AMERICAN JOURNAL OF INDUSTRIAL MEDICINE 33:55–60 (1998)

Urine Vanadium Concentrations in Workers Overhauling an Oil-Fired Boiler

Russ Hauser MD, ScD, MPH[1]* Salma Elreedy SM, ScD,[1] P. Barry Ryan PhD[2] and David C. Christiani, MD, MPH[1,3]

Since fuel oil ash contains vanadium (V), the measurement of urinary levels of V may provide a biological marker in workers exposed to fuel oil ash. The usefulness of urine V samples as a biological monitoring tool ultimately depends on determining the appropriate time of sampling relative to when exposure occurs. Twenty boilermakers were studied during the overhaul of a large oil-fired boiler. A total of 117 urine samples were collected, 65 start-of-shift (S-O-S) and 52 end-of-shift (E-O-S) samples. Air V exposures were estimated with personal sampling devices and work history diaries. Air V concentrations ranged from 0.36 to 32.19 μg V/m³, with a mean ±SD of 19.1 ± 10.7, and a median of 18.5. On the first day of work on the overhaul, the V urine levels at the E-O-S (mean ±SD were 1.53 ± 0.53, median was 1.52 mg V/g creatinine) were significantly higher than those at the S-O-S (0.87 ± 0.32, median was 0.83), P *= 0.004. However, the V concentrations of the S-O-S urine samples on the last Monday of the study were not significantly different from the S-O-S urine levels on the previous Saturday, a time interval of about 38 hr between the end of exposure and sample collection. The Spearman correlation coefficient (r) between the S-O-S urine V and the workplace concentration of V dust during the previous day was r = 0.35. In summary, the results suggest a rapid initial clearance of V (elevating the E-O-S V concentration on the first day of work relative to the S-O-S concentration), followed by a slow clearance that is not complete 38 hr after the end of exposure, as evidenced by the Monday morning urine V concentrations. The Spearman correlations suggest that the S-O-S urine is preferred to the E-O-S urine for across-shift biological monitoring of V exposure.* Am. J. Ind. Med. 33:55–60, 1998. *© 1998 Wiley-Liss, Inc.*

KEY WORDS: urine vanadium; biological monitoring; fuel oil ash

INTRODUCTION

Vanadium oxides and vanadium sulfates, known respiratory irritants [Dutton, 1911; Wyers, 1946; Vintinner et al., 1955; Sjoberg, 1956], are found in varying proportions in fuel oil and, consequently, in fuel oil ash [Wyers, 1946; Williams, 1952; Henry and Knapp, 1980]. The concentration of vanadium in the ash is proportional to the amount of oil burned and the oil's vanadium content. During the repair and overhaul of oil-fired boilers, workers are exposed to fuel oil ash containing vanadium. The inhaled respirable vanadium dust is absorbed through the lungs and is subsequently eliminated in the urine. Ingestion of vanadium dust is also a possible route of exposure. Urine is an appropriate medium for biological monitoring of vanadium exposure: it is easy to

[1]Department of Environmental Health (Occupational Health and Environmental Science and Engineering Programs), Harvard School of Public Health, Boston, Massachusetts.

[2]Department of Environmental and Occupational Health, Rollins School of Public Health of Emory University, Atlanta, Georgia.

[3]Pulmonary and Critical Care Unit, Massachusetts General Hospital, Department of Medicine, Harvard Medical School, Boston, Massachusetts.

Contract grant sponsor: National Institute of Environmental Health Sciences; Contract grant number: ES05947; Contract grant number: ES07069; Contract grant number: ES00002; Contract grant sponsor: National Institute for Occupational Safety and Health; Contract grant number: U60/CCU10997; Contract grant sponsor: Environmental Protection Agency; Contract grant number: CR-822061-1-2

*Correspondence address: Russ Hauser, Harvard School of Public Health, Occupational Health Program, Building I, Room 1415, 665 Huntington Avenue, Boston, MA 02115

Accepted 11 August 1997

obtain and has been found to be associated with occupational levels of airborne vanadium [White et al., 1987].

