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Studies on the Models of Electronic Supervision in Methyl Bromide Fumigation of Wood Packing Materials

Jin Guangyao, Tang Zheng, Wu Xinhua, Ma Jianhua and Huang Jiaping

Abstract: Methyl bromide fumigation is widely used for plant quarantine treatment. However, the traditional supervised approach always has problems of poor accuracy and veracity in dealing with the quarantine inspection data, and practical work can not meet the technical requirements of MB fumigation of AQSIQ (Administration of Quality Supervision, Inspection and Quarantine). After more than two years of system development and field testing, the project of "*studies on the models of electronic supervision in methyl bromide fumigation of wood packing materials*" has achieved the following three results: 1. we adopt infrared spectra absorption of methyl bromide sensor (SM95 – S2) as a systematic methyl bromide Detector; 2. the MB sensor will be placed far away from the dosed pipeline and as close as possible to the top; 3. we find by the field testing that the specificity, stability, reliability and accuracy especially supervision of MB concentration of this system accords with the related requirements of No. 69 and proclamation No. 105 by the general bureau and the national standard named《JJG693 – 2004 flammable gas detection alarm》 In this standard, the accuracy of fumigation system has reached to 5% scope. It has accomplished the long-distance electronic supervision of MB fumigation by CIQ supervised platform. The system accomplished long-distance automatic supervision of MB concentration and temperature in the fumigant warehouse during wood packing fumigation, recording time and concentration. It has also accomplished the automatic generation and print of the reports, such as Bill of Documents, and warrants of fumigant results. The data can not be modified by hand in the system. Several practical applications prove that this method can not only reduce burdens on enterprises, but also save inspection and quarantine departments a lot of human resources, and reduce work intensity and contradictions. Thus it achieves the goals of "accelerating, reducing burdens, increasing efficiency, and tightening supervision".

Key words: wood packing materials, methyl bromide, quarantine treatment, electronic supervision

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1 Preface

Wood packing materials are extensively used in international trade. As they have many advantages such as economy, convenience, security and invulnerability, in many cases wood packing materials cannot be replaced by other ones. Because wood packing materials can easily contain forest noxious creatures and transmit them through international trade, strict quarantine measures are established in many countries. Methyl bromide is a kind of fumigation medicine, which has the characteristics of deep penetrability, stable chemical properties and strong toxicity. Methyl bromide fumigation is one of the important methods of wood packing quarantine treatment. In the traditional supervised way, supervisors sample and test over time. However, this way has problems of poor accuracy and veracity in dealing with the quarantine inspection data; it wastes time, is highly hazardous, and has many hidden safety troubles and interference factors so that it cannot truly reflect the change state of MB concentration in the fumigant warehouse. To standardize the supervision of wood packing quarantine, according to No. 69 and proclamation No. 105 by the general bureau, quarantine institutions decided to supervise the process of pest and disease control. After studying survey meters for MB and temperature, designs of data collecting and data transmitting, supervised platforms for corporations and bureau, and systematic integration and accuracy, we successfully accomplished a system of *electronic supervision in methyl bromide fumigation of wood packing materials*. In field investigations, this electronic supervision system has the advantages of specificity, stabilization, reliability and integrity (because figures cannot be easily modified), These achievements conformed to the related requirements of No. 69 and proclamation No. 105 by the general bureau and the national standard named JJG693 – 2004 *flammable gas detection alarm.*

Changshu Exit – Entry Inspection and Quarantine Bureau, Jiangsu, China

2 Materials and Methods

2.1 Experimental Materials

Standard fumigant warehouse: It contains 25 m^3, conforming to the requirements of SN/T1143 – 2002 (simple fumigant warehouse regulations of plant quarantine);

Wood packing: pine/miscellaneous wooden block (specification: 110cm × 110cm);

MB: concentration: 98.5%, produced by Shandong Changyi Chemical Plant (authorized MB producing factory by the bureau);

Aluminium phosphide: concentration: 56%, Lianyungang Haitang jintiandi Chemical Plant;

