. Accuracy ranged from 40% to 100%, decreasing over the course of the study. The 40% accuracy level resulted from 0.5 ppm phosphine levels that the device read as 0.2 ppm.

The percent accuracy on the last day of the study for all electronic monitors is

shown in Figure 3. Monitor #3 had the lowest accuracy at 78% and 60% for the low- and high-range sensors, respectively. Monitor #1, at 88%, had the next lowest accuracy level. Monitors #2 and #4 tied at 100% for the highest accuracy level.

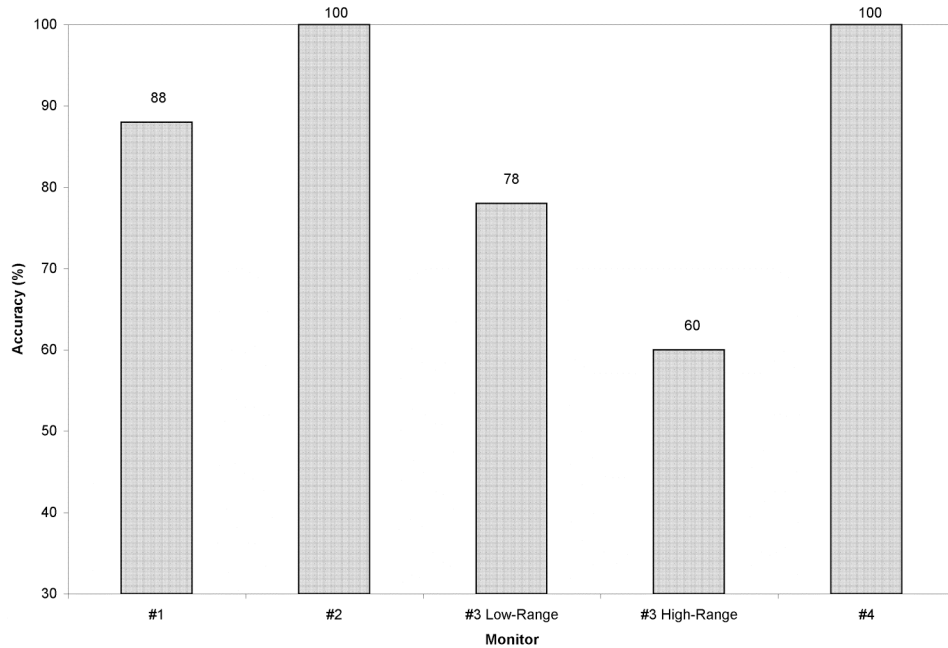


Figure 3. Accuracy of electronic monitors on day 31.

The average accuracy over the 31-day study and time required to achieve a stable reading is shown in Figure 4. Monitor #3 had the lowest average accuracy, at 82% for the low-range and

71% for the high-range sensor. Monitor #1 averaged 84% accuracy. Monitor #4 was second highest with a 95% average, and Monitor #2 was highest with 98% average accuracy.