In workers cleaning an oil-fired boiler, White et al. [1987] found urine vanadium levels ranging from nondetectable to 30 mg V/g creatinine. The urine samples were taken at the start of each working day. Sabbioni and Maroni [1985] found similar urinary vanadium levels in workers (i.e., scaffolders, burner operators and welders) overhauling an oil-fired boiler. Urine vanadium levels were within the range of 0.6 to 2.0 mg V/g creatinine in burner operators, 0.7–19.5 mg V/g creatinine in scaffolders, and 2.3–125 mg V/g creatinine in welders. In comparison, studies on nonoccupationally exposed individuals found all urinary vanadium values of $<$0.4 mg V/L [White et al., 1987] and below 0.1 mg V/L [Arbouine and Smith, 1991].

The kinetics of vanadium elimination in the urine are uncertain. Sabbioni and Maroni [1985] studied workers exposed to fuel oil ash during the repair of a large boiler. Their results suggest that vanadium clearance is slow and that there is the possibility of accumulation of vanadium during long-term low-level continuous occupational exposure. An earlier study by Kiviluoto et al. [1979] also showed slow excretion (after an initial rapid excretion) of vanadium in workers processing vanadium pentoxide.

Although there is an incomplete understanding of the kinetics of vanadium excretion, urine vanadium levels can be used as a biological monitor in occupationally exposed workers because of the very low background exposure, and the elimination of vanadium in urine. The usefulness of urine vanadium samples as a biological monitor ultimately depends on determining the appropriate time of sampling relative to when exposure occurs. The present study was designed to determine (1) the range of urinary vanadium levels in workers during the overhaul of a large oil-fired boiler, (2) the relationship between exposure levels of inhalable vanadium dust and urinary vanadium excretion, and (3) the appropriate time of urine sampling for vanadium exposure. When designing biological monitoring programs for workers occupationally exposed to vanadium, the sampling time, such as start-of-shift (S-O-S) versus end-of-shift (E-O-S) urine samples, is an important factor. Therefore, in this study we were specifically interested in the relationship between air vanadium levels and in the S-O-S and E-O-S urine sample.

MATERIALS AND METHODS

The study was approved by the Institutional Review Board of the Harvard School of Public Health (HSPH). The study was explained to the subjects before written and informed consent was obtained. This study population was recruited from participants in a larger study examining the upper and lower respiratory tract responses among workers overhauling an oil-fired boiler [Hauser et al., 1995a,b].

Urine Samples

The subjects were asked to give urine samples prior to the S-O-S and immediately upon finishing a work shift, i.e., at E-O-S. The work shift was 10 hr, from 7:00 AM to 5:00 PM, 6 days a week (Monday through Saturday). The urine samples were collected in 15 ml polypropylene tubes, and stored on ice until arrival at the laboratory, where they were frozen at -20°C until analysis.

The analysis of vanadium in the urine was carried out according to standard operating procedures developed at the HSPH [1994] based on the work of Arbouine and Smith [1991]. The procedure for samples and calibration standards may be summarized as follows: 5 ml of the sample (or standard) is placed into a plastic centrifuge tube, its pH adjusted to pH 1 to 2 by adding 10% (v/v) H_2SO_4 solution, and it is mixed. For chelation, 500 ml of a 5% (w/v) aqueous Cupferron solution is added, and the solution is vortex-mixed for 30 sec and allowed to stand for 10 min. The chelated vanadium is then extracted into 4-methylpentan-2-one by adding 1 ml of the solvent to the sample, vortex mixing it for 30 sec, then mixing it on a mechanical shaker for 10 min. The organic and aqueous phases are separated by centrifugation at 3,000 rpm for 5 min. The organic solvent layer is then removed and stored in a tightly capped container (at 4°C) until it is ready for analysis. The vanadium concentration was determined using a Perkin-Elmer model 4100 ZL graphite furnace atomic absorption spectrometer (GF-AAS) equipped with a THGA graphite furnace, a model AS-70 automatic sampler, and a fume extraction unit.

