MONITORING OF OCCUPATIONAL EXPOSURE IN MANUFACTURING OF STAINLESS STEEL CONSTRUCTIONS. PART I: CHROMIUM, IRON, MANGANESE, MOLYBDENUM, NICKEL AND VANADIUM IN THE WORKPLACE AIR OF STAINLESS STEEL WELDERS

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Abstract

Exposure to workplace airborne pollutants was examined in a group of 20 workers dealing mainly with welding, polishing, drilling and assembling of stainless steel constructions. Monitoring of airborne particulate matter (APM) was performed using both personal and stationary samplers. For the personal full-shift monitoring, a SKC 224 PCRX-4 constant flow rate pump was used which was connected to a sampling head with mixed cellulose matched-weight filters having a diameter of 32 mm and a 0,8 μm pore size. The constant flow rate amounted to 2 L min^{-1}. For the stationary sampling, the "Gent" stacked filter unit PM10 sampler was used, operating at a flow rate of 16 L min^{-1}. It collects particles having an equivalent aerodynamic diameter (EAD) of less than 10 μm in the separate "coarse" (2-10 μm EAD) and "fine" (< 2 μm EAD) size fractions on two sequential polycarbonate (Costar, Nuclepore) filters with a 47 mm diameter. The filters of both types were analyzed by instrumental neutron activation analysis (INAA). Of the elements determined, results for chromium, iron, manganese, molybdenum, nickel and vanadium are presented. Procedures of quality assurance of both sampling and analytical stages are described. Sampling of biological material for elemental analysis (hair, nails, urine and blood and/or serum) of exposed and control persons in contamination-free conditions was also performed. In addition, saliva samples were collected for studying immunological and genotoxicity aspects of occupational exposure.

1. INTRODUCTION

The substances with the known and/or possible adverse health effects in occupational settings are numerous. Workers in mining, metal refining and metal working industries are exposed to airborne particulate matter containing various levels of metals with known neurotoxicity, genotoxicity, carcinogenic, allergenic and immunological effects [1]. In manufacturing of stainless steel constructions, the main health risk is associated with inhalation of welding fumes and APM originating from manufacturing of the constructions, which contain elevated levels of steel-alloying elements, such as Cr, Mo, Mn, Ni, V, etc. A growing need to harmonize activities in the field of toxicological methodology and approaches to risk assessment results in the expanding use of both direct and biological monitoring as has already been pointed out in our previous report [2].

In the present work, occupational exposure was examined in a group of 20 workers of a plant manufacturing storage and production vessels for the pharmaceutical, food and chemical industries made of austenitic stainless steel containing on average 18 % of Cr, 2-2.5 % of Mo, 1-2 % of Mn, 9-10 % of Ni and traces of V (~ 0.01 %). The main sources of exposure to these

metals are welding fumes and APM originating from polishing, shaving and drilling of the vessels and/or stainless steel sheets from which the vessels are made. Exposure to workplace airborne pollutants was monitored using both personal and stationary samplers. Multielemental analysis of airborne particles on filters was carried out by INAA. For biological monitoring, samples of hair, nails, blood, urine and saliva were collected. Of these, multielemental analysis of hair and nails by INAA will be performed, while the elements of the main concern, i.e. chromium, manganese and nickel will be determined in urine, and the elements chromium and manganese also in serum and blood, respectively, by neutron activation analysis with radiochemical separation (RNAA). The blood and saliva samples will also be used for immunological and genotoxicity testing.

2. METHODS

2.1. Subjects and their exposure

The group of exposed workers consisted of 18 men and 2 women of the average age of 43 years who have been working in the plant for various periods of time, and were occupationally exposed to welding fumes and/or APM originating from various activities in the production of stainless steel vessels, mainly shaving and polishing. Only women of this group were involved in one type of activities (polishing), men were changing their activities during a week (or even during a shift). Workers involved in polishing were equipped with respirators, while welders did not use them.

The control group was formed by 20 men (of a similar age structure as in the exposed group) employed in an agricultural enterprise located about 5 km from the plant producing stainless steel vessels.

2.2. Sampling of airborne particulate matter

For the personal full-shift monitoring, an SKC 224 PCRX-4 (USA) constant flow pump was used connected to a sampling head with mixed cellulose ester (MCE) matched-weight filters having a 32 mm diameter and a 0.8 μm pore size (SKC Cat. No. 225-502). The constant flow rate was set to 2 L min^{-1} and checked with the aid of a flow meter three times during sampling. Each worker was sampled twice for the whole 8-hour shift (working activities took place usually in the range of 6 to 7 hours).

Stationary sampling was carried out in the center of the assembling hall (50 x 40 x 5 m), where all welding, polishing and assembling activities were carried out. The "Gent" stacked filter unit was employed with the PM10 inlet and stacked cassette with two sequential polycarbonate (Nuclepore) filters of a diameter of 47 mm with a pore size of 8 μm and 0.4 μm, operating at a flow rate of 16 L min^{-1}. Under these conditions, size fractionating of APM occurs so that the former filter collects APM having equivalent aerodynamic diameter (EAD) in the range of 2-10 μm EAD (so-called "coarse" fraction), while the latter filter collects APM with EAD < 2 μm (so-called "fine" fraction).

2.3. Sampling of biological material

Blood and urine for elemental analysis were sampled in conditions preventing external contamination as much as possible. Both exposed workers and controls took shower and were given a clean laboratory coat prior to sampling. Approximately 5 mL of blood were obtained from cubital vein using a Teflon canula that was first flushed with 15 mL of blood collected for immunological and genotoxicity testing. Blood was collected in a polyethylene (PE) cryogenic vial (Nalgene) that was pre-cleaned as given below. About 1 mL of blood was

immediately transferred to another Nalgene vial for determination of manganese, while the rest of the sample was centrifuged to obtain serum for chromium determination