ENVIRONMENTAL MONITORING OF ATMOSPHERIC LEAD PARTICULATES IN A RECLAIMING SMELTER

M. KUSUMOTO and S. IWAO

Department of Preventive Medicine and Public Health, School of Medicine, Keio University, Shinjuku-ku, Tokyo, Japan

ABSTRACT

Environmental monitoring of lead particulates, with regard to the determination of concentration, particle-size measurement and identification of compounds, was carried out from 1963 to 1978 in a small reclaiming smeltery in Japan.

The concentration of lead in the air, measured by stationary sampling, decreased from an average of 621 μg Pb/m³ at the beginning of observation before 1965 to an exposure level of 73 μg Pb/m³ in June 1978. The decrease was due to hygienic measures, taken by the company during the period.

The working conditions of the sampling devices such as collecting force, air velocity, and sampling time, had no effect on the values of lead in the air. Lead concentrations in the workshop air differed significantly in different operation processes in the plant. The time-weighted average in lead concentration, measured by personal samplers on sample workers during 8 hours, agreed well with its expected value, which was calculated from the lead concentrations at stationary sampling sites. The evidence leads to the conclusion that the "dose" can be evaluated equivalently either by direct measurement of the time-weighted average, or by averaging the lead in the air at stationary sites according to time, if exposure does not vary greatly during 8 hours.

The specific gravity of the blood (an "effect" variable) decreased as a logarithmic function of the lead concentration in the air (a "dose" variable) in all lead workers, except the fork-lift operators, who showed no effect despite the highest exposure level in time-weighted average. Particulates sampled in their working area were, at a significantly low percentage, in a respirable micrometer range (under 5 μm in an aerodynamic dimension), as compared with particulates from the workshops for other workers. The evidence suggests that lead concentration could not be a unique index of the "dose", unless particle-size information is available. There was no positive finding as regards differences in the composition of samples from different workrooms.

The dose-effect relationship in lead workers has not been thoroughly studied, due to the scarcity of dose data in most studies. Furthermore, respirable particle monitoring and identification of compounds in addition to concentration measurements are indispensable to dose evaluation, since the respiratory retention of particulates is a direct function of aerodynamic size, while absorption rates via the respiratory tract into organs depend on their solubility.

The aim of the present study was to obtain information about the concentration, respirable size, and composition of particulates, in relation to the dose-effect relationship in lead workers.

METHOD

Exposure situation

The factory (1 000m²) consists of two plants. One plant smelts the lead of electrode plates from batteries (smeltery) and the other founds electric wares (foundry). Of a total of 51 males in May 1978 33 were lead workers. In the smeltery there were 24 smelters, 3 crushers whose job was to dismantle battery cells of electrodes and crush them, and 1 fork-lift operator whose task was to weigh the raw materials, mix them and put them into hoppers, while in the foundry there were 3 melting-bath operators, 1 caster and 1 welder. Smelters work in three 8-hour shifts and their exposure to lead varies during the scheduled sequence of operations such as filling furnaces, stirring and pouring the molten lead into molds. Exposure of a fork-lift operator ranges from low to high, continuing for short intervals. Other workers have a more continuous exposure during 8 hours. There are great variations in the use of protection masks by the workers.

Dust sampling, lead determination, and identification of chemical compounds

Environmental monitorings were done 19 times every 6 months throughout the whole period from May 1963 to June 1978. Before 1976, only stationary samples for measuring the lead in the air had been taken. Since May 1976, both stationary sampling for a concurrent determination of the lead in the air and particle-size, and personal sampling for measuring the time-weighted average of lead in the workshop air during 8 hours were carried out.

Stationary sampling sites were selected at random within the working areas of 6 different operations in the smeltery and foundry: the surroundings of the smelting furnaces, the working area of the fork-lift operation including a storeroom, an open-air material store for crushing, the surroundings of a melting-bath, and workshops for casting and welding. At these sites 143 particulate samples for measuring the lead concentration, and 15 samples for the determination of particle size were collected throughout the whole period. Four samples were taken outside the factory as references.

