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Serum and urinary vanadium of vanadium-exposed workers

by MARKKU KIVILUOTO, M.D.,¹ LAURI PYY, M.Sc.,² and ARTO PAKARINEN, M.D.³

KIVILUOTO, M., PYY, L. and PAKARINEN, A. Serum and urinary vanadium of vanadium-exposed workers. *Scand. j. work environ. & health* 5 (1979) 362—367. In this investigation the environment of vanadium workers was studied. It was found that low concentrations of vanadium (0.01—0.04 mg/m³) in the air do not correlate with vanadium serum levels or its urinary excretion. The results, however, suggest that values of vanadium in serum and urine samples reflect absorption of vanadium because vanadium could not be detected in the urine of referents. In higher vanadium exposure (0.2—0.5 mg/m³), the concentration in the air inhaled remaining unknown due to the use of dust masks, urinary vanadium excretion and serum vanadium level decreased significantly with exposure-free time.

Key words: serum vanadium, urinary vanadium, vanadium, vanadium dust, vanadium excretion, vanadium exposure.

Vanadium is used in the steel industry as an alloy substance to improve the properties of steel, as well as in the chemical industry as a catalyst. Exposure to vanadium is possible during the various stages of its separation, in the steel industry, and in certain branches of the chemical industry. It may also occur when oil- or gas-fired boilers are being cleaned or repaired (2, 19) because some oils and gases contain vanadium.

Vanadium enters the body mainly through the lungs; it is excreted in the urine and, to a minor degree, in feces (3,

14). The injurious effects of vanadium have been described elsewhere (3, 8, 9).

This study was undertaken in the vanadium factory of the Otanmäki Mine of the Rautaruukki Company, Finland, which has been manufacturing vanadium since 1956. The annual output of the factory is up to 2,400 tons. During the process, magnetite is roasted with sodium carbonate into pellets. The roasted product is leached, and vanadium is precipitated from the leach liquor as vanadates.

The "red cake" thus produced is filtered, washed, and smelted into vanadium pentoxide. Controlling vanadium dust has been very difficult at the smelting furnaces and during the packing of the vanadium pentoxide smelt, the processing of the filtered precipitate, and the grinding of laboratory samples.

The concentration of vanadium in the factory air has been measured occasionally in the past. A summary of the previous

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measurements is given in table 1. There it can be seen that in the dustiest work areas the total concentration of vanadium in the air exceeded or was equal to the threshold limit value (TLV) of 0.5 mg/m³ (1). The vanadium concentrations have been determined from the total dust collected during 1–3 h. The urinary vanadium concentrations of the exposed workers had been, in many cases, higher than recommended by the Institute of Occupational Health in Finland (0.6 µmol/l). Therefore thorough measurements of vanadium exposure and determinations of serum and urinary vanadium were undertaken.

MATERIAL AND METHODS

Subjects

The subjects of the study were process workers, dayworkers, repairmen, foremen, and a laboratory worker, 60 men in all. The normal urinary vanadium excretion was measured from 24 referents unexposed to vanadium.

Dust sampling

The concentrations of vanadium in the factory air were determined by measurements covering two shifts just before the biological sampling in March–May 1976. The number of samples taken from the breathing zones was 112, and that of the stationary samples 80. The samples were

taken by methods commonly used by the Institute of Occupational Health in Finland (15, 16).

Biological sampling

In order to determine the excretion rate of vanadium, we measured vanadium from successive blood and 18- to 24-h urine samples (8 men) in December 1975. The first blood samples were taken just before the workers left the factory for 3 d of rest. The second and third blood samples were taken 18 and 42 h after they had left the factory. The urine samples were taken 0–18, 18–42 and 42–66 h after the beginning of the 3-d rest period.

The serum vanadium levels of all the workers exposed to vanadium (60 men) were examined in March–May 1976 at the end of a work shift. At the same time the urine collections for the next 18 h were started to determine the amount of excreted vanadium. In August 1978 we determined the urinary vanadium excretion of the reference group.