Analysis of the urinary vanadium sample proceeded according to the standard operating procedure (SOP) at the HSPH [1994]. Quality assurance procedures are specified as part of the SOP. Briefly, a sample batch consisted of 10 samples, a spike, and a blank. Prior to the analysis of a batch, a calibration was performed using sample concentrations of 0.0, 2.5, 5.0, 7.5, and 10.0 ppb. Additionally, a sample of NIST SRM 1648 was dissolved in MIBK and diluted 4 : 1 v/v to produce a known standard in the appropriate concentration range. The calibration curve was then determined and, in accord with laboratory QA procedures [HSPH, 1995], the calibration slope was evaluated. If the slope fell out of the control limits, it was discarded, the instrument was evaluated, and a new curve was run. The extraction fraction associated with the NIST SRM was used to correct the data collected for the sample batch with respect to extraction efficiency. Instrumental and method limits of detection were determined using moving average blank values to ensure that the system remained in control [HSPH, 1995].

Reagent blanks were obtained by performing the above procedure on a sample of deionized water. The reagent blanks were used to determine the method's limit of detection (LOD). The LOD obtained in this study is 0.3 mg

V/L urine. The LOD is defined as three times the standard deviation of the reagent blanks (after adjusting for the volume reduction in going from 5 ml of urine to 1 ml of solvent). The value for the LOD obtained is in good agreement with values quoted in the literature for studies involving solvent extraction and subsequent analysis by atomic absorption spectroscopy: 0.06 mg/L [Buratti et al., 1985], 0.4 mg/L [White et al., 1987], and 0.1 mg/L [Arbouine and Smith, 1991].

Urinary creatinine concentrations were measured to adjust for variability in the dilution of the urine. The vanadium concentration in the urine is then reported as a ratio of the vanadium level to the creatinine level. The determination of creatinine was carried out on a sample aliquot analyzed by Bioran Medical Laboratory (Cambridge, MA), using the alkaline picrate method and following established quality assurance and quality control steps. The range of values observed is 11–446 mg/dl.

Air Sampling

Occupational exposures to inhalable particulate matter with an aerodynamic diameter of 10 μm and smaller (PM_{10}) were assessed with a personal sampling device consisting of a pump and an impactor [Spengler et al., 1989; Thomas et al., 1993]. The personal air samples, collected on a Teflon membrane filter, underwent two sequential acid extractions using a combination of concentrated hydrochloric, hydrofluoric, and nitric acids, modified from procedure by Yamashige et al. [1989]. The vanadium concentration was determined using the previously described GF-AAS instrument. The ratio of the mass of V extracted in the second to first extraction was calculated. This extraction ratio was used to calculate the theoretical mass of V that would be expected if four more extractions were performed. A ''total'' V mass was calculated as the sum of the two actual and the four theoretical extractions. The filter extraction efficiency was determined as a ratio of the actual V mass extracted to the theoretical ''total'' mass of V extractable and was expressed as a percentage; values were within the range of 86–100%. In addition, the bulk extraction efficiency of removing vanadium from fuel oil ash was estimated by determining the percentage of vanadium extracted from Standard Reference Material 1648 (''Urban Particulate Matter'') of the National Institute of Standards and Technology (Gaithersburg, MD). For the exposure-response analyses, the vanadium concentrations were adjusted by both the filter extraction efficiency of the sample batch in which each sample was extracted, as well as the average bulk extraction efficiency (86%).