For the collection of particles at stationary sites before 1975 an electrostatic precipitator was used. Precisely 1 m³ of air was sampled at a flow rate of 100 liters/min (equivalent to 220 cm/sec as linear velocity) in 10 minutes. Since May 1975, particulates were collected by means of low-volume and high-volume filtering devices for the measurement of the lead concentration. The low-volume sampler filtered 0.8 to 1.5 m³ of air through 55 mm-diameter millipore filters at an air-flow of 10 to 30 liters/min (equivalent to 7 to 22 cm/sec as linear velocity) within a sampling time ranging from 20 min to 2 hours. The high-volume sampler filtered 150 to 450 m³ of air through 20 × 25 cm glass-fiber webs at a flow rate of 1.1 to 2.3 m³/min (equivalent to 40–80 cm/sec as linear velocity) within a sampling time ranging from 40 min to 7 hours. Hounam's 4-stage cascade centripeter[2-6] and Andersen's 8-stage centrifugal unit[1] were used for the concurrent determination of concentration and particle size. The cascade centripeter collected particles on glass-fiber filters from 3 to 12 m³ of air at a

constant rate of 30 liters/min within a sampling time ranging from 2 to 7 hours, and automatically separated the particulates into 4 size categories according to the aerodynamic particle size. Andersen's unit sampled particles and separated them into 8 size-categories on polyethylene sheets tightened on the collection plate of each of the 8 stages, operating at an air suction rate of 28.3 liters/min in 2−7 sampling hours. Separation of particles according to size gives the mass-median diameter and standard geometric deviation expressed as an equivalent aerodynamic diameter d $\sqrt{\rho}$ where d is the physical diameter, and ρ the density of a particle. On the assumption that the particulate is spherical and has a density equal to that of metallic lead, i.e. 11.3, the size parameters are expressed by the physical dimension.

A total of 59 personal samples were collected on 24 workers in the course of 6 measurements since May 1976. Using portable low-volume samplers, particulates were collected on glass-fiber filters 55 mm in diameter from 0.3 to 0.5 m³ of air at an air suction rate of 0.4 to 1 liter/min (equivalent to 17−41 cm/sec as linear velocity) during 8 working hours.

Particulates precipitated in the collection tubes or collected on the filters were dissolved in a 2.5 N nitric acid solution. Lead determination was made by means of dithizone-chloroform-spectrophotometry until October 1973. In April 1974 the colorimetric method was replaced by atomic absorption spectrometry using a single-beam spectrometer with an acetylene-flame atomizer.

The qualitative identification of the lead compounds was made within 8 samples collected by high-volume samplers at stationary sites in May 1978, using the method of X-ray diffractometry over an angle range of $\theta = 15$ to 65 degrees.

Selection of target group

Cross-sectional observation was made with a retrospective collection of dose and effect data. All workers who had ever been involved in lead operations and were still employed in June 1978 were included in the exposed target group. Workers who had never been exposed to lead and had no exposure at the time of observation were included in the reference group. In June 1978, the average duration of employment of workers classified according to operation was 9.8 years for smelters, 7.3 years for melting-bath operators, 13.7 years for other target workers, and 14.3 years for the reference workers. Average ages in these 4 groups were 37.4, 34.0, 35.6 and 38.3 years, respectively.