Analysis of vanadium

The Millipore filters (type AAWP 03700, pore size 0.8 µm) on which the dust samples were collected were wet ashed with a mixture of nitric acid and hydrochloric acid. The rest was dissolved in 5 % nitric acid. The vanadium concentrations were determined with an atomic absorption spectrophotometer with a flameless graphite atomizer (Perkin-Elmer 300, HGA 74).

Table 1. Previous total vanadium concentrations in the air (mg/m³).

Site or job	Time of measurement							
	Jan. 1957	March 1970	Feb. 1972	April 1972	May 1972	Oct. 1973	March 1974	May 1975
Sintering furnaces (discharge)	0.1	0.1	0.0					
Packing of smelt	3.9	0.9	0.2	0.2	0.05	0.1	0.1	0.6
Smelt furnaces		1.9	0.5	0.2	0.8		1.0	
Packing of precipitate	0.0	0.1	0.3				0.3	
Grinding of samples					1–10			
Sintering furnaces (charging)	0.2							
Filtering		0.01	0.2			0.2		0.5
Pelleting machine	0.1	0.1				0.0		

The sensitivity of the method was 0.002 mg for 1 % absorption, and the coefficient of variation within runs 6 % at a concentration level of 0.05 mg/m³. The particle size was determined by a modified Andreasen sedimentation method (10) from five dust samples, which were taken separately with a high-volume sampler.

The content of vanadium in the urine and serum of the subjects was determined in the Technical Research Center of Finland with an atomic absorption spectrophotometer with a graphite furnace (Perkin-Elmer 503, HGA 72). The reliability of the method was checked with five duplicate urine and serum samples spiked with 0, 0.1, 0.2, 0.5 and 1 µmol/l.

The range of recovery of standard additions was 70–120 %, and the given sensitivity of the method was 0.08 µmol/l. The coefficient of variation within runs of the method was 34 % (random) for the urine

determination at a concentration level of 0.2 µmol/l, and 38 % for the serum determination at the same level.

The urinary vanadium excretion of the referents was determined in the Oulu Regional Institute of Occupational Health (Perkin-Elmer 603, HGA 74). The sensitivity (1 % absorption) of the method was 0.04 µmol/l, and the coefficient of variation within runs at a concentration level of 0.2 µmol/l (spiked samples) was 20 % (random).

Statistical methods

The differences in the urinary excretions and serum levels of vanadium were investigated with the Wilcoxon signed-ranks test. The correlation coefficients between the concentrations of vanadium in factory air, serum, and urine were calculated.

Table 2. Total vanadium concentrations in the air (mg/m³).

Site or job	No. of workers or sites	No. of samples	Range	Time weighted mean concentration
Breathing zone samples covering whole shift	58	112	0.002–0.42	0.028
Breathing zone samples at grinding (1 h samples)	1	2	0.25–4.7	1.7
Stationary samples covering whole shift	15	80	0.002–0.043	0.012
Packing of smelt (1 h samples)	1	7	0.020–0.37	0.13
Grinding room	1	1	2.3	2.3

Table 3. Serum concentration and urinary excretion (18 h) of vanadium and their correlation with vanadium (V) concentration in the air.

Determination	No. of samples	Mean ± SD	Coefficient of correlation
<i>Vanadium group</i>			
Serum vanadium	60	0.22 ± 0.14 µmol/l	
Urinary excretion (18 h)	60	0.26 ± 0.17 µmol	
Serum V vs. total V in breathing zone	60		0.04
Serum V vs. total V in workroom air	60		0.05
Urine V vs. total V in breathing zone	60		0.07
Urine V vs. total V in workroom air	60		0.08
Urinary V vs. V in serum	60		0.04
<i>Reference group</i>			
Urinary excretion (18 h)	24	not detectable	

^a The sensitivity of the determination method was 0.04 µmol/l.

RESULTS

Concentration of vanadium in the air

The concentration of vanadium in the air (table 2) was considerably lower than earlier (table 1). The mean respirable fraction of the dust (particle size $< 5 \mu\text{m}$ in diameter) was 20 %, and the range of variation 6–32 %. Concentrations exceeding the TLV, $0.5 \text{ mg}/\text{m}^3$, were found only during the grinding of laboratory samples. Notable concentrations of vanadium were also found during the packing of smelt. These work periods are very short, and the workers wear dust masks. In the other parts of the factory the vanadium concentration was constantly below $0.1 \text{ mg}/\text{m}^3$.

