Biological Monitoring of Styrene in FRP-Making Small Industries in Kumamoto, Japan—Winter-Summer Difference and Effect of Protective Masks in Practical Working Conditions—

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Objective: Studies were carried out in Kumamoto, Japan to examine 1) the winter-summer differences in the average individual exposure to styrene (8hr-TWA) and to end-shift-urinary mandelic acid (MA in g/g Cr), 2) the possible seasonal difference in their relationship, and 3) the protective effect of a disposable particulate respirator containing charcoal fiber (called a "charcoal mask") and a charcoal granule cartridge-mask (called a "gas mask") in the real working conditions. Methods: Approximately 100 male and female workers from about 10 small industries were subjected to the studies first in winter and second in summer. Individual exposure to styrene was monitored with a passive sampler during work time, and end-shift-urine was collected to determine urinary MA excretion. The content of their activities and the types of protective equipment were observed and recorded by the minute throughout the working day. Results: Neither individual exposure to styrene nor urinary MA excretion differed at the time of the study in both "no-mask" and "gas mask" groups. The urinary MA excretion was related to individual exposure to styrene in both seasons, with the highest correlation coefficient in the "no-mask" group. Since the regression slope for the "charcoal mask" group did not differ from that for "no-mask" group, the "charcoal mask" was judged to have little protective effect in practical working conditions. From the difference in urinary MA values at 50 ppm (previous TLV-TWA by ACGIH) of individual exposure to styrene in the two regressions for "no-mask" and "gas mask" groups, 49% of styrene was protected against by the "gas mask" in winter, and 45% in summer. Conclusions: Despite different physical environmental conditions, individual exposure to styrene and urinary MA excretion did not differ by season in FRP-making industries. A "gas mask" is more recommended than a "charcoal mask" when treating styrene, although their protective effects are decreased in practical working settings. It is basically necessary to give correct information on and free access to such protective equipment to styrene-treating workers.

Key words: Biological monitoring, Styrene, FRP, Protective equipment, Seasonal difference, Practical working conditions

Occupational exposure to styrene can result in various health effects not only on the central and peripheral nervous system¹,², especially impairment of color vision³,⁴ and hearing ability⁵, but also on the respiratory tract⁶, liver, kidneys⁷,⁸ and skin⁹. Those health defects are reported to occur at a relatively low dose, and the reduction of individual exposure to styrene is essential in those industries making fiberglass-reinforced plastics (FRP) with styrene. Styrene exposure could preferably be reduced by the ventilation systems, but as in Japan where the FRP-industries are too small to install them, individual protective equipment is alternatively required for use during work. Nevertheless, there are few reports on the biological monitoring of styrene in Japan, partly for the reasons given below. Moreover, there is almost no report on the effectiveness of protective equipment use in practical working situations. In fact, workers have little chance to get sufficient information and education
about them, and in many cases even the employees or administrators do not know the right way to use them. Workers often incorrectly use protective equipment and unnecessarily inhale styrene vapor, especially when they feel uneasy wearing it. The problems relating to biological monitoring of styrene in Japan can be summarized as follows: Firstly, individual exposure to styrene during work time is estimated by the average styrene concentration in the workplace that is calculated after meshed samplings of air for only 10 min, but consecutive monitoring with a personal passive gas-sampler is preferred. Secondly, concentrations of the main metabolites of styrene, mandelic acid (MA), is expressed in gram/liter. An MA concentration of 1.0 g/l is presumed to be equivalent to an environmental styrene concentration of 50 ppm, which had been used as Threshold Limit Value-Time Weighted-Average (TLV-TWA) until recently and is now reduced to 20 ppm. This is different from the US, for example, where the MA concentration is expressed in gram/gram creatinine (Cr) and 0.80 g/g Cr had been proposed as the Biological Exposure Indices (BEI) corresponding to individual exposure to 50 ppm styrene by ACGIH.

There are three distribution categories in the Japanese standard: “distribution 1” is urinary MA below 0.3 g/l, “distribution 2” is between 0.3 g/l and 1.0 g/l and then “distribution 3” is above 1.0 g/l. When urinary MA of “some” workers in a plant drops in the “distribution 3” category, improvement of their working environments are immediately recommended by the Labor Standards Bureau with additional suggestions to use protective equipments such as gas-masks, though the extent of their effect in protecting against the urinary MA concentration in practical situations is unknown.

As a multi-centre study on health risks among workers exposed to styrene, we have collected extensive data on their working environment and health twice a year, in winter and summer, and tried to elucidate causal relationships between them and seasonal variations. As the first part of the studies, this report mainly deals with biological monitoring of styrene, i.e., the relationship between urinary MA excretion and individual exposure to styrene, and its variations with seasons and protective masks. In both winter and summer time, individual exposure to styrene and its concentration in the working environment were simultaneously and continuously measured among FRP-making workers. The protective effects of masks on urinary MA excretion in practical situations were also examined, and on MA concentration corresponding to individual exposure to 50 ppm styrene was calculated in g/g Cr for each season.

Materials and Methods

Subjects

Because it is easy to make without requiring a lot of capital or facilities, FRP-making plants were established in many parts of Japan about 2–3 decades ago. In Kyushu, in the southwest of Japan, relatively large-scale fiberglass-reinforced plastic (FRP) plants are now operating and making boats, bathtubs, pools and septic tanks. In Kumamoto, one of the 7 Prefectures in Kyushu, more than ten small to medium sized FRP plants have been operating for more than twenty years. The main products of our subject plants, workers’ job types, the list of organic solvents used in the workplace and the environmental styrene concentrations and ventilation systems in their work sites will be reported elsewhere (Nagano et al., in preparation). The number of workers in one plant ranged from 2 to about 50, many of whom were process workers, i.e., hand laminators, spray laminators, rollers and operators of semiautomatic processors, and others were non-process workers, i.e., grinders, cutters and forklift truck drivers. The main organic solvent used in our subject enterprises was styrene, but acetone was usually put in a corner of the workplace to wash out the laminators in the intervals between making FRP products.

The maintenance staff of the plants often suggest that workers should wear a protective mask at least when treating styrene, but some workers do not listen because according to them it sometimes interferes with their work by making their visual field narrower and breathing harder. And actually some have eczema around the mouth and nose especially in hot and wet seasons. Although many types of protective masks are designed and provided to the workers depending on their work, e.g., some for dusts and others for organic solvents, use of a wrong mask in treating styrene often happens—in some cases even the maintenance staff do not know the right mask to put on. During our study roughly two types of masks were used for organic solvents: a mask containing a charcoal granule cartridge (called a “gas-mask” in this paper), and a disposable particulate respirator containing charcoal fiber (called a “charcoal mask” in this paper).

One hundred and five people from 10 small plants (92 males aged 18–67 (42 on average) and 13 females aged 28–61 (46 on average)) participated in winter (Nov. 1997–Jan. 1998), whereas 103 people from the same 9 plants and 2 new ones (93 males aged 15–71 (39 on average) and 10 females aged 29–78 (53 on average)) joined in summer (July–Sep. 1998). Since there have been observed no gender-related differences in urinary MA excretion or in the correlation between environmental styrene levels and exposure indices, all of the subjects were pooled in the rest of the analyses.

Each subject was put in a category for the mask type they used on our research day because he/she never used two kinds of masks in one day. The following analyses were carried out mainly according to mask type and the season of the research (Table 1, Fig. 1), but it should be mentioned briefly how the workers usually wore the
masks: actually most of them did not change either the “charcoal-mask” or the cartridge of “gas-mask” in the right manner, i.e., they usually wore them for longer than instructed, and the timing of changing masks mostly depended on the worker’s judgment. In the light of our research aims, i.e., to know their practical working conditions, we didn’t tell them to change masks to new ones. We also failed to obtain information about how long they had already been using the masks up to the research day, although very few were seen to wear the new mask on the research day. Moreover, misuse of the masks, e.g., putting knitted cotton gauze between the mask and the jaw to make breathing easier, was observed from time to time and recorded in our time study (described below), but its effect on the relationship between individual styrene exposure and urinary MA excretion was unable to be evaluated since each kind of mask use was not controlled, as mentioned above.

Environmental styrene concentration and individual exposure to styrene

The research protocol was same both in winter and summer. Basically on Monday (the first weekday) one FRP plant was visited and examined. The environmental styrene concentration and individual exposure to styrene were measured with the same passive gas-sampler (Organic gas monitor, 3M Co. Ltd.). Just after they started working, several passive samplers were placed about 1.5 m high at distances to cover the whole workplace, and the cover caps were opened after recording the exact time. For each subject, the same passive gas-sampler was hooked on to the collar near the neck at the beginning of the work shift, and the cover cap was opened and the time was recorded. He/She was asked to carry it wherever he/she went on that day.

At the end of the work shift, all the samplers were collected from the workplace and the subjects. After removing the membrane sheet, the sampler was sealed with the attached cap and put into an aluminum-container with the record of time. The samplers were carried back to our department laboratory and kept in the refrigerator (at around 4°C) until analysis within one week.

The styrene concentration in each sampler was determined by gas chromatography with a flame ionization detector and PEG 20M chromosorb WAW as a column. The eight-hour-time-weighted-average (8hr-TWA) was then calculated for each sampler. The geometric mean of the styrene concentration (8hr-TWA) in a workplace, which is taken as the environmental concentration of styrene in that workplace, was also calculated, and the values will be presented in another paper (Nagano et al., in preparation). The styrene concentration (8hr-TWA) in each worker’s sampler thus determined indicates the individual exposure to styrene.

Urine collection and the measurement of MA

The urine sample was collected just before the beginning of the shift (around 8 o’clock) from all the workers and its urinary metabolites were checked on site with the semi-quantitative dipstick-test (Uro-hemocomb-stics, Terumo Co. ltd.). Those morning samples were brought back to the laboratory for further analysis to confirm the disappearance of MA during the previous weekend. Followed by urination during the afternoon rest around 3 o’clock, the end of shift urine was also collected at the end of the work shift (around 5 o’clock). All the urine samples thus obtained were kept in a portable freezer and taken back to the laboratory to be stocked.

The urine samples were thawed within one week after collection, and the urinary MA concentration was determined by high performance liquid chromatography (HPLC) with HA Pak-II as a column.

Time study and analysis

Each subject was continuously observed by one of the authors throughout his/her working time, and his/her activity together with information about having any exposure to styrene and wearing any protective equipment was recorded in the sheet minute by minute. From this personal record, total time spent for working and total time with having exposure to styrene and wearing protective equipment were calculated for each subject.

The styrene concentration in the gas-sampler being used in monitoring both the environmental styrene concentration and individual exposure to styrene were measured by gas chromatography immediately after reaching our department. At the same time, the urinary MA concentration was measured with high-pressure liquid chromatography within one week after putting the samples in the freezer.

An SPSS package was used for the statistical analyses.

Results

Table 1 shows the means and standard deviations of the individual exposure to styrene (8hr-TWA) and urinary MA concentrations in the end-shift samples (in both g/l and g/g Cr) by season and the type of mask used. The winter-summer difference in the individual exposure to styrene (8hr-TWA) was presumed due to different weather and working conditions, but it was not statistically significant. In both “no-mask” and “gas-mask” groups, the urinary MA (g/g Cr) excretion did not differ by season, whereas urinary MA expressed by the Japanese unit (g/l) was understandably higher in summer (p<0.05), reflecting the enrichment of urine.

Fig. 1 indicates the relationship between urinary MA excretion (g/g Cr) and individual exposure to styrene (8hr-TWA) by season and the kind of mask used. In both seasons, urinary MA excretion was significantly related to individual exposure to styrene in the “no-mask” group,
whereas the relationship was not so close in either season in other groups. Though statistically insignificant, the slope of regression for the “gas-mask” group was the lowest in the two seasons, which indicated a significant protective effect of the mask with remarkable variation among the subjects, whereas the regression slope was similar for “no-mask” and “charcoal mask” group in both seasons, which meant that the “charcoal-mask” was not effective in preventing the subjects from inhaling styrene in practical working conditions.

Although the TLV-TWA of individual exposure to styrene was reduced from 50 ppm to 20 ppm, the urinary MA value at 50 ppm of individual exposure to styrene was estimated from the two linear regressions for “no-mask” and “gas-mask” groups. And from their difference, it was estimated that the charcoal granule cartridge protected against inhaling 49 and 45% of styrene in winter and summer, respectively, in actual working conditions. Of course these protective percentages for the charcoal granule cartridge can be calculated at any level of individual exposure to styrene, but they did not differ markedly from those calculated at 50 ppm styrene.

According to the regression for the “no-mask” group, the urinary MA excretion equivalent to 50 ppm of individual exposure to styrene was calculated to be 0.59 and 0.51 g/g Cr, respectively in winter and summer. Those values were 26–36% lower than the previous BEI standard (0.80 g/g Cr). Lower values than the BEI standard are assured even if the rates are calculated against new BEI standard (corresponding to 20 ppm of individual exposure to styrene).

**Discussion**

The first finding in this study is that the individual exposures to styrene and urinary MA excretion (g/g Cr) in winter did not differ significantly from those in summer. As far as we know, however, there is no comparable report concerning such seasonality. Essentially there are many possible factors relating to those seasonal differences: 1) physical environmental factors such as air temperature, ventilation frequency, and the rate of evaporation of styrene, 2) individual

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<th>Table 1. Individual exposure to styrene and urinary MA by season and protective mask (mean ± sd)</th>
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<td><strong>Individual Exposure</strong></td>
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*: Means in winter and summer are significantly different in each mask group (p<0.05).
behavioral/educational factors to protect against styrene inhalation, and 3) socioeconomic factors deciding the amount of daily products and thus their work loads and eventually individual exposure to styrene. In our study time, however, there were observed marked differences only in physical environmental factors, although the average percentage of workers using protective equipment did not differ and the amount of FRP-production actually seemed rather constant due to economic stagnation. Variations in the mean individual exposure to styrene are further discussed in another paper (Nagano et al., in preparation), but it should be stressed again that different physical environmental conditions did not produce any difference in the means of individual exposure to styrene and urinary MA excretion.

Urinary MA excretion expressed in Japanese units (g/l) showed significant seasonal difference, reflecting enrichment of most urinary metabolites in summer. Condensed Cr in summer time has mechanically caused greater variation in urinary MA (g/g Cr) in that season (Fig. 1). Of course other factors such as the amount of sweat and drinking water should have contributed to the enrichment of urinary metabolites in summer. These facts further also indicate that the Japanese unit for MA (g/l) should be carefully used in the biological monitoring of styrene.

The second finding is to confirm the high correlation coefficients in the relationship of urinary MA (g/g Cr) and individual exposure to styrene (8hr-TWA) especially in the “no-mask” group (Fig. 1). These correlation coefficients were compatible with those mentioned in previous reports, although Ong et al. showed a little bit better correlation when MA+PGA was applied for MA only. We believe that ours have been attained with the help of intensive recording of activities, in which the time of handling styrene and putting on masks was also checked. There were a few workers who used styrene only either in the morning or in the afternoon—this should have caused urinary MA excretion either lower or higher than it should be for the same individual exposed to styrene (8hr-TWA).

The third finding is related to the protective effect of face masks: the “charcoal mask” was found to be not very effective in our working conditions because the regression of urinary MA (g/g Cr) and individual exposure to styrene was similar in the “charcoal group” and the “no-mask group” (Fig. 1). Needless to say, the charcoal mask prevents workers from absorbing styrene for some time, but most of them use the same one for a long period without knowing the right time to change to new one.

On the other hand, the reasons why urinary MA values in the “gas-mask” group varied in both seasons (Fig. 1) can be attributed to the fact mentioned in the Subjects and Methods section, that they put a charcoal granule cartridge on the mask for longer than its effective time, or that they misused the mask, for example by putting knitted cotton gauze between the mask and jaw to make breathing easier. If they keep changing the cartridge and using the mask properly, the protective effect of the mask should be bettered than those calculated in our study. There are some reports on measuring such protective effects of respirators and/or developing comfortable face masks in real working situations, but it should be noted that effective use of such protective devices could not be attained without appropriate health education to the workers and administrators as well.

The fourth and last finding in this study is that the values corresponding to 50 ppm (previous TLV-TWA) of individual exposure to styrene, i.e., 0.51 and 0.59 g/g Cr in respective summer and winter, were 26–36% lower than the previous BEI value of 0.80 g/g Cr (corresponding to 50 ppm). The lower rates in our study are consistent as far as the BEI value changes with TLV-TWA. Our predicted values were also lower than that in Ikeda et al.’s report on FRP boat production plants in Japan. The reasons are unknown, but they can possibly be explained by overestimation of individual exposure to styrene in our subjects due to the placement of passive samplers, or by the unique practice of making a variety of FRP-products in Japan. If the latter is thought to be more plausible, the biological monitoring of styrene should be carried out according to the FRP product or subject’s job type in Japan. It is a welcome trend that the TLV-TWA was reduced from 50 ppm to 20 ppm in some developed countries because the health effects of styrene on the central and peripheral nervous system was clarified even at low concentrations. Consequently, biological monitoring of styrene would also demand more delicate and strict protocols in measuring urinary MA excretion in actual working conditions.

References