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### OCCUPATIONAL HAZARDS IDENTIFICATION AND THE EXPOSURE ASSESSMENT IN A CHINESE VISCOSE RAYON PLANT

#### XIAODONG TAN

Dept. of Public Health, Hubei Medical University & Dept. of Public Health, University of Gent

#### YONGYI BI

Dept. of Public Health, Hubei Medical University

#### JUN HE

Hubei Chemical Group, Hubei, P.R. of China

#### YONGJUN SU

Dept. of Public Health, Hubei Medical University

#### FUYANG WANG

Dept. of Public Health, Hubei Medical University

**Abstract** - Carbon disulfide is a well-known occupational hazard in the viscose industry world wide, and studies have shown considerable health effects when the workers were exposed to high concentration carbon disulfide. Some contradictory facts still remain. The present study tries to identify the occupational hazards and assessment the exposure levels in a Chinese viscose rayon plant.

**Methods:** an industrial hygiene survey and industrial hygienic sampling campaign were carried out. The industrial hygienic campaign included the multi-gas monitoring, on-line measurement, stationary assessment at spinning hall and personal exposure sampling for spinners (by charcoal tube absorbing and GC-FPD analysis); All of the data was introduced into the foxpro database, and was analyzed by Epi info (6.0) and SPSS.

**Results:** Online measurement showed the carbon disulfide exposure amount to  $12.73 \text{ mg/m}^3$  in geometric mean in 'exposure' and amount  $0.08 \text{ mg/m}^3$  in 'non-exposure' worksites. These concentrations in the air were related to the subject's activities showing the highest levels when the subjects have to open the shield windows of the spinning machines. Stationary exposure measurements of carbon disulfide in the spinning hall amounted to  $23.29 \text{ mg/m}^3$  on geometric mean (range  $5.8\text{-}97.94 \text{ mg/m}^3$ ). Personal exposure of spinners was about  $17.3 \text{ mg/m}^3$ . Comparing these above methods, the personal exposure sampling could exactly express the exposure levels of the worker's contacting situation, and on-line measurement by multi-gas monitor could also recommend to the factory as it has own advantages of rapid, and independent assessment.

## ***Introduction:***

Carbon disulfide (CS<sub>2</sub>) is widely used to produce rayon, carbon tetrachloride, rubber chemicals and cellulose film, and also a by-product of widely used dithiocarbamate pesticides. Chronic low level and long term exposure to CS<sub>2</sub> could cause eye, ear, heart, nervous system and reproductive effects.<sup>1-7</sup> The largest use of CS<sub>2</sub> is made in the viscose industry which it is used to yield sodium cellulose xanthate from alkali cellulose. The concentrations of CS<sub>2</sub> in viscose plants varied a lot worldwide from the published literature.<sup>8-17</sup> In generally idea from published papers, the CS<sub>2</sub> concentrations in Western countries are higher than the CS<sub>2</sub> in Asian and Far East countries, but the CS<sub>2</sub> concentration in Taiwan is exception. Most of these studies except the Belgian and German studies, were based on the stationary sampling, which does not exactly express the occupational exposure levels of the workers that may had to the misclassification problems.<sup>12; 18</sup> Up to now, no English paper about the Chinese workers who occupational exposed to carbon disulfide based on the personal exposure sampling technique be founded, only one paper in 1992<sup>15</sup>, which presented the results of the stationary measurement method.

## ***Aims of the study***

Within the framework of a cross-sectional epidemiological study of carbon disulfide health effects in China, we investigated the carbon disulfide exposure levels at a big viscose group located in central China, with three sampling methods: on-line assessment, stationary assessment, and personal assessment. The objectives of the present study were required to answer the following questions:

1. What are mainly occupational hazards at this factory, and what are the exposure levels at the mainly production location and exposure levels of the mainly production process workers?
2. Which exposure assessment method is more exactly to express the exposure level for the workers?
3. Could the on-line assessment be recommended to the factory as the routine monitoring method?