Every subject completed a self-administered detailed work diary for each day of air sampling. The work diary listed the tasks performed (i.e., welding, cutting and grinding), and the specific location (i.e., boiler, airheater and condenser) at which they were performed. Twenty-nine task/location categories were identified. The mean of the personal air samples (1- to 10-hr time-weighted average) for each task/location category was used as the exposure level assigned to each task/location category. By using the mean exposure for each task/location category, we estimated occupational exposures for each subject on each day; all exposure concentrations represent the mean of the personal air samples for a given task/location.

TABLE I. Boilermaker Subject Demographics and a Description of the Air and Urine Data

	Range	Median	Mean (SD)
Age in years (n = 20)	28–60	43.4	43.1 (8.3)
Years on job (n = 20)	5–35	19	18.6 (7.2)
S-O-S urine V concn (n = 65)[a]	0.30–3.62	0.98	1.15 (0.68)
E-O-S urine V concn (n = 51)[a]	0.19–4.30	1.25	1.44 (1.02)
Air V concn (n = 98)[b]	0.36–32.19	18.5	19.1 (10.7)

[a]Start-of-shift (S-O-S) and end-of-shift (E-O-S) urine vanadium concentration (μg V/g creatinine). Note that the E-O-S urine V concentrations exclude one outlier.
[b]Air vanadium concentration (μg V/m^3)

Data Analysis

Wilcoxon signed-rank tests were used to compare (1) the S-O-S versus E-O-S urine vanadium concentrations on the first day of work on the boiler overhaul, and (2) the S-O-S urine vanadium on the last Monday of the study versus the S-O-S urine vanadium on the previous Saturday (48 h separates these two urine samples). Note that during the overhaul, boiler work was performed on Saturday. Since the workers worked a 10-hr shift on all workdays, the S-O-S urine on the final Monday was performed approximately 38 hr after finishing work on Saturday.

We calculated Spearman correlation coefficients between the S-O-S urine vanadium concentration and the workplace air vanadium concentration during the previous day, as well as between the E-O-S urine vanadium concentration and the workplace air vanadium concentration on that same day. All our statistical analyses were performed with Stata [StataCorp, 1995].

RESULTS

Twenty male boilermakers participated in the present study. Subject demographics and a description of the air and urine data are presented in Table I. A total of 117 urine samples were obtained, 65 at the S-O-S and 52 E-O-S samples. The mean and standard deviation of the S-O-S samples were 1.15 ± 0.68 mg V/g creatinine (range 0.3–3.62), the median was 0.98. The mean and standard

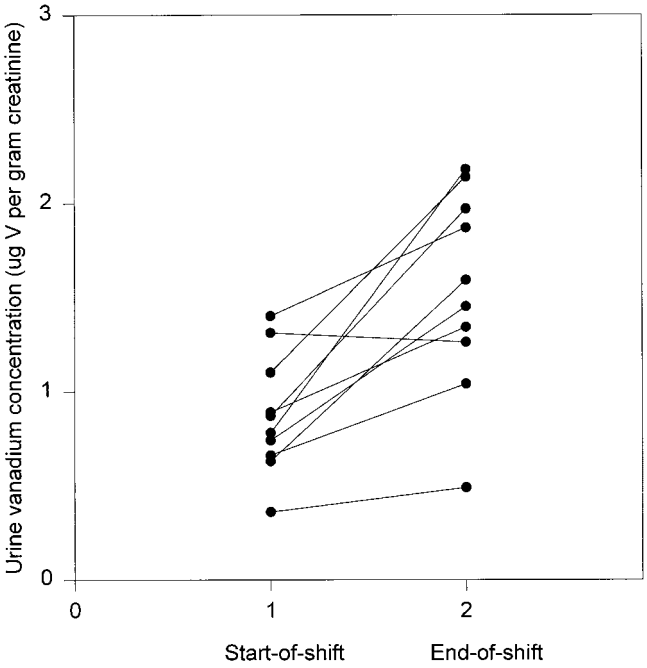

FIGURE 1. Start-of-shift and end-of-shift urine vanadium concentrations on the first day of boiler work. Mean of 10 urine vanadium concentrations (μg V/g creatinine); 10 workers were missing either start or end-of-shift samples. Start-of-shift mean = 0.87 and end-of-shift mean = 1.53; $P = 0.004$.