Sulfuric fluoride: concentration: 99%, Shandong Longkou Chemical Plant;

Fumigation gas concentration survey meter:

①solid catalyzed burning type MB transducer (produced by American IST Co., full range 150g/m^3 (35 000ppm), permissive value ±5%, ie. ±7.5g/m^3);

② infra – red spectral absorption type MB transducer SM95 – S2 (produced by American IST Co., full range 150g/m^3 (35000ppm), permissive value ±5%, ie. ±7.5g/m^3

③heat conduction XK – Ⅲ MB survey meter;

④TM3 type XK – Ⅲ MB survey meter, produced by U.K;

⑤MINIRAE2000 VOC gas survey meter, produced by American RAE SYSTEM INC.

Temperature survey meter: PT100 type temperature transducer;

Data collecting reading instrument: JS05D intelligent electronic monitoring station for kiln;

Electronic platform instrument: TCS – A electronic platform instrument for both alternating and direct current (produced by Shanghai Youshenghanhengqi Co. ltd., measured by Changshu Measurement Bureau);

Data transmitting equipment: RS485, RS232;

Computer: CPU1.8G, 256K memory, hard disk 60G/7200 turn;

INTERNET: Telecom Broadband (broadband 2m).

2.2 Testing Method

2.2.1 Design Principle of the System Experiment

The electronic supervision system in this study consists of six functional modules: MB transducer, temperature transducer, intelligent supervised platform, RS485 communication equipment, supervised platforms for corporations and bureau. The design principle Fig. ture is shown in Fig. 1:

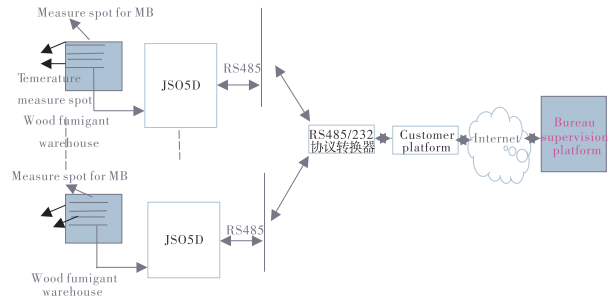

Fig. 1 principle of work

2.2.2 MB transducer filtration

Because the electronic supervision system in this study requires that all the data should be able to be collected and transmitted, the transducers must have data output ports. However, in this study, only 5 transducers have data output function: solid catalyzed burning type MB transducer, infra-red spectral absorption type MB transducer SM95 – S2 and MINI2000, etc. However, MINI2000 cannot be used since it has too short a measurement range (0ppm – 2000ppm), which is not suitable for high concentrations. The other two transducers are tested for their accuracy. The result shows that solid catalyzed burning type transducer cannot be used since it is easily poisoned, which can not reflect the concentration of MB in the fumigant warehouse (see Fig. 2); as infra-red spectral absorption type MB transducer (SM95 – S2) has the advantages of wide measure range, high sensitivity, good selectivity, long life and is not easily poisoned, it suits the study.

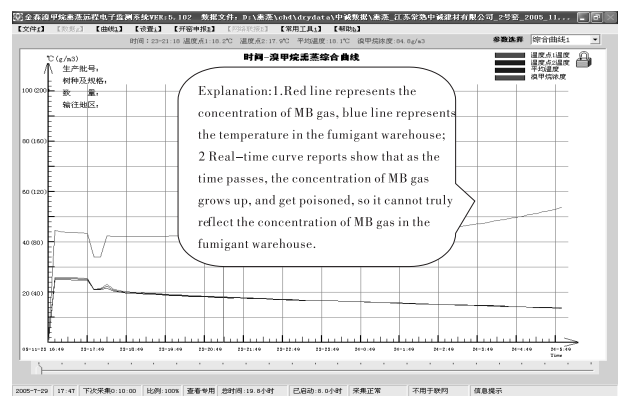

Fig. 2 poisoning symptom of solid catalyzed burning type transducer

2.2.3 Calibration Test of the Instruments

2.2.3.1 Measuring Instruments (except MB, temperature transducer)

Measuring instruments such as scales, mercury thermometer, and digital multimeter should be sent to the national legal measuring units for testing, and to obtain the corresponding certifications.