RESULTS AND DISCUSSION

Lead concentration in the air

Variations of lead concentrations measured at all sampling sites throughout the whole period are shown in Figure 1. The earliest data obtained before 1968 gave a variation ranging from 64 to 1 912 µg Pb/m³ (N = 10) with an average of 621 µg Pb/m³ and standard deviation 697 µg Pb/m³. The last 9 samples obtained in June 1978 varied between 33 and 115 µg Pb/m³ giving an average of 73 µg
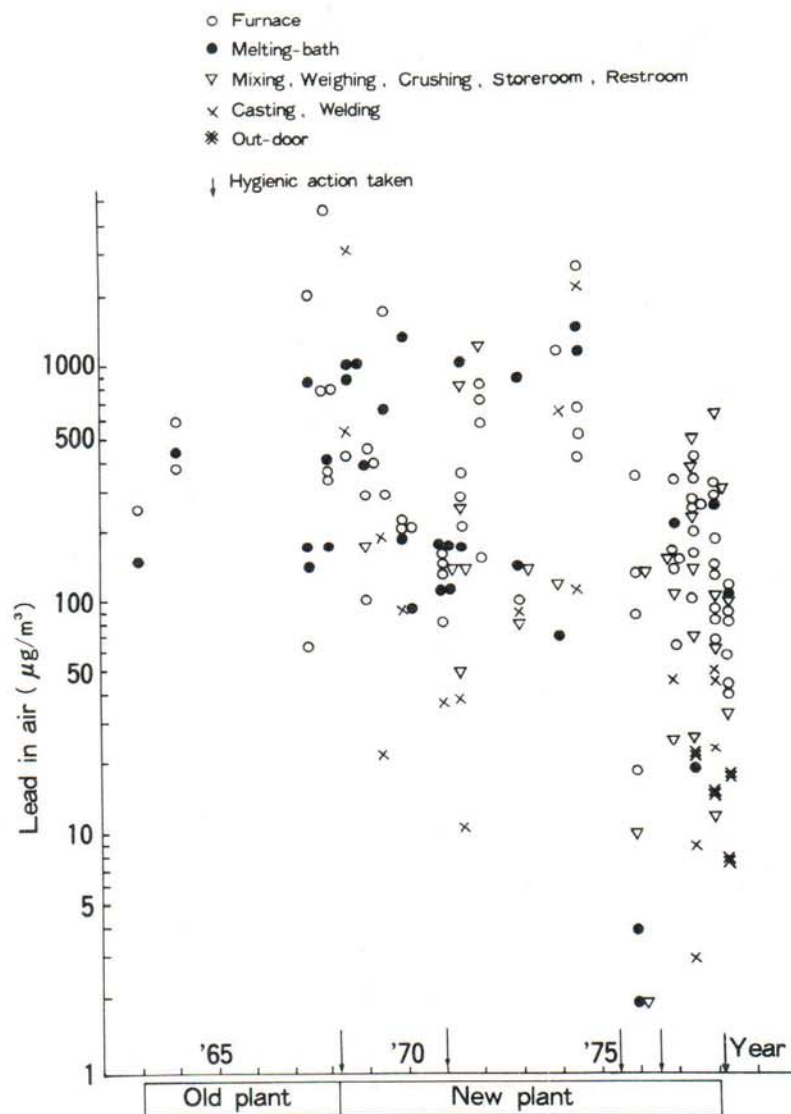
FIG. 1 – Atmospheric lead concentrations.

Pb/m³ and standard deviation 31 µg Pb/m³. Despite the variation of almost 10 – 100 times, an annual decrease in lead was established with a decreasing average and standard deviation over the period of the monitorings. The hygienic measures taken by the company (Table 1) had obviously led to the decline. The removal of the plant to a new building in July 1968 and the installation of

TABLE 1
Hygienic measures which have influenced lead exposure.

Time	Type of measure
July 1968	Factory moved into a new building Use of protection masks frequently required by the company
April 1971	Frequent health education of the workers
September 1975	Local ventilation equipment installed
July 1976	Restroom air-conditioned Additional ventilation and wet-scrubber installed
June 1978	Closure around hopper of smelting-furnaces installed Frequent sprinkle on the floor of workroom

ventilation equipments in September 1975 appeared to be the main cause of the decrease in lead concentrations.

There were significant differences in the mean lead concentrations in different working areas as shown in Table 2. According to the significant differences between the mean levels in two different working areas in the same operation, the whole working area of the two plants could be divided into two categories of lead exposure. Smelting and fork-lifting in the smeltery plant and the melting-bath operation in the foundry plant belonged to the high exposure area, while the crushing operation in the smeltery plant and casting and welding in the foundry belonged to the low exposure area. Due to the limited amount of samples no differences could be established between the mean lead concentrations in the low exposure and the reference area.

TABLE 2
Lead in air at operation processes 1963–1978, stationary sampling.

	Sampling sites grouped by operation process					Outdoor air (Reference)
	Smelting furnace	Melting-bath	Mixing, weighing, fork-lifting	Crushing	Casting, welding	
N	71	29	24	6	13	4
Group average	398	481	470	91	100	16
S	656	452	719	96	155	5
Significance by t between △ groups						
Smelting furnace	—			**	**	**
Melting-bath		—		**	**	**
Mixing, weighing, fork-lifting			—	*	*	**
Crushing				—		
Casting, welding					—	
Reference air						—