deviation of the E-O-S samples were 1.44 ± 1.02 mg V/g creatinine (range 0.19–4.30), the median was 1.25. One E-O-S urine sample (43.9 mg V/g creatinine) was dropped from the analysis because it was found to be a statistical outlier, being 10 times larger than the next largest sample concentration. Air vanadium concentrations were within the range of 0.36–32.19 μg V/m^3, with a mean ±SD of 19.1 ± 10.7, and a median of 18.5 μg V/m^3. The OSHA PEL for vanadium is 50 μg V/m^3.

To assess short-term clearance patterns, we compared the urinary vanadium concentrations from the S-O-S and E-O-S samples on the first day of work on the boiler overhaul (defined as the day when the boiler was opened and entered by workers). Prior to the opening of the boiler, the workers were present on site, placing staging and preparing the worksite for the overhaul. The nature of the boilermakers' trade is such that between large commercial boiler overhaul jobs they do not work; the time interval between jobs may be days, weeks, or months. In the present cohort of workers, workers had not worked for at least 17 days prior to being assigned to this job. On the first day of work on the overhaul, the vanadium urine levels at the end-of-shift (median 1.52, and mean ±SD 1.53 ± 0.53 mg V/g creatinine) were significantly higher than those at the S-O-S (median was 0.83, 0.87 ± 0.32 mg V/g creatinine), $P = 0.004$ (Fig. 1). Among the twenty subjects, 10 had both S-O-S and E-O-S urine samples on the first day of work; the 10 subjects without both S-O-S and E-O-S urine samples on the first day of work were not included in this analysis.

The vanadium concentrations of the S-O-S urine samples on the last Monday of the study were compared with the S-O-S urine levels from the previous Saturday, a time interval of 48 hr between urine samples but of only 38 hr between the end of exposure on Saturday afternoon and the sample collection time on Monday morning. The Monday S-O-S urine vanadium levels (median 1.03 mg V/g creatinine) were not significantly different from the Saturday S-O-S urine vanadium levels (median 1.12).

The correlation coefficient (r) for the E-O-S urine vanadium and the workplace concentration of inhalable vanadium dust on that same day was 0.005 (n = 42, nine air measurements were missing). However, the correlation coefficient between the S-O-S urine vanadium and the workplace concentration of inhalable vanadium dust during the previous day was 0.35 (n = 55, 10 air measurements were missing). In Figure 2, the S-O-S urine vanadium concentrations are plotted against the previous day's air vanadium concentrations, which are estimated using personal sampling and work history diaries (the mean of the personal air samples for each task/location category is used as the exposure level for each category). The air vanadium concentrations plotted in Figure 2 are limited to 10 values, corresponding to the ten distinct task/location categories identified in this cohort of workers. The limitation of air vanadium exposure concentrations to 10 values partially accounts for the appearance of Figure 2: the air vanadium