2.2.3.2 PT100 Temperature Transducer Calibration

Calibrate with the tested mercury thermometer the PT100 temperature transducer. From +14℃ to +29℃, there are 18 data spots. The permissive error of the data is ±0.5℃, the real calibration error is ±0.1 – 0.2℃, which conforms to the requirement. About the reports, see appendix 3.

2.2.3.3 On – the – site Calibration of Supervision System

On – the – site calibration on MB transducer requires:

a. Electrifying the MB transducer, warming up 12 hours before the fumigant, according to the service instruction, then warm up about 30 minutes before using.

b. Calculating the concentration of MB by the weighing method. Measure the volume of the warehouse V (m^3), weigh MB of weight M (kg), plunge MB after aerification through pipeline of medicine. Turn on circulating fan to distribute MB equally in the warehouse.

c. Calculate the concentration of MB with $C(g/m^3) = M(kg)/V(m^3)$; the permissive error should be in the range of operating error. (Generally, the range of the operating error should be about 5%).

d. Run supervising software and hardware system.

e. After MB was equally distributed, (about half an hour after application, the reading of MB transducer is stable), the supervising instrument shows the concentration of MB (C_1), and the computer software shows the data (C_2) ($C_1 = C_2$); calibrate the readings of MB with the instrument, to make C_1 equal C, which is calculated concentration of MB by the calculating method, i. e., $C_1 = C$.

f. After the installation of the system at the scene, the legal unit will measure the system with a MB standard. About the result, please see the report on the scene by Jiangsu Province Measure Testing Tech Institute.

2.2.4 Experiments and Steps

2.2.4.1 Testing Method of Accuracy of the indicative value of concentration of MB——Empty Warehouse Experiment

To validate the accuracy of the system testing, this experiment is conducted in an empty warehouse in advance of commercial fumigations. Put the MB transducer onto the top of the fumigant warehouse (the place of lowest MB concentration), compare the weighing (calculated) concentration to the indicative concentration in the system. On the condition of no wood packing, apply fumigant in the warehouse, then turn on the circulating fan in the warehouse, at the same time, switch on the electronic supervising system to measure and collect automatically the concentration of MB and temperature at certain times. After 24 hours, open the door of the warehouse to spread the poison. Analyze the data collected by the system (we will take the data collected at the point of 0.5 hour as the original data), validate the accuracy and reliability of the testing system; assess long – distance transmit, supervising long – distance, data analysis and automatic printing of the data and report.

2.2.4.2 Study on the specificity of the MB transducer

To study the specificity of the system, we fumigate with aluminium phosphide and sulfuryl fluoride at 11 – 25℃ in the empty warehouse for 24 hours, then obtain and record the readings of the MB sensor.

2.2.4.3 Testing Method of Accuracy of the Experiment——Full Warehouse Experiment

Put the MB transducer onto the top of the fumigant warehouse, place some wood packing into the warehouse and close the door of the warehouse. Apply a determined amount, turn on the circulating fan, switch on the automatic supervising system to test and collect the data on concentration of MB and temperature, then open the door of the warehouse to spread the poison after 24 hours. When the experiment is finished, compare the concentration of 2 hours, 4 hours, 12 hours and 24 hours required by the No. 105 with the actual concentration.

2.2.4.4 Test Experiment of Different Locations Where MB Transducer Is Put

As MB gas is heavier than the air, in the same closed container, lamination will happen, so in this experiment MB transducer will be put on the top, the middle and the bottom of the fumigant warehouse. Compare the calculated concentration with the indicative concentration in the system. Apply fumigant to the warehouse with the same quantity and volume of wood packing and turn on the circulating fan and electronic supervising system to measure and collect concentration of MB and temperature. Open

the door of the warehouse to spread the poison after 24 hours, and make a comparative analysis of the concentration of the theoretical data and collected data when the transducers are placed in the different locations.