* $p < 0.05$
** $p < 0.01$

The values of lead concentration measured of all sampling sites since October 1976 were classified according to the existing sampling conditions such as collection forces, air flow velocity and sampling time as shown in Figure 2. There was no evidence of the sampling conditions having any effect on the measurement of lead in the air.
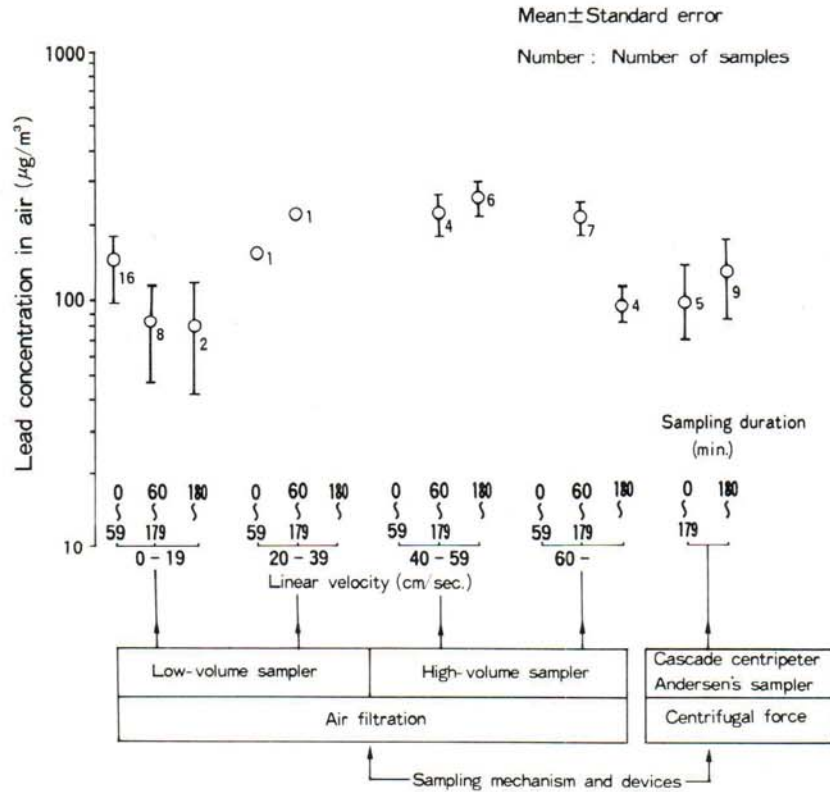

FIG. 2 – Lead concentrations in workshop air by sampling conditions.

Time-weighted average

Fifty-nine samples measured on 24 sample workers throughout the monitoring from 1976 to 1978 gave a time-weighted average lead concentration during 8 hours ranging from 14 to 1 692 μg Pb/m^3 with a mean of 175 μg Pb/m^3 and standard deviation 214 μm Pb/m^3. The highest exposure was observed in 7 fork-lift operators (average 336 μg Pb/m^3, standard deviation 555 μg Pb/m^3), followed by 32 smelters (average 135, standard deviation 105) and 17 melting--bath operators (average 170, standard deviation 104), while the lowest exposure was observed in a group of one crusher, one caster and one welder (average 77,

standard deviation 50) as shown in Figure 3. Applying the statistical method of variance analysis with a one-way layout model, the variation in the values of the time-weighted average was divided into two components: the system variation, deriving from the operation of sample workers, and the residual part of variations including error in sampling and analysis and error from other undefined causes. As can be seen in Table 3, the significant difference in the time--weighted average derives from the different amounts of lead emission from the operations. The same statistical method was repeated in the variance analysis
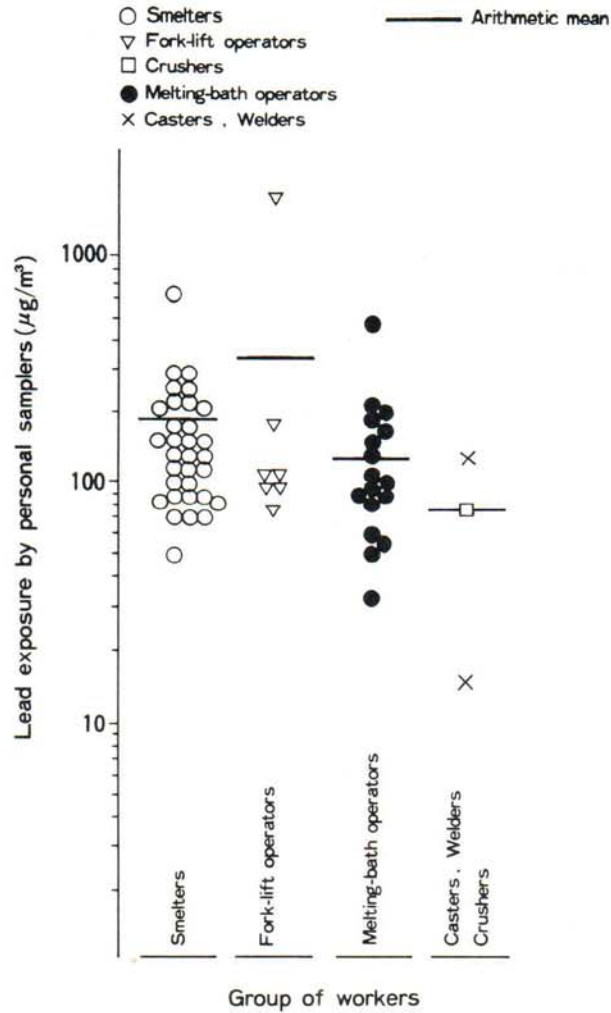