## ***Material and Methods***

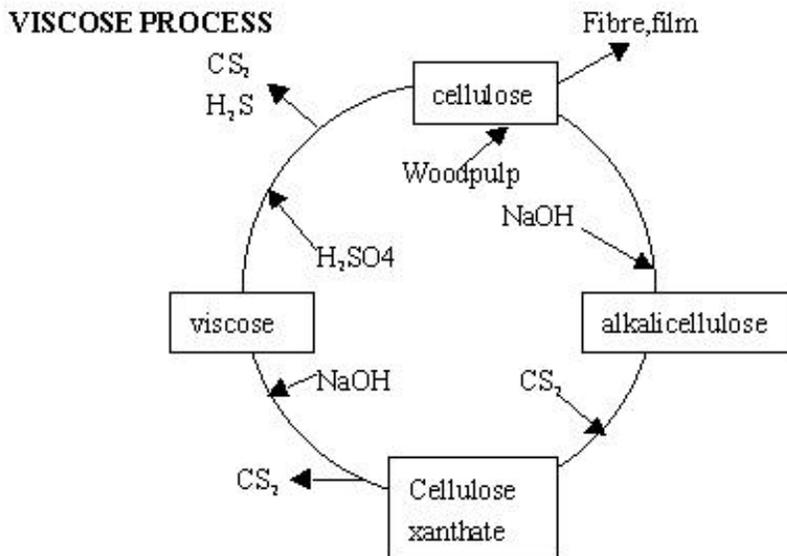
### ***Production process and potential hazard identification***

The study was conducted in a Chinese viscose rayon group which had been established around 1976. The main viscose factory is functionally divided into four main departments: the preparation, spinning, bleaching and spooling departments. The main production process of filament is shown in figure 1.

The first step of viscose production takes place in the preparation department. Cellulose is first dissolved with sodium hydroxide (NaOH), to produce alkalicellulose. After the following stage of aging, sulfuration takes place by means of CS<sub>2</sub> in closed rotating churns whereby cellulose xanthate, which is soluble in lye, is formed from the insoluble cellulose. The churns are emptied and cleaned with water automatically. The potential hazard in this department is related to the maintenance of the churns, which takes place only once a year. Therefore these workers were not included in our study.

Figure 1 schematically represents the overall production processes. Basic substance (stages) in the process are shown in the rectangles. Substances added during the process are shown within the circle. Those released outside the circle.

In the spinning department, liquid cellulose xanthate (viscose) is pressed through a spinneret into a bath containing an acid solution. At this stage the viscose partially decomposes and coagulates forming the rayon filament yarn, releasing CS<sub>2</sub> and H<sub>2</sub>S. The freshly formed rayon filament is wound onto a rotating axis behind the spinning bath. The spinning cakes so formed are removed manually (lifting) from the spinning machines, which are then completely open. Most of the time, however, the spinning machines are closed with mobile windows except during the lifting process.



**Fig.1 The viscose productive process ( Michel Vanhoorne,1992<sup>3</sup>)**

There is exhaust ventilation at the spinning machines, but since CS<sub>2</sub> vapour is heavier than air, this seems inefficient and probably increases the exposure of the workers, while the spinning cakes are being lifted. The lifting process is considered as one of the exposure periods to CS<sub>2</sub> and H<sub>2</sub>S. The spinners are required to make routine inspections during the non-lifting period. The spinners were thus selected as the first subjects to be examined.

Immediately after the cakes are removed from the spinning machines, they are put on a small cart, while still releasing considerable amounts of CS<sub>2</sub> to the atmosphere, and transported to the cakes hall. Workers spend only a short time in this hall. From there, the cakes are transported to the bleaching department where they are washed, centrifuged and dried in ovens. Finally, the filament is rewound onto spools on textile machines in a separate spooling department.

The bleaching and spooling processes are fully automated. Therefore, there are no relevant toxic exposures in these departments.

***Exposure measurement campaign***

The exposure data of this factory was composed of three levels: routine exposure data performed by the industrial hygienists and environmental engineers who designed the machines, external exposure measurements and biomonitoring. The exposure measurement campaign consisted of the online measurement of CS<sub>2</sub> by multi-gases monitor, stationary assessment, and personal exposure measurement.

**Table 1 Contents of Exposure assessment campaign**

Type of the assessment	Sampling and analysis methods
Routine data	Spectrophotometry
External exposure	Multi-gases monitoring
online assessment	Sampling pumps
stationary assessment	Personal sampling
personal exposure	

The routine exposure data by spectrophotometer method were obtained from the industrial hygienists and environmental safety engineers in the factory. These data mainly were used as a reference for the further assessment campaign design. The exposure assessment was mainly performed by our team, and was carried at the spinning department of the factory. The online measurements were firstly taken as screening of the CS<sub>2</sub> concentrations at the worksite, stationary measurements and personal exposure assessments were then used for the exact exposure levels measurements.