3 Results and Analysis

Experiment of Accuracy of MB indicative value

In the warehouse of Xingfu and Huasen Co., the theoretical doses are 80g/m^3, 64g/m^3, 56g/m^3 and 48g/m^3 respectively. Test 3 times of the same group, to make sure the temperature in the warehouse conform to the requirement of the fumigation. The data is in the table 1.

Table 1. Table of Indicative Value Error

Experiment condition: Drug in the empty warehouse, and turn on the circulating fan.

No.	Experiment site	Theoretical value	CK(g/m^3)	Initial concentration	Test value (0.5h)	Data number	Average	Value error(%)
				0	76.6	2006-4-23-13-16ch4		
1	Xingfu	80g/m^3	0.1	0	76.0	2006-5-6-17-29ch4	75.6	-2.93
				0	74.2	2006-5-31-15-20ch4		
				-2	59.8	2006-11-30-15-28ch4		
2	Xingfu	64g/m^3	0.1	-2	59.3	2006-11-30-17-59ch4	61.0	-2
				-5.9	63.9	2006-12-1-16-9ch4		
				-5.8	55.3	2006-11-29-16-49ch4		
3	Huasen	56g/m^3	0.1	2	53.6	2006-12-1-17-18ch4	55.1	-0.6
				-4.5	56.4	2006-12-3-15-59ch4		
				10	46.5	2006-12-1-14-26ch4		
4	Huasen	48g/m^3	0.1	10	46.4	2006-12-1-15-32ch4	46.57	-0.93
				8	46.8	2006-12-1-16-23ch4		

Note: testing value = actual value - original value

According to the indicative error of the instrument ≤5FS% (FS is full range) of the regulation in JJG693 - 2004 *Combustible Gas Testing Annunciator*, the formula of the error should be:

$$\text{Indicative value error} = \frac{averageval\ ue - theoretice\ lvalue}{fullrange} \times 100\%$$

From the data in the table 1: indicative value of the four groups 80g/m^3, 64g/m^3, 56g/m^3, 48g/m^3 are 2.93%, 2%, 0.6% and 0.93%, the errors are all less than 5%. In the regulated range and conform to the related testing standard of the state.

3.2 Study on the Specificity of the MB Transducer

The experiment is made in Xingfu Wood Factory, we set 3 treatment experiments in the range of 11 - 25℃, i.e., blank test, aluminium phosphide and sulfuryl fluoride experiments. Each will be treated 3 times, blank contrastive experiments (24 hours), aluminium phosphide experiments (48 hours) and sulfuryl fluoride experiments (24 hours). Collect data of transducer after 2, 4, 12, 24 and 48 hours and make contrastive analysis (see table 2).

Table 2. Data Analysis of Study on the Specificity of MB Transducer

No.	Fumigant medicine type	quantity (g/m^3)	Time (h)	2h	4h	24h	48h
1			48	1.9	1.5	1.5	3.2
2	phosphine	7.5	48	-0.3	-0.4	1.5	1.5
3			48	0.9	0.8	1.2	1.4
4			24	-1.7	-2.0	-0.7	
5	sulfuryl fluoride	80	24	-0.6	-0.6	1.0	
6			24	0.5	0.6	0.7	
7			24	2.0	2.0	1.1	
8	contrast with no fumigant	0	24	1.5	1.9	2.7	
9			24	1.1	1.4	1.5	

According to the data in the blank experiment of aluminium phosphide and sulfuryl fluoride, MB transducer has no reaction to phosphine and sulfuryl fluoride. The transducer has good specificity and stability.

3.3 Validating Experiment of Accuracy of the System

According to requirements No. 60 and No. 105, integrated with the actual work, we classify the data of different concentration and compare them with the related MB fumigation technical requirements regulated by the bureau. The full warehouse MB data classification is in table 3; related technical requirements of MB fumigation treatment are in table 4.