FIG. 3. — Time-weighted average of lead concentration in air in different operations, 1976—1978.

owing to personal behavior of the sample workers during work. As shown in Table 3, personal behavior has no significant effect on the values of the time-weighted average.

TABLE 3

Variation in time-weighted average by (A) operation process and by (B) behavior of sample workers, tables of variance analysis by one-way layout model.

Factor	Sum of square	Degree of freedom	Variance	F-value	Estimate of variance
Total	2 934 710	58	50 598		
A. Operation process (P)	231 358	4	578 360	11.6**	$\sigma^2 + p\sigma^2_P$
Residual error	2 703 352	54	50 062		σ^2
B. Behavior of workers (W)	613 029	23	26 653	0.402	$\sigma^2 + w\sigma^2_W$
Residual error	2 321 681	35	66 334		σ^2

** $p < 0.01$

The values of the time-weighted average, measured in 1977 and 1978 on 19 smelters and 8 melting-bath operators, were plotted against each expected value in a scatter diagram of Figure 4. The expected values were obtained from the lead
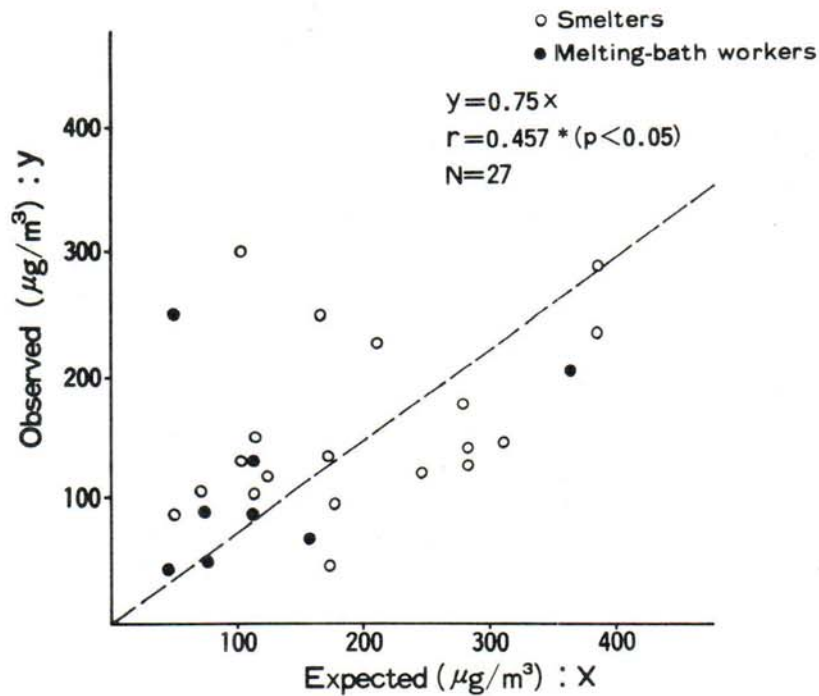

FIG. 4 — Time-weighted average values of lead concentration in air measured by personal sampling (y) and calculated from time-study (x).

concentrations at stationary sampling sites and the time distribution in the workers standing at each site during their operations. The observed values correlated significantly with the expected values with a correlation coefficient of $r = 0.457$ ($p < 0.05$). The regression line between the two variables is given by $y = 0.75x$, where x and y are the expected and observed values, respectively.