Urinary excretion and serum level of vanadium

The vanadium values of urine collections and successive serum samples taken from eight workers (filter men and workers who packed and smelted) are shown in fig. 1 and 2.

Due to the dust masks no correlation could be determined between the concentration of vanadium in the air and the biological samples. It was found that the excretion of vanadium in urine and the vanadium level of serum decreased significantly with the time the workers spent out of exposure.

The concentration of vanadium in the serum and the urinary excretion of the 60 vanadium workers and the 24 referents were measured. The results can be found in table 3, along with the correlation coefficients between the vanadium concentration of factory air, serum, and urinary excretion.

DISCUSSION

In the thorough measurements of the vanadium concentrations in the workroom air and respiratory zones carried out in

the vanadium factory, the values measured were $0.01\text{--}0.04 \text{ mg}/\text{m}^3$, which are clearly below the TLV of $0.5 \text{ mg}/\text{m}^3$. These values are considerably lower than corresponding earlier determinations, probably due to the intensified flushing of the floors of work sites that was started at the beginning of 1976. The mean urinary 18-h vanadium excretion of the

Fig. 1. Urinary excretion pattern of vanadium. (Significance of difference between excretions: 42 — 18 h = $p < 0.005$; 66 — 42 h = $p < 0.1$; 66 — 18 h = $p < 0.005$)

Fig. 2. Serum vanadium levels after exposure. (Significance of difference between levels: 18 — 0 h = $p > 0.2$; 42 — 18 h = $p < 0.1$; 42 — 0 h = $p < 0.05$)

exposed workers was 0.26 μmol . The concentration of vanadium in the urine of the referents was below 0.04 $\mu\text{mol/l}$, which was the sensitivity of the vanadium assay. Therefore we did not measure the concentration of vanadium in the serum of the referents. The mean vanadium concentration in the serum of the exposed workers was 0.2 $\mu\text{mol/l}$.

Thus our results agree with Sjöberg's figures of lower than 3 $\mu\text{g/l}$ (0.06 $\mu\text{mol/l}$) for urine and serum (13). On the other hand, for urine, Perry and Perry (11) have reported values of 1–20 $\mu\text{g/l}$ (0.02–0.4 $\mu\text{mol/l}$), and Watanabe et al. (18) 3.5–11.0 $\mu\text{g/l}$ (0.03–0.2 $\mu\text{mol/l}$). Heydorn and Lukens (4) have given 4.6 ± 0.8 $\mu\text{g/l}$ (0.09 ± 0.016 $\mu\text{mol/l}$) as the normal vanadium level of serum. We found no significant correlation between the vanadium concentration in the factory air and the serum level and the urinary excretion of vanadium.

Jaraczewska and Jakubowski (5) have determined the correlation between the vanadium content of the urine and the vanadium concentration in the workroom air. Neither did they find a statistically significant correlation between the two. Vintinner et al. (17) found an increased urinary vanadium excretion for exposed workers. However, they did not state a correlation coefficient between the vanadium concentration of the inhaled air and urinary vanadium excretion. Roshchin and Ordjonikidze (12) claimed that there is a correlation between vanadium in urine and in the air of work sites, but they did not give the coefficient.

In higher vanadium exposure (0.2–0.5 mg/m^3) — the vanadium concentration in the air inhaled remaining unknown due the use of dust masks — the urinary vanadium excretion and serum vanadium level decreased significantly with exposure-free time. In the study of Kent and McCance (6) it was found that vanadium was excreted in urine, for the most part, in a week. They administered vanadium intravenously to two volunteers in their study.

The lack of correlation in our study between a low vanadium concentration (0.01–0.04 mg/m^3) in air and serum and the urinary excretion of it could be due to

the following reasons: a nonuniform distribution of vanadium dust particle size, interindividual differences in inhalation and absorption even though personal dust sample collection was employed, or analytical problems. The detection limit of the method used was just below the concentration measured, and it explains the high coefficient of variation, which could obscure a possible correlation.

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