Table 3. Data classification table of wood packing in the full warehouse

No.	Treatment site	Theoretical medicine concentration	System test value (g/m^3)						Data No.
			0.5h	2h	4h	12h	16h	24h	
1	Xingfu	$80g/m^3$	80.6	83.3	77.8	66.4	62.6	55.7	2006-7-22-18-7ch4
2	Xingfu	$80g/m^3$	86.9	77.7	70.3	55.5	51.8	45.1	2006-7-24-10-32 ch4
3	Xingfu	$80g/m^3$	82.3	80.3	75.6	65	60.1		2006-7-25-14-6 ch4
4	Xingfu	$80g/m^3$	87.8	82.2	72.8	60.1	56.8	49.9	2006-7-26-14-5 ch4
5	Huasen	$80g/m^3$	80.2	80.8	75.5	62	55.4	45.7	2006-8-30-18-53 ch4
6	Xingfu	$64g/m^3$	71.4	55.3	48.5	43.0	40.8		2006-9-4-16-26 ch4
7	Xingfu	$64g/m^3$	68.6	69.3	66.5	61.2	58.5	51.4	2006-9-9-15-2 ch4
8	Xingfu	$64g/m^3$	59.5	68.1	65.5	58.7	55.7	49.8	2006-9-10-17-14 ch4
9	Xingfu	$64g/m^3$	64	65.5	64	56.7	53.5	47.1	2006-9-11-18-22 ch4
10	Huasen	$64g/m^3$	64	66.2	62.9	56.0	54.1		2006-11-24-13-25ch4
11	Huasen	$48g/m^3$	45.1	46.3	45.4	39.1	33.5	30.5	2006-9-2-16-40 ch4
12	Xingfu	CKg/m^3	1.5	1.6	1.4	0.8	1.3	1.1	2006-12-12-10-36 ch4

Table 4. Related technical requirements of MB fumigation treatment

Reports	Temperature (℃)	Dosage (g/m^3)	Min concentration (g/m^3)					
			0.5h	2h	4h	12h	16h	24h
NO. 69	≥21	48	36	24	17		14	
	≥16	56	42	28	20		17	
	≥11	64	48	32	22		19	
No. 105 (from 2006.10.1)	≥21	48		36	31	28		24
	≥16	56		42	36	32		28
	≥11	64		48	42	36		32

The data compared with requirements of fumigation in No. 60 and No. 105 shows: in the concentration 80 g/m^3, 64g/m^3, 48g/m^3 and the time 0.5, 2, 4, 12, 16 and 24 hours, the results conforms to the requirement of the lowest concentration. "The automatic supervising system of MB fumigation of wood packing" has stable properties in the treatment process of MB fumigation in the full warehouse, and truly reflects and report the process of fumigation treatment. All the data in the fumigation process are true and efficient, conforming to the requirements of No. 60 and No. 105.

3.4 Test Experiment of Different Locations where MB Transducer Is Placed

In Xingfu Wood factory, MB transducer will be put on the top, the middle and the bottom of the fumigant warehouse. The theoretical concentration is 80g/m^3, and we collect the data in 0.5, 2, 3, 12 and 16 hours (see table 5). Then calculate the average of each group, and draw the graph (see Fig. 2).

Table 5. Selected Measuring Points Table of Transducers of MB Concentration

Experiment condition: circulating fan is turned on, fumigant is dropped into the empty warehouse;
Environment temperature ≥20℃, the same fumigant, the same weighing system; MB concentration measuring value(g/m^3) = testing indicative value(g/m^3) − original concentration(g/m^3)