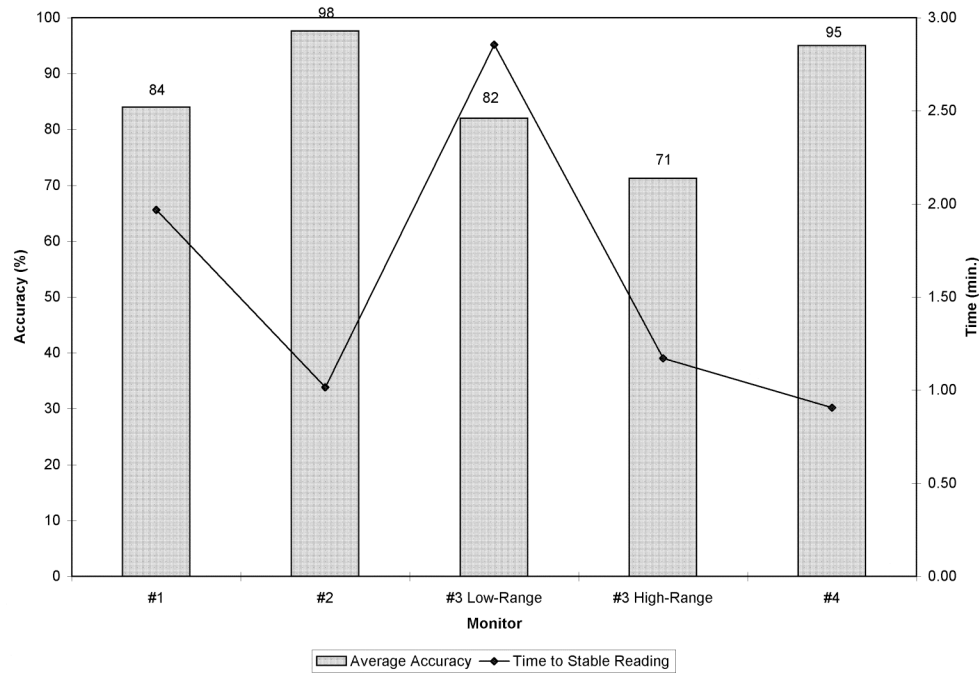


Figure 4. Average Accuracy of Electronic Monitors during 31-Day Study and Time Required to Reach Stable Reading.

The period of time required for readings to stabilize differed among devices. The longer a monitor takes to stabilize, the more opportunity there is for phosphine levels to reach dangerous concentrations before the monitor provides adequate warning. However, if the user is adequately protected, the biggest issue becomes one of cost (i.e., extra time spent waiting for stable readings). Monitor #3, using the low-range sensor took the longest time to stabilize at 2.86 minutes. Monitor #1 stabilized in 1.97 minutes. Monitor #3, using the high-range sensor, stabilized in 1.17 minutes. Next fastest was Monitor #2 at 1.02 minutes, and fastest, was Monitor #4, stabilizing in 0.91 minutes.

Thus, as Figure 4 shows, Monitors #2 and #4 achieved the highest average accuracy readings in the shortest amount of time. When comparing costs, these two are also the least expensive of the four electronic monitors, in terms of both initial purchase price and yearly cost (Danley et al., 2004).

Accuracy of Tube-Type Monitor

When read properly, the tube-type monitor provided gas concentration readings very close, essentially 100% accuracy, to the true concentration of the laboratory samples. However, elevator operators did not always read them properly. The true gas concentrations and the corresponding elevator operator readings of those concentrations are shown in Table 1.

Table 1. Actual Concentration vs. Readings by 28 Grain Elevator Operators Using Tube-Type Phosphine Monitor.

Sample	Actual Concentration (ppm)	Average Reading (ppm)	Average Accuracy (%)	Lowest Reading (ppm)	Accuracy (%)	Highest Reading (ppm)	Accuracy (%)
1	1.5	1.64	90.7	0.65	43.3	3.0	0.0*
2	0.2	0.18	90.0	0.01	5.0	0.2	100.0
3	0.4	0.36	90.0	0.02	5.0	0.4	100.0
4	0.2	0.23	85.0	0.01	5.0	0.4	100.0
5	0.4	0.38	95.0	0.02	5.0	0.6	50.0

* Reading is twice as high as actual concentration

While the average reading of each of the five samples was very near the actual phosphine concentration, and average accuracy ranged from 85.0% to 95.0%, the range of observations by the 28 operators was wide. For example, phosphine concentration in Sample 1 was 1.5 ppm. The average of the 28 readings (1.64 ppm) was near the true value, with an accuracy of 90.7%, however at least one grain elevator operator read the concentration as 3.0 ppm, twice as high as the actual

concentration. At least one operator read it as 0.65 ppm, for an accuracy of 43.3%. The same pattern was observed in the other four samples.

In several cases the accuracy of the lowest reading was only 5%. For example, the concentration of both Sample 3 and Sample 5 was 0.4 ppm, but at least one elevator operator for each sample read the concentration as 0.02 ppm. Thus, although the tube-type devices are technically more accurate than the electronic devices, in practice

they may be less accurate because of operator error in reading the tubes.