It should be noted that the lead exposure of workers can be evaluated either by a direct measurement of the time-weighted average using personal samplers, or by calculation from stationary-sampled lead concentrations in the workshop air, if the operation is precisely scheduled. Even a simple arithmetic mean of stationary-sampled lead concentrations may give a good estimate of the exposure level in workers, if the daily fluctuation of lead in the air is not extremely great.

Comparison of dose variables and the effect variable

Table 4 shows an association between the specific gravity of the blood and the time-weighted average lead exposure in workers grouped into 5 groups. This association could be established in all groups except in fork-left operators. These showed no decrease in specific gravity, as compared with the value for references workers, despite the highest exposure to lead. This evidence is presented only approximately in Table 4, because of the limited number of coherent dose data available, which were measured only during the last 3 years. This weakness is noticeable in Figure 5 which indicates the direct plotting of the group average of specific gravity against the arithmetic average lead concentration in the air which

TABLE 4

Specific gravity of blood in workers grouped by operation, 1968–1978.

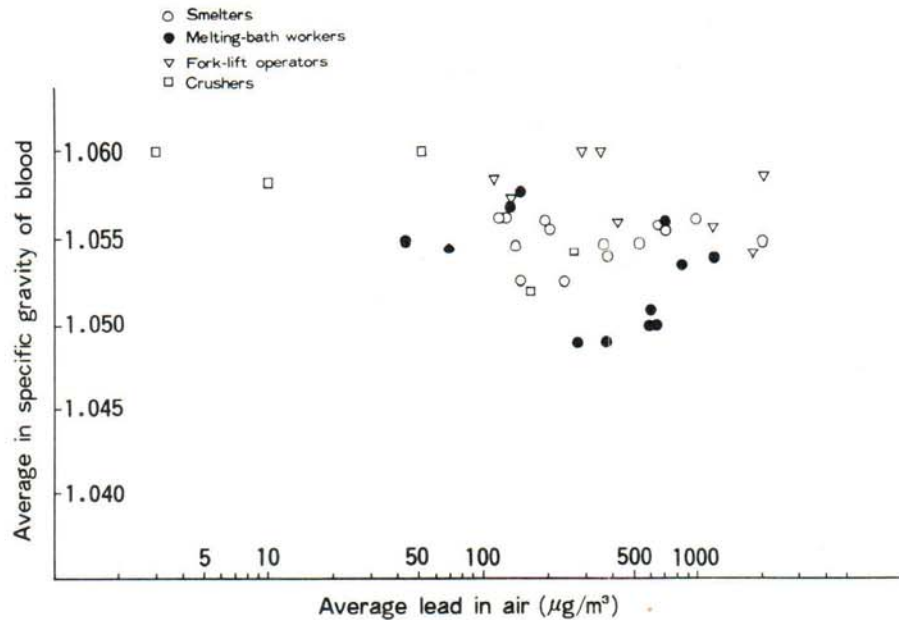|	Group of workers				
	Smelters	Melting-bath operators	Fork-lift operators	Casters, welders, crushers	Office- -workers
Time-weighted average lead in air, mean $\pm$ standard deviation (μg Pb/m^3)	170 ± 105	135 ± 104	336 ± 555	77 ± 50	—
N	439	29	49	41	113
$\overline{X}$	1.0558	1.0542	1.0573	1.0547	1.0566
S.D.	0.0029	0.0037	0.0029	0.0026	0.0029
Significance by t between $\triangle$ groups					
Smelters	—	**	**	**	**
Melting-bath operators		—	**		**
Fork-lift operators			—	**	
Casters, welders, crushers				—	**
					—

** $p < 0.01$

FIG. 5 – Specific gravity of blood in workers as a function of average lead concentration in air, 1968–1978.

is consistent with the time of measurement. The decrease in specific gravity follows a logarithmic function of the lead concentration in the workshop air. A significant correlation coefficient of $r = -0.320$ ($p < 0.05$ with $N = 37$) is obtained for workers excluding the fork-lift operators. A significant correlation coefficient for the workers could not be established when the fork-lift operators were included ($r = -0.182$ with $N = 45$).