Location of transducer	Standard value(g/m^3)	Test times	Corresponding curve	Concentration value of MB(g/m^3)				
				0.5h	2h	4h	12h	16h
top	80	1	2006 − 4 − 23 − 13 − 16ch4 (Xingfu)	76.6	73.7	71.8	66.3	
		2	2006 − 5 − 6 − 17 − 29ch4 (Xingfu)	76.1	73.9	71.5	63.8	59.2
		3	2006 − 5 − 31 − 15 − 20ch4 (Xingfu)	74.2	72.3	71.5	62.4	59.2
			Average	75.6	73.3	71.6	64.2	59.2
mid	80	1	2006 − 6 − 4 − 13 − 8ch4 (Xingfu)	76.6	76.6	73.3	64.6	61.0
		2	2006 − 6 − 2 − 15 − 59ch4 (Xingfu)	72.3	73.8	72	63.7	59.6
		3	2006 − 11 − 26 − 10 − 13ch4 (Xingfu)	84.3	84.5	78.3	63.8	58
			Average	77.7	78.3	74.5	64.0	59.5
bottom	80	1	2006 − 4 − 29 − 9 − 38. ch4 (Xingfu)	79.0	83.1	75.8		
		2	2006 − 5 − 27 − 15 − 13. ch4 (Xingfu)	81.7	80.7	72.3	68.3	65.7
		3	2006 − 5 − 28 − 16 − 0. ch4 (Xingfu)	82.5	84.9	81	70.5	55.4
			Average	81.1	82.9	76.4	69.4	60.6

The data in table 5 and curve in Fig. 3 show that concentration of MB in the fumigation warehouse on the top is relatively low, in the middle less, at the bottom highest. As the time passes, the difference gets less; after 16 hours, the top, middle and bottom concentrations are approaching the same value.

There are abundant studies on distributing MB in the fumigation warehouse at home. One summarises: about MB fumigation in the container, the gas in the container is not distributed equally. If the gas inside is not mixed transmit by an outside force, generally there will be 24 hours to reach balance. The dose quantity in empty or full container, top or bottom, single or multi locations to drug and the at the horizon level can be balanced more quickly but it is hard to get the gas to be distributed uprightly to reach balance[3]. The testing data shows when the transducer is put on the top, the concentration at the lowest point is reflected. Thus, the MB transducer should be placed far from the pipeline of drugging; the closer to the top place, the better. Secondly, we set the circulating fan in the warehouse, to make sure the fumigation gas in the warehouse is balanced; setting a transducer in the warehouse can reflect the concentration of MB in the warehouse.

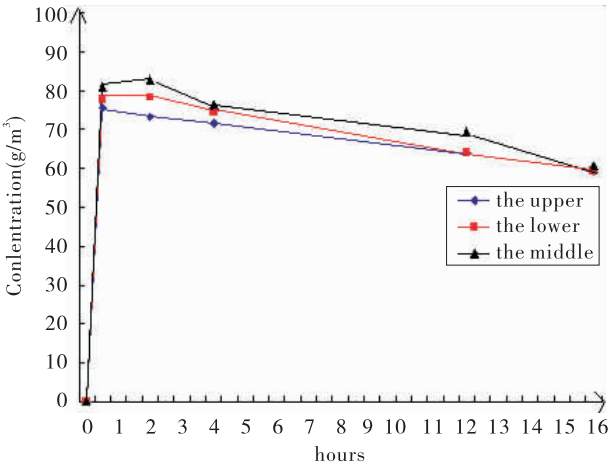

Fig. 3 **location of MB transducer**

4 Conclusion

"Studies on the models of electronic supervision in methyl bromide fumigation of wood packing materials" started in 2005. After studying and making experiments at the scene for over a year, the system accomplished long – distance automatic supervision of MB concentration and temperature in the fumigant warehouse during wood packing fumigation in given time and quantitative amount; and it has also accomplished the automatic generation and print of the reports and warrants of fumigant results. The data is very true and cannot be modified by hand in the system. Stability, reliability and accuracy especially supervision of MB concentration of this system accords with the related requirements of No. 69 and proclamation No. 105 by the general bureau and the national standard named JJG693 – 2004 *flammable gas detection alarm.*

Several practical application in commercial enterprises prove that this method can not only reduce burdens of enterprises, but also save a lot of human resources for the inspection and quarantine departments, and reduce work intensity and the contradictions, thus achieve the goals of " accelerating, reducing burdens, increasing efficiency, and tightening supervision". The study also accomplishes the long – distance electronic supervision in methyl bromide fumigation of wood packing materials for the inspection and quarantine departments, thus achieving the goals of " accelerating, reducing burdens, increasing efficiency, and tightening supervision", meanwhile, reducing burdens of enterprises.

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