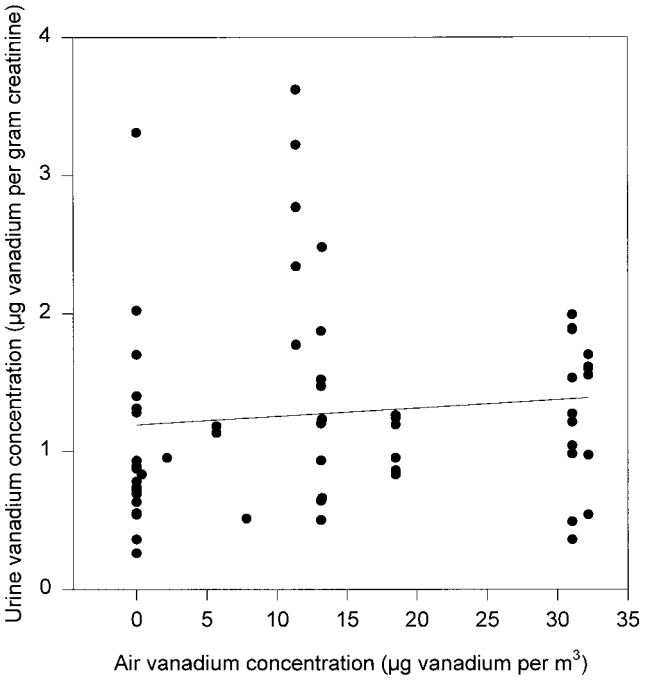

FIGURE 2. Start-of-shift urine vanadium concentrations plotted against previous day's air vanadium concentration.

concentrations (x-axis) are categorical and restricted to 10 distinct values, whereas the urine vanadium concentrations (y-axis) are continuous.

DISCUSSION

In comparison to earlier studies on workers repairing oil-fired boilers [White et al., 1987; Sabbioni and Maroni, 1985], the urine vanadium concentrations in the present study were relatively low. The creatinine adjusted urine vanadium levels in the present study were within the range of 0.19–4.3 mg V/g creatinine, as compared to 0.4–2.8 mg V/g creatinine for burner operators, 2.3–18.8 mg V/g creatinine in scaffolders, and 2.3–125 mg V/g creatinine in welders [Sabbioni and Maroni, 1985]. In the Sabbioni and Maroni study personal exposure concentrations of air vanadium for the workers were unavailable. However, the authors state that exposure is expected to be low for the burner operators working outside the boiler wall and high (though variable) for the scaffolders and welders working inside the boiler. In another study in which 8-hr time weighted average air vanadium levels were high (0.11–6.41 mg/m^3), the urine vanadium concentrations ranged from nondetectable to 30.0 mg V/g creatinine [White et al., 1987]. Possible explanations for the relatively low urine vanadium levels seen in our cohort may include: low air concentrations of vanadium (0.36–32 μg V/m^3 in our study), improved work practices, the type of work performed on the boiler, and the use of respirators. In the present study, workers were offered respirators and some were observed to use them.

Insight into the clearance of vanadium is provided by the observation that the vanadium levels at the E-O-S urine on the first day of work on the boiler are significantly higher than those of the S-O-S urine on the first day of boiler work. This suggests that there is an initial rapid clearance of vanadium, occurring over less than 10 hr, the length of the work shift. In addition to the initial rapid clearance of vanadium, there is evidence that the time needed for complete clearance may be long. This is supported by the lack of a significant difference between the S-O-S urine vanadium on the last Monday at work (after a day away from work following six consecutive days at work) and the previous Saturday urine vanadium level. This suggests that clearance is not complete 38 hr after the end of exposure. These two observations together suggest that, following exposure, there is a rapid initial clearance of vanadium (elevating the E-O-S concentration on the first day of work relative to the S-O-S concentration), but that the clearance is not complete 38 hr after the end of exposure, as evidenced by the Monday morning urine vanadium concentrations. The initial rapid clearance may represent only a fraction of the total vanadium dose, though it may be a large enough fraction to elevate the E-O-S urine relative to the S-O-S (pre-boiler work) urine.

The study by Sabbioni and Maroni [1985] supports our findings of an initial rapid clearance of vanadium followed by a period of slow clearance. In that study, the E-O-S samples were higher than the S-O-S samples. Furthermore, they found that workers sampled 36 hr after the end of exposure continued to show elevated urine vanadium levels as compared to baseline, suggesting that the rate of elimination of vanadium is rather slow. In another study, Kiviluoto et al. [1979] describe a similar clearance pattern: rapid excretion followed by slow excretion.