#### ***On-line exposure measurements:***

On-line exposure measurement was performed with multi-gases monitoring equipment 1302 ( Brüel & Kjaer, Denmark). Air was aspirated through a 3.9 meters long tube, the air was injected into an automated system, every 3 minutes, between spinning machines. Screening of the CS<sub>2</sub> concentrations at the whole worksite was firstly performed and a whole work day continuous monitoring was subsequently performed.

Whole work day monitor took 9 hours continuous sampling at a fixed sampling site which was located at the middle of the spinning machines in spinning hall, and sampling height was 150 cm, the sampling interval was every 3 minutes. The sampling was taken 9 hours during from 11:56 to 20:30.

#### ***Stationary exposure measurements:***

Stationary measurement was designed according the results of the on-line measurement. Nine sampling sites were selected at different representative sites in the worksite. (see detail at the fig.3 the layout of the worksite) Sampling pumps (Gilair 3) were fixed at 150 cm height at a flow rate of 140-180 ml/min. The basic sampling method we used was an improved method based on the NIOSH and EPA recommended methods. In general, it includes charcoal tube absorbing and capillary GC analysis. A complete description of the method and detailed sampling data of the exposure assessment campaign will be separately reported elsewhere (Tan et al. In preparation).

#### ***Personnel sampling assessment.***

Pumps: The personal sampling pumps (Gilair-3) were used. They were calibrated immediately before and after sampling with the soap-film calibrator (Gilair calibrator-2). The average sampling time was about 150 min (120-180min), the flow was about 130 ml/min (100-170 ml/min); the minimum of the sampling volume was 2L, the maximum of the sampling volume was 25L. Samples were discarded if the flow changed more than 10% during the sampling process.

Sampling: the pump was attached to the belt of the subject. The pump was connected to the absorbent tube (charcoal tube of SKC), Drier tube (SKC) with a silicone rubber tube. The opening of the drier tube was fixed on the shoulder or collar of the employee.

#### ***Analysis of the stationary and personal assessment samples:***

desorption: After the cooled samples recovered to the room temperature (20-22), 1 ml toluene was add to the absorbent tube and left standing for 30 minutes.

Gas Chromatographic conditions: sulfur FPD (flame photometric detector) detector; helium carrier, flow: 20 ml/min; Glass column (2m x 6m) with 5% ov-17 on 80/100 mesh Gas Chrom Q; the temperatures: injection:150, detector: 145, column: 30; injection volume:1µl, range: 0.05-05 mg per sample.

#### ***Quality control of the campaign***

The quality control was carried out through all of the campaign, focusing on two aspects: sampling control and analytic control. The sampling control included air flow rate calibration and breakthrough control.

Air flow rate control: the calibration was performed with a calibrator (calibrator-2, Gilair, USA). All sampling pumps were strictly controlled. The air flow rate variation before and after sampling should be less than 10%, otherwise, the sample had to be discarded. The successful samples was cooled immediately to -20 °C until the lab analysis.

Analytic methods were controlled using control samples provided by the VITO, University of Gent, Belgium. The control samples were made by spiking exactly known amounts of carbon disulfide to empty

charcoal tubes, and sealing the samples. The concentrations of control samples was not communicated to the Chinese technicians before the analytic method was established.

The charcoal absorption tube (SKC) consists of two parts: a front and backup section. The CS<sub>2</sub> amount absorbed in the backup section of the charcoal tube should not be more than 10% of the amount in the front section. Otherwise, the sample was considered invalid and was discarded. In order to overcome the problems with this breakthrough, a drier tube, a big charcoal tube of 200 mg (SKC nr 226-25) and a 100 mg/50 mg charcoal tube (SKC nr226-01) were serially connected during sampling at the end of the sampling campaign.

## Results

### Routine exposure measurement results

The routine exposure data was provided by the industrial hygienists of the factory. They performed the CS<sub>2</sub> assessment by spectrometer method every week, which give us a general idea of the exposure levels at the factory. In the cotton pulp production process hall, considered as non-exposure site in the present study, the level is below the 2 mg/m<sup>3</sup>, in the spinning hall it is about 10 mg/m<sup>3</sup>.

### On-line exposure measurement results

On-line exposure measurements were performed in two ways by multi-gases monitor: overview assessment and a whole work shift monitoring at a fixed sites(only in spinning hall). The global results of the overview assessment of the factory are shown in table 2.

