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Serum and urine monitoring of fluoride exposed workers in aluminium smelting factory*

K. Kono, Y. Yoshisda, M. Watanabe, K. Usuda, H. Nagaie, Y. Takahashi

Department of Hygiene and Public Health, Osaka Medical College, 2—7 Daigakumachi, Takatsuki City, Osaka, 569, Japan

Sun G

Department of Preventive Medicine, China Medical University, Shenyang 110001, China

Ding G, Hu Y

The Hospital of Aluminium Smelting Factory, Fushun, China

Abstract——To define the relationship between F concentrations in the serum and urine of workers and the amount of gaseous F in the workplace, postshift serum and urine samples of exposed and unexposed workers of an aluminium smelting factory were examined.

Average gaseous F concentration in each work environment was 1.89 mg/m^3 to 4.82 mg/m^3. Although serum F concentrations in unexposed workers increased with age, those in F exposed workers did not change, and the levels of F in serum and urine of them were more than twice as high as those in the controls. The serum and urinary F of exposed workers were well correlated ($r = +0.66$) with each other.

Keywords: serum and urine monitoring; fluoride exposed workers; aluminium smelting factory.

1 Introduction

The occupational health control of workers exposed to inorganic fluoride has focused on the measurement of environmental fluoride at the work place and on medical surveillance of the workers, particularly the biological monitoring of exposed workers.

In recent years, increased use of inorganic fluoride such as hydrofluoric acid (HF), and acute or chronic fluoride poisoning has often been reported (Hodge, 1977; Mayer, 1985; Chan, 1987). The major pathway for fluoride elimination from the body is via the kidney. Fluoride concentration in urine has therefore been recognized as a good indicator of occupa-

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tional fluoride exposure. Zober *et al.* (Zober, 1977) suggested that urinary fluoride analysis of postshift samples is suitable for monitoring workers exposed to HF. According to the National Institute for Occupational Safety and Health of the United States(1975) up to 7 mg/L fluoride in postshift urine can be considered safe with respect to the development of chronic fluoride poisoning.

Compared with urinary fluoride , serum fluoride has not been fully evaluated and measuring the fluoride concentration is often much more difficult than in the case of urine. In the previous reportes, we demonstrated a linear relationship between mean urinary fluoride concentration or serum fluoride concentration and HF levels in air (Kono, 1987; 1992).

The aim of this investigation were to define the relationship between serum, urine and the amount to inorganic gaseous fluoride in the work environment, and to clarify the usefulness of the biological monitoring of fluoride exposed workers to prevent the occupational fluoride poisoning.

2 Materials and methods

2.1 Subjects

To determine serum and urinary fluoride, serum and urine samples from 200 fluoride exposed workers were studied. The subjects were aged 20 to 70 years and had been engaged in smelting aluminium for making the virgin ingots and other alloys. These workshops were opened rooms in which gaseous fluoride such as HF was vaporized from the silicon smelting furnaces and various types of aluminium pots. Post shift serum and urine samples were taken on either Thursday , Friday or Saturday. In postshift specimens, the levels of fluoride were expected to be highest. As a control group, 121 unexposed workers of the same age group were examined. To investigate the effects of retained fluoride and biological fluids as an indicators of fluoride exposure, the serum and urine specimens of 29 retired workers who had been exposed to fluoride at the same factory for long periods were taken. External contamination of urine samples was minimized using polyethylene bottles.

2.2 Analysis of fluoride in serum and urine specimens

Serum and urinary fluoride were measured using a previously described fluoride specific electrode method(Yoshida, 1978). The fluoride electrode gives a selective response to fluoride ion in specimens. The measurement must be made at a certain hydrogen ion concentration, namely, by fixing at pH 5.25, to dissociate hydrofluoric acid complex formation in the acid zone. Furthermore, the electrode potential is also influenced by the total ion strength. For such reasons the same volume of total ion strength urinary buffer (TISUB), and a one-tenth volume of acetate buffer were added, respectively, to the serum and urine. The measured concentrations in the urine were corrected using a specific gravity of 1.024.

2.3 Measurement of gaseous concentration in air

To measure gaseous fluoride concentration in the air a volumetric method was used. The air was aspirated into an absorbing solution, and fluoride in the solution was measured using a fluoride-specific electrode. At least five measurements were made in each workplace, and

the mean concentration was calculated.