When designing a biological monitoring program for workers occupationally exposed to vanadium, an important factor to consider is the time of sampling. In the present study, the association between the S-O-S urine vanadium and the previous day's exposure is stronger than the association between the E-O-S urine vanadium and the same day's exposure. This suggests that the S-O-S urine is preferred to the end-of-shift urine for biological monitoring of vanadium exposure. Although the S-O-S urine vanadium and the previous day's exposure to vanadium were associated, the association was not strong (Spearman $r = 0.35$). Possible explanations for the low correlation include (1) the lack of information on respirator usage, (2) exposure misclassification, (3) the use of spot versus cumulative urine samples; and (4) incomplete vanadium clearance from the previous day's exposures.

Information on respirator usage (type and duration) was incomplete and not sufficient to account for it in the analysis; this would produce exposure misclassification and may partially explain the low correlations seen between air and urine vanadium concentrations. For instance, in Figure 2, if individuals exposed to comparatively ''high'' air vanadium levels (>15 μg V/m^3) wore respirators (e.g., half-face cartridge respirators) more often than those working in areas of ''low'' air vanadium levels (below 15 μg V/m^3), the urine vanadium concentrations in the ''high'' exposed workers wearing respirators may actually be lower than that in the ''low'' exposed workers not wearing respirators. Consequently, respirator usage may partially explain the appearance of the data in Figure 2: some of the workers exposed above 30 μg V/m^3 had lower urine vanadium concentrations than some workers exposed at 12–14 μg V/m^3.

Exposure misclassification may have occurred since the mean of the personal air samples for a given task/location category was used to estimate exposure for every workday in a task/location category. The estimation of personal exposure using the task/location category may produce nondifferential misclassification of exposure that would likely attenuate the relationship between exposure and urinary vanadium levels. Therefore, if personal exposure measurements (using sampling devices) had been available for each worker on each workday, the relationship between air and urine vanadium levels may improve.

In addition, the use of spot urine samples may also partially explain the low correlations. One of the limitations of using spot urine samples is that they integrate vanadium exposure over an unknown number of hours. This unknown, and variable, integration time may introduce random variation in the urine vanadium levels relative to air levels, possibly contributing to the low correlations seen. Finally, our observation of no significant difference between S-O-S urine vanadium concentrations on the last Monday of the study compared to the S-O-S urine levels from the previous Saturday, and the clearance rates of Sabbioni and Maroni [1985], half-life = 15 hr, suggest incomplete clearance over a 24-hr period. Therefore, the S-O-S urine vanadium sample may not only reflect exposure from the previous day, but also days prior to that, but with exponentially decreasing amounts.

In summary, the results of this study, designed to determine the appropriate sampling time for urine vanadium in workplace exposure programs, suggest that biological monitoring programs for urine vanadium in workers exposed to fuel oil ash should include a S-O-S urine sample (collected approximately 14 hr after the end of exposure) to monitor exposure from the previous workday. Furthermore, an E-O-S urine sample, though not as strongly correlated with air levels as the S-O-S urine, will detect clearance of vanadium from exposure during the worker's first work shift. Although this study was not designed to investigate the kinetics of vanadium elimination, the results suggest that there may be an initial rapid clearance of vanadium, followed by a more prolonged slower clearance extending to at least 38 hr after the end of exposure. This may suggest a double-exponential decay of urine vanadium concentrations. However, another possibility is that there is one exponential decay and the initial rapid clearance represents the steep part of the curve. Further study is needed to determine the complete kinetics of vanadium elimination, which is essential to improving the utility of urine vanadium levels as a biological monitor for vanadium exposure in both the working population, as well as the general population which is exposed to fly ash from oil-fired power plants.

ACKNOWLEDGMENTS

The authors thank the following individuals for research assistance: Marcia Chertok, Tom Dumyahn, Janna Frelich, Jane A Hoppin, Lucille Pothier, Marlys Rogers, Nick Weidemann, and Dorie Wolf. We thank Michael Nkwah for performing the laboratory work. We also thank Boston Edison Co., specifically Forrest Carr, Director of Safety, and John Embriano, the Outage Coordinator; the staff and boilermakers of the International Brotherhood of Boilermakers, Iron Ship Builders, Blacksmiths, Forgers, and Helpers of Local Lodge No. 29, Quincy, Massachusetts, with a special thanks to their president Paul Meade; and Thomas O'Connor Co., especially James Murray.