**Table 2 The results of the overview CS<sub>2</sub>exposure in the factory (mg/m<sup>3</sup>)**

Location	N	GM	GSD	UCL	LCL
Spinning hall	92	12.73	0.27	16.64	9.74

N= sampling size; GM= Geometric mean (mg/m<sup>3</sup>) ; GSD= Geometric Standard Deviation; UCL= Upper Confidence Limit (mg/m<sup>3</sup>) LCL= Lower Confidence Limit (mg/m<sup>3</sup>)

Overview of carbon disulfide exposure assessment by multi-gas monitoring was also performed in the cotton pulp production hall. Thirty nine samples were obtained, eighty percent of samples were below the detection limit of the equipment, only 8 samples were between 0-1.6 mg/m<sup>3</sup>.

A whole working day continuous sampling was then taken at a fixed sampling site. One hundred and seventy samples were obtained, the carbon disulfide concentrations variations during the sampling period are shown in Fig.2.

It is clear that the carbon disulfide concentrations at the spinning hall were subject to big variation according to the worker's activities. The CS<sub>2</sub> concentrations were low when the workers were at rest or out of the worksite (16:00-17:30). At the end of a workshift when spinning cakes were removed from the spinning machines and the beginning of next shift when the workers were required to check the machines, the windows of these machines were opened. At this time (19:20-19:50) peak exposures up to 33 mg/m<sup>3</sup> of CS<sub>2</sub> occurred. Between these operations the CS<sub>2</sub> concentrations remained at "background" concentrations of 15-25 mg/m<sup>3</sup>.

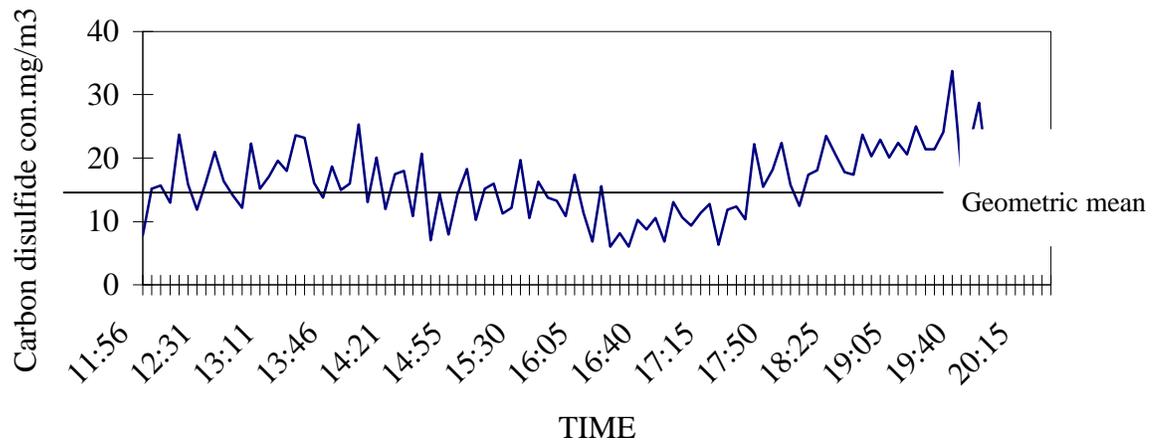


Fig.2 Results of whole work day continuous monitoring of spinning hall

*Stationary exposure measurement results*

The stationary exposure measurement was performed only in spinning hall. It was performed 3 days of 8-12 hours. The results of the exposure measurements are shown in table3.

**Table 3 Results of the stationary measurement in the spinning hall (mg/m<sup>3</sup>)**

Locations	N	GM	GSD	UCL	LCL
1	12	20.71	1.16	22.76	18.85
2	12	63.61	1.17	70.28	57.57
3	12	26.37	1.16	28.98	24.00
4	12	47.21	1.18	52.44	42.50
5	12	21.90	1.19	24.56	19.61
6	12	11.74	1.42	14.67	9.40
7	12	20.36	1.10	21.63	19.16
8	12	11.01	1.20	12.36	9.81
9	12	21.31	1.26	24.68	18.40
Sum	108	23.29	1.35	44.97	12.06

N= sampling size; GM= Geometric mean (mg/m<sup>3</sup>) ; GSD= Geometric Standard Deviation; UCL= Upper Confidence Limit (mg/m<sup>3</sup>) ; LCL= Lower Confidence Limit (mg/m<sup>3</sup>)

It is clearly shown that the carbon disulfide concentrations at most places are below the TLV value ( $<31 \text{ mg/m}^3$ ) and higher than Chinese MAC value ( $10 \text{ mg/m}^3$ ), but only at the area of upper right of the workplace, the concentrations were very high, which may be due to:

1. the exhaust pipes of the spinning machine were not connected well. As each spinning machine have two exhaust pipes (upper and down tube) which draw the  $\text{CS}_2$  out of the workplace, if one of the tubes is not connected well, the  $\text{CS}_2$  is released into the air of workplace.
2. design error of the ventilation system. The whole workplace was installed the ventilation system which includes an amount of openings of the ventilating system in the ceiling of the workplace and exhaust pipes system. Everywhere in the spinning hall should theoretically be covered by the systems. In fact, some places in the spinning hall where we took samples are excluded from either of the ventilation system or the exhaust system and the concentrations of carbon disulfide could be higher than in other locations, such as the high  $\text{CS}_2$  area located at the upper right corner of the spinning hall. It is possible that the one of the systems did not work well thus inducing the high  $\text{CS}_2$  concentration.

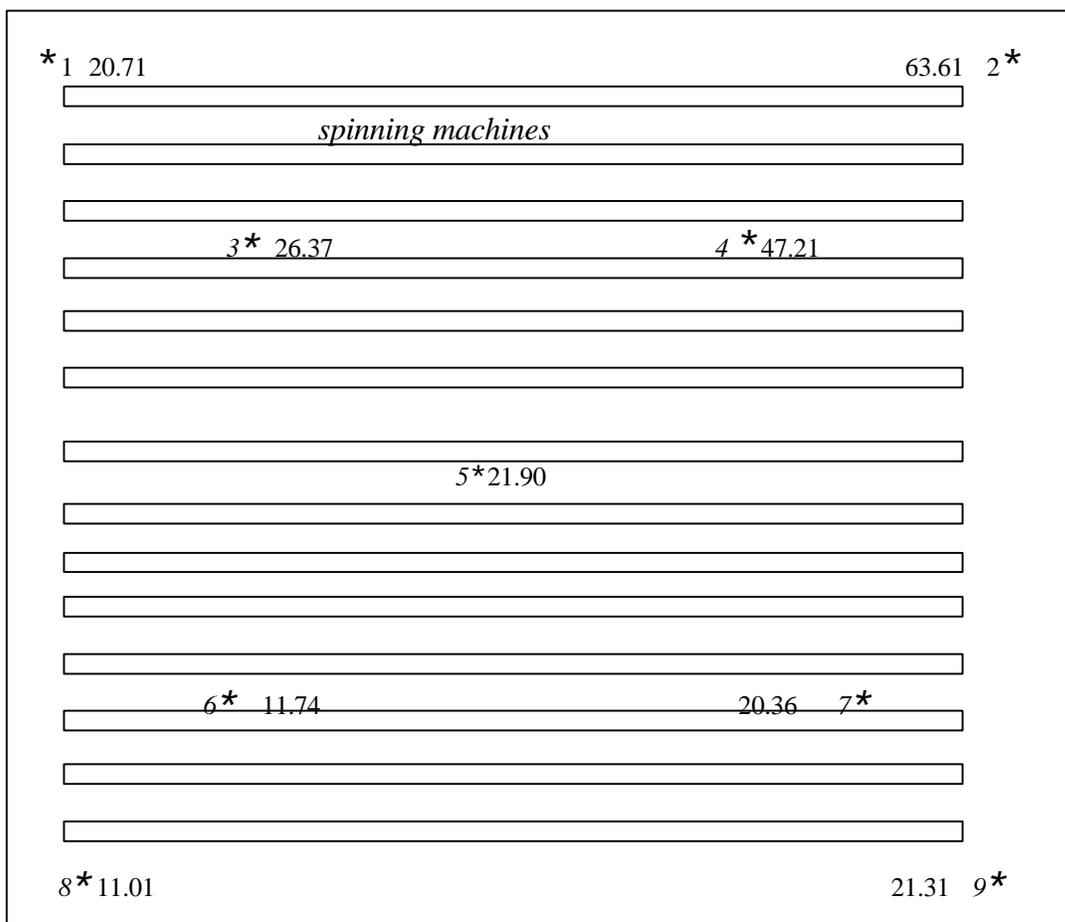


Fig. 3 Layout of the spinning hall A and results of the stationary measurement ( $\text{mg/m}^3$ )

Number with star = the number of the sampling location and sampling location;  
 Number besides the star = the concentration of carbon disulfide  $\text{mg/m}^3$

### Personal exposure measurement

Personal exposure measurements were performed among the workers who worked in the cotton pulp process a priori considered as the non-exposed subjects and spinning hall workers as exposed subjects. Eight samples were obtained from subjects who worked at the cotton pulp hall, only one sample have a very low carbon disulfide concentration ( $0.01 \text{ mg/m}^3$ ), and others are below the detection limit of the method. This result indicates that it is not necessary to take more sample and it confirmed that the cotton pulp workers could indeed be used as non-exposed control subjects.

The personal exposure sampling of workers in spinning hall was also performed in 3 days by different subjects wearing the sampling pumps in the spinning hall. All the results are summarized in the table 4.

**Table 4 The personal exposure measurement results ( $\text{mg/m}^3$ ) in spinning hall**

N	GM	GSD	UCL	LCL
78	20.05	1.33	23.13	17.38

N= sampling size; GM= Geometric mean ( $\text{mg/m}^3$ ) ; Gsd= Geometric Standard Deviation; UCL= Upper Confidence Limit ( $\text{mg/m}^3$ ) ; LCL= Lower Confidence Limit ( $\text{mg/m}^3$ )

### Discussion:

Some papers<sup>11; 12</sup> have summarized the history of the exposure measurements in viscose rayon industry history. Most the studies examine exposure by reference to historical data, i.e. measurements performed by the company staff, using stationary air measurements (ambient air monitoring). Personal air sampling was only carried out in individual field studies with few workers. The internal exposure assessment to carbon disulfide was developed in recently years. The exposure assessment presented here includes the current exposure of the employee and was verified as thoroughly as possible through valid personal exposure sampling technique as well as through biological monitoring.

The on-line monitoring assessment at the filament spinning field is rarely reported.<sup>3</sup> The aim of on-line measurement is to assess peak values at worksites. The results of such measurements in the Belgian study was  $420 \text{ mg/m}^3$  during removal of the spinning cakes from spinning machine pots in the spinning baths, and the background concentrations at the worksite was about  $120 -180 \text{ mg/m}^3$ . Our results only catches the peak period of a whole workday which equate the whole filament production process in the spinning machines. We found that the peaks appeared when the spinning cakes were removed from the spinning machines and also at the period of shift changes, which is obviously due to the opening of the shield windows of the spinning machines.

Stationary measurements were used a lot in the industrial hygiene, and most viscose studies reported such results.<sup>3; 12; 19-24</sup> In general, the concentrations reported from the above studies are around  $30-50 \text{ mg/m}^3$ , but the study performed in Taiwan reported much higher values than the western studies, namely about  $150 \text{ mg/m}^3$ . The carbon disulfide concentrations presented here are very low (around  $30 \text{ mg/m}^3$ ), compared to other studies. The reason for this might be that the factory where we took the samples was founded in 1976 and therefore relatively modern compared to Western viscose rayon plants.

Personal exposure monitoring more exactly reflects the exposure level of the subjects at the worksites compared to the other two kinds exposure assessments methods. The average personal exposure level we found in this study is  $20.05 \text{ mg/m}^3$ , which is in agreement with Drexler's study.<sup>12</sup> Our results also showed that there is an

enormous variation in personal exposure between individuals, depending on the activities of the subjects who wore the sampling pumps. The longer they stayed inside of the spinning hall, the higher the CS<sub>2</sub> concentrations.

### **Conclusions:**

The four definitive elements of industrial hygiene are the anticipation, recognition, evaluation, and control of health hazards arising in or from the workplace. The anticipation and recognition of health hazards have primacy. Upon anticipation or recognition of a health hazard, the industrial hygienist should be able to identify measures necessary for proper evaluation. Upon completion of evaluation, the industrial hygienist then is in a position-in consultation with other members of the occupational health and safety team- to recommend and implement controls need to reduce risks to within tolerable limits.<sup>7; 18</sup> According to this definition, the present study finished the industrial survey of productive process, identify the occupational hazards arising from the production process, and evaluation the exposure levels at the main hazards for the contacting workers, and found that:

1. The occupational hazards of this factory is mainly due to the carbon disulfide, the noise and other chemicals might not be included.
2. The exposure levels of the workers who exposed to carbon disulfide are not higher than the average international levels, which is lower than the TLV level recommend by the American Congress of Governmental Industrial Hygienists (ACGIH), 31mg/m<sup>3</sup>.
3. The personal exposure assessment method is better than the other measurement methods from the present study, as it can exactly express the worker's contacting situation. The online measurement by multi-gases monitor could be also recommended to the factory as it has advantages of rapid, independent assessment.

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