Aerodynamic particle-size and chemical composition

In all 15 samples taken in the smeltery and foundry plants the particles were distributed log-normally by size. The mass-median diameter ranged from 0.5 to 23.5 with an arithmetic average of 8.3 equivalent aerodynamic diameter while the geometric standard deviation ranged from 2.7 to 24.4, as listed in Table 5. On the assumption that particles are spherical with a density of 11.3, which is equal to that of metallic lead, the range of the actual mass-median diameters of lead particles is 0.1–7.0 μm, and the arithmetic average as 2.5 μm. Particulates sampled from a storeroom, one of the fork-lift operators' working areas, were less frequently within a respirable size range (under 5 μm as equivalent aerodynamic diameter) as compared to the particulates collected in the working areas of smelters and melting-bath operators (Table 5). Because the respiratory penetration and retention of particulates decreases reversely as a direct function

TABLE 5

Aerodynamic size of lead particulates following log-normal distribution 1977–1978, stationary sampling by cascade centripeter.

Sampling site	Mass-median diameter (μm)	Geometric standard deviation (μm)	Weight percentage of particles having a diameter < 5 μm (%)
Smelting-furnace	9.8	2.7	25
	8.4	5.5	39
	3.5	6.0	58
	23.5	3.3	10
	0.5	8.5	87
	4.8	5.0	51
	1.1	6.1	81
	1.8	3.7	78
	6.0	5.2	46
	6.7	5.1	43
			52 ± 24[*a]
Storeroom in smeltery plant	7.0	3.9	41
	21.5	5.5	22
	14.6**	4.6**	25**
			29 ± 10[*a]
Melting-bath	1.6	24.4	65
	13.5	19.3	37
			51 ± 10*

[*]Mean ± S.D.
[**]Measured by Andersen's sampler
[a]: t = 2.53, p < 0.05

TABLE 6

Lead compounds identified by X-ray diffractometry.

Compound of lead	Sampling site	
	Smelting-furnace (N = 6)	Storeroom in smelting plant (N = 2)
$PbSO_4$	+	+
α-Pb_3SO_6	+	−
PbS_2O_3	+	−
PbS	+	+
$PbSO_4 \cdot 3PbO \cdot nH_2O$	±	+
$PbSO_4 \cdot 3PbO \cdot H_2O$	±	+
PbO (yellow)	±	±
$PbO \cdot nH_2o$	±	−
Pb_3O_4	±	−
$Pb_9(PO_4)_6$	+	−
$Pb_3P_4O_{13}$	−	+
$Pb_2P_2O_7$	±	+
$Pb(N_3)_2$	+	−
$PbCrO_8$	+	±
$Pb(OH)Cl$	+	−
$Pb_2Cl_3(OH)$	±	+

− not identified; ± not obviously identified; + identified at least in one sample

of the increase in aerodynamic size, the lack of negative biological effect in the fork-lift operators may be due to the lower weight percentage of respirable particulates.

The lead compounds qualitatively identified in 8 particulate samples from stationary sites in the workshop for smelters and fork-lift operators are shown in Table 6. There is a slight change in the chemical composition of lead compounds identified in the two workrooms: compounds such as α-PbS_3O_6, PbS_2O_3, $Pb_9(PO_4)_6$, $Pb(N_3)_2$ and $Pb(OH)Cl$ were found only in samples from the smelting process, and $Pb_3P_4O_{13}$ was found only in samples from the working area of the fork-lift operators. However, it is difficult to draw conclusions regarding the difference between th types of compound from the two different workshops.

REFERENCES

1. *Andersen, A. A*. A sampler for respiratory health hazard assessment. Am. Ind. Hyg. Assoc. J., **27** (1966) 160–165.
2. *Hounam, R.F*. The cascade centripeter. Ann. Occup. Hyg., **8** (1965) 335.
3. *Kusumoto, M. and Toyama, T*. Determination of concentration and size distribution of aerosols. Air-pollution Handbook, Korona Pub., Tokyo, 1975, p. 121–127 (in Japanese).
4. *Kusumoto, M., Toyama, T. and Momotani, H*. Particle-size measurement of respirable dust by cascade centripeter (Hounam and Sherwood). Medical Progress, **65** (1968) 604–610 (in Japanese).
5. *Sherwood, R. J*. On the interpretation of air sampling for radioactive particles. Am. Ind. Hyg. Assoc. J., **27** (1966) 98–109.
6. *Sherwood, R. J. and Hounam, R.H*. The cascade centripeter; A device for determining the concentration and size distribution of aerosols. An. Ind. Hyg. Assoc. J., **26** (1965) 122–131.