REFERENCES

Arbouine MW, Smith NJ (1991): Determination of vanadium in urine and its application to biological monitoring of occupationally exposed workers. Atomic Spec 12:54–58.

Buratti M, Pellegrino O, Caravelli G, Bettinelli M, Colombi A, Maroni M. (1985): Sensitive determination of urinary vanadium by solvent extraction and atomic absorption spectroscopy. Clin Chim Acta 150:53–58.

Dutton WF (1911): Vanadiumism. JAMA 1:1648–1652.

Harvard School of Public Health (1994): ''Trace Metal Analysis Laboratory Standard Operating Procedure. Procedure for Extraction and Analysis of Vanadium in Urine.''

Harvard School of Public Health (1995): ''Trace Metal Analysis Laboratory. Universal Quality Control/Quality Assurance Guidelines.''

Hauser R, Elreedy S, Hoppin JA, Christiani DC (1995a): The upper airway response in workers exposed to fuel oil ash: Nasal lavage analysis. Occup Environ Med 52:353–358.

Hauser R, Elreedy S, Hoppin JA, Christiani DC (1995b): Airway obstruction in boilermakers exposed to fuel oil ash: a prospective investigation. Am J Respir Crit Care Med 152:1478–1484.

Henry WM, Knapp KT (1980): Compound forms of fossil fuel fly ash emissions. Environ Sci Technol 14:450–456.

Kiviluoto M, Rasanen O, Rinne A, Rissanen M (1979): Effects of vanadium on the upper respiratory tract of workers in a vanadium factory. A macroscopic and microscopic study. Scand J Work Environ Health 5:50–58.

Sabbioni E, Maroni M (1985): A study on vanadium in workers from oil fired power plants. Commission of the European Communities. Environmental and quality of life. Report EUR 9005 EN.

Sjoberg S-G (1956): Vanadium dust, chronic bronchitis and possible risk of emphysema: A follow-up investigation of workers at a vanadium factory. Acta Med Scand 154:381–386.

Spengler JD, Ozkaynak H, Ludwig J, Allen G, Pellizzari ED, Weiner R (1989): Personal exposures to particulate matter: Instruments and methodologies of P-TEAM. In ''Proceedings of EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants.'' Raleigh, NC: APCA (VIP 13), Pittsburgh, pp 449–463.

StataCorp (1995): ''Stata Statistical Software: Release 4.0.'' College Station, TX: Stata Corp.

Thomas KW, Pellizzari ED, Clayton CA, Whitaker DA, Shores RC, Spengler J, Ozkaynak H, Froehlich SE, Wallace LA. (1993): Particle total exposure assessment methodology (PTEAM) 1990 study: Method performance and data quality for personal, indoor, and outdoor monitoring. J Exp Anal Environ Epidemiol 3:203–226.

Vintinner FJ, Vallenas R, Carlin CE, Weiss R, Macher C, Ochoa R (1955): Study of the health of workers employed in mining and processing of vanadium ore. Arch Ind Health 12:635–642.

White MA, Reeves GD, Moore S, Chandler HA, Holden HJ (1987): Sensitive determination of urinary vanadium as a measure of occupational exposure during cleaning of oil fired boilers. Ann Occup Hyg 31:339–343.

Williams N (1952): Vanadium poisoning from cleaning oil-fired boilers. Br J Ind Med 9:50–55.

Wyers H (1946): Some toxic effects of vanadium pentoxide. Br J Ind Med 3:177–182.

Yamashige T, Yamamoto M, Sunahara H (1989): Comparison of decomposition methods for the analysis of atmospheric particulates by atomic absorption spectrometry. Analyst 114:1071–1077.