Accuracy problems are potentially dangerous, because even though the concentration of phosphine gas in Samples 3 and 5 was high enough to require safety equipment, at least one grain elevator operator for each sample would have incorrectly concluded that the storage facility was safe to enter. In contrast, all of the electronic monitors (with the exception of two days of observations using Monitor #3 with the high-range sensor) would have provided adequate warning that safety equipment was still required.

Conclusion

None of the electronic phosphine monitors tested was 100% accurate although some were more accurate than others. With one exception, on two of the 16 days, each was accurate enough, however, to alert users to potential danger. Monitors varied in how quickly they were able to supply stable readings. The tube-type device was more accurate in lab tests, but its potential for reading error allowed at least one operator in our tests to incorrectly read dangerous levels of phosphine as 'safe'.

Only one unit of each of the electronic devices was tested in the studies reported above. Readers should not consider our results to be a comprehensive, replicated study in quality control for these products, nor can our results be used for purchase recommendations. However, we purchased these individual electronic units and multiple tube-type monitors on the open market, as would any pesticide applicator, and we experienced some unacceptable results from some of the

monitors. Thus, phosphine applicators should acquire information and extensive hands-on experience with any monitoring system they might purchase, and be sure to exercise caution when using a monitor to make decisions impacting worker safety.

Our results may tempt some phosphine applicators to avoid purchasing any phosphine monitor due to uncertain accuracy and the relatively high initial purchase price of an electronic device compared to that of a tube-type monitor. However, phosphine applicators should not use the potential for reading errors with a tube-type device, or the high initial purchase price of an electronic monitor, as a basis for deciding against purchasing any phosphine monitoring device. A low-cost tube-type monitor would clearly be better than not using any monitor at all, and would satisfy the legal requirements for proper application of this dangerous fumigant. To ensure safest use though, users should seek training and exercise extra care to read tube-type phosphine monitors correctly.

It is important for safety educators to fully understand the benefits and limitations of each monitoring device. Cost should not be the only influence in purchasing considerations; thoroughly understanding the ease of use and limits of accuracy of the equipment should also weigh heavily in a purchase decision. It is imperative for safety educators to fully explain these tradeoffs to fumigators using phosphine. Also, it is critically important to educate those fumigators using tubes in the proper techniques for accurately reading these devices to best ensure the safety of workers and bystanders.

References

Anonymous. 2001. Amendment to Reregistration Eligibility Decision for aluminum and magnesium phosphide; Notice of availability, 66 Fed. Reg. 23 (February 2, 2001). [<http://www.epa.gov/fedrgstr/EPA-PEST/2001/February/Day-02/p2773.htm>].

Anonymous. 1998. Initiation of aluminum and magnesium phosphide stakeholder process; Notice of availability of the aluminum and magnesium phosphide Reregistration Eligibility Decision document; and proposed risk mitigation measures for comment, 63 Fed. Reg. 246 (December 23, 1998). [<http://www.epa.gov/fedrgstr/EPA-PEST/1998/December/Day-23/p34049.htm>].

Danley, R. 2002. An economic evaluation of phosphine fumigant monitoring devices in commercial grain elevators. Unpublished master's thesis, Oklahoma State University, Stillwater.

Danley, R., Adam, B. D., Criswell, J., Noyes, R., & Phillips, T. W. 2004. Choosing a monitoring device for phosphine fumigation in commercial grain elevators: An economic analysis using a multiple attribute decision making model (Working Paper #AEJ-256). Oklahoma State University, Department of Agricultural Economics.

Degesh America. 2004. Applicator's manual for Phostoxin r tablets and pellets. Weyer's Cave, VA: D&D Holdings, Inc.

Phillips, T. W., Bonjour, E. L., Payne, K., Noyes, R. T., Cuperus, G. W., Schmidt, C., et al. 1999. Effects of exposure time, temperature and life stage on mortality of stored grain insects treated with cylinderized phosphine. *In* Zuxun, J., Quan, L., Yongsheng, L. Xianchang, T., & Langhua, G. (Eds.), *Proceedings of the Seventh International Working Conference on Stored-Product Protection* (pp. 320-325). Beijing: Sichuan Publishing House of Science and Technology, Chengdu, Sichuan, People's Republic of China.