Differences between the two groups were examined using Student's t test if the variances were equal, and Welch's t test if the variances were unequal(F test).

3 Results

The maximum and minimum concentrations of gaseous fluoride in the air at each workshop varied from the mean by less than 30%.

The postshift serum and urinary fluoride concentrations in fluoride exposed workers among different workshops are summarized in Table 1. The mean gaseous fluoride concentration in the workplaces were relatively high, ranging from 1.89 to 4.28 mg/m^3. We could not obtain a good correlation between serum or urinary fluoride and gaseous fluoride concentration in the air.

Table 1 Serum and urinary F concentrating of F exposed workers in different workshops

	Workshop	n	Mean±SD	F in air
Serum F,	100	79	63.6±27.3	1.89
μg/L	101	57	54.1±19.1	4.28
	103	14	49.8±21.2	3.87
	110	4	44.8±20.6	40.03
	D	29	40.4±17.6	—
	F	6	29.0±7.4	—
Urinary F*,	100	80	3.33±2.07	1.89
mg/L	101	57	2.70±1.54	4.28
	103	14	2.42±1.16	3.87
	110	4	4.55±3.24	4.03
	D	33	1.71±0.91	—
	F	6	1.65±1.46	—

* Corrected with specific gravity 1.024

The results of the cross-sectional analyses in fluoride exposed workers and healthy controls by 10-year age group on serum and urinary fluoride are shown in Table 2. Although serum fluoride concentration in controls slightly increased with advancing age, that in fluoride exposed workers did not paralleled to the changes in controls. Urinary fluoride concentrations in both exposed and non-exposed groups did not change with advancing age. The levels of fluoride in serum and urine among fluoride exposed workers were more than twice as high as those in control subjects.

Table 2 Serum and urinary fluoride analysis in exposed workers and controls by ten-year age group

		Fluoride exposed workers		Control	
	Age, year	*n*	Mean ±*SD*	*n*	Mean ±*SD*
Serum F, μl/L	20—29	1	46.0 —	20	18.3±4.40
	30—39	12	62.9±20.74**	32	17.3±4.03
	40—49	56	66.6±27.18**	38	18.6±5.12
	50—59	85	50.4±21.92**	12	20.1±4.08
	60<	35	42.8±17.66*	6	25.8±13.82
Urinary F[1],	20—29	1	0.70 —	20	0.75±0.25
mg/L	30—39	12	3.38±1.87**	32	0.74±0.36
	40—49	59	3.62±2.07**	38	0.75±0.30
	50—59	85	2.51±1.62**	12	0.85±0.35
	60<	37	1.92±1.06**	11	0.67±0.30

* $p<0.05$, ** $p<0.01$ compared with controls; 1. corrected with specific gravity 1.024

Table 3 shows the mean serum and urinary fluoride levels in fluoride exposed workers, retired persons, and controls. Serum and urinary fluoride concentrations in fluoride exposed workers and retired persons were remarkably higher ($p<0.01$) than those in control subjects. This result suggests that the excretion of retained fluoride from the body continues for long period.

Table 4 shows that serum and urinary fluoride analysis in fluoride exposed workers by duration of fluoride exposure. There were no differences between the levels in both serum and urine with advancing duration of exposure. This means that the serum and urinary fluoride concentrations reached the maximum level after chronic exposure and maintained the high level during the exposure to fluoride.

Fig. 1 shows the relationship between the serum and urinary fluoride concentrations of the fluoride exposed workers. A good correlation ($r=0.66$), as shown by the straight regression line, was obtained.

Table 3 Serum and urinary fluoride levels in exposed workers, retired workers and controls

		n	Mean ±*SD*
Serum F, μg/L	F workers	161	58.1±24.0
	Retired	28	34.5±15.2**
	Controls	108	18.7±5.6
Urinary F*,	F workers	165	3.00±1.85
mg/L	Retired	29	1.51±0.71**
	Controls	113	0.75±0.31

** $p<0.01$; * corrected with specific gravity 1.024

Table 4 Serum and urinary fluoride analysis in exposed workers by duration of exposure

	Duration of exposure, year	*n*	Mean ±*SD*
Serum F, μg/g	>9	3	46.3±27.5
	10—19	28	55.9±25.2
	20—29	106	54.1±26.0
	30<	52	55.4±20.5
	Non-HF	108	18.7±5.6
Urinary F*,	>9	2	2.81±2.99
mg/L	10—19	28	3.15±12.05
	20—29	109	2.81±1.85
	30<	55	2.52±1.57
	Non-HF	113	0.75±0.31

* Corrected with specific gravity 1.024

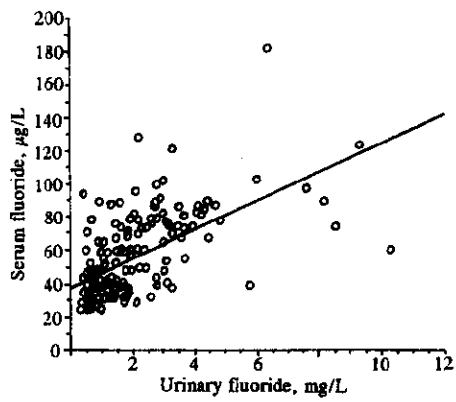

Fig. 1 Relationship between serum and urinary fluoride in fluoride exposed workers

$n=182$, $r=0.66$, $p<0.01$

4 Discussion

It is accepted practice to evaluate fluoride exposure by analysis of fluoride in the work environment (Brown, 1985). Such an examination, however, does not always reflect the status of fluoride in the body. Determining the fluoride concentration in the urine is considered to be an appropriate way to evaluate the status of exposure, even when the exposure time and the concentration of atmospheric fluoride are irregular (Yoshida, 1978; Toyota, 1979; Kono, 1987). In the case of urine, a 24-hour urine analysis is necessary to monitor atmospheric fluoride exposure. However, it is difficult to examine a large number of workers and ensure accuracy in the measured values. Therefore, measurement of fluoride concentration in the postshift urine is more practical for routine evaluation of environmental fluoride exposure. Our previous study showed that the biological effects of HF could be monitored by

determining the postshift urinary fluoride concentrations (Kono, 1987).

Compared with urinary indices , with serum measurements it is often difficult to maintain accuracy in the measured values. The variation in serum fluoride among fluoride exposed workers is rather wide even if the atmospheric fluoride levels are fairly constant. The main reason are that serum fluoride is readily affected by various foods and by the time of specimen collection. In particular, intake of tea, which contain much fluoride, obviously influences the serum and urine levels (Kono, 1992; 1994). As shown in the results, the serum and urinary fluoride in the exposed workers were well related each other. The results show that serum fluoride also presents a suitable monitoring method for workers exposed to fluoride.

The physical and chemical states of inhaled fluoride (e. g. gaseous fluoride or containing fluoride dust) are important for the biological monitoring of the workers. The subjects observed in this study were exposed to various type of fluoride compounds in the workshops. Although we could determine only gaseous fluoride in the environment, measured serum and urinary fluoride in the exposed workers well reflected the status of exposure.

The serum and urinary fluoride concentrations in the retired person who had been chronically exposed to fluoride were still higher than those in control subjects. This result show that the biological half life of inorganic fluoride is very short (Kono, 1994), and retained fluoride in the hard tissue is not easy to excrete from the body.

Beside serum and urine analyses, frequent monitoring of the biological indicators of chronic exposure such as hair is necessary for the health care of fluoride exposed workers, even if they are retired.

5 Conclusions

Measuring the fluoride (F) concentration in the postshift serum and urine is considered to be an appropriate way to evaluate the F exposure in the work environment.

To define the relationship between F concentrations in the serum and urine of workers and the amount of gaseous F in the workplace, postshift serum and urine samples of 200 F exposed workers and 121 unexposed workers of an aluminium smelting factory were examined. For the measurement of gaseous F concentration in the air a volumetric method was used.

Average gaseous F concentration in each work environment was 1. 89 mg/m^3 to 4. 82 mg/m^3. Although serum F concentrations in unexposed workers increased with age, those in F exposed workers did not change, and the levels of F in serum and urine of them were more than twice as high as those in the controls. The serum and urinary F of exposed workers were well correlated ($r=+0.66$) each other.

From the present results the environmental exposure to gaseous F in aluminium smelting factory could be monitored by determining the postshift serum and urinary F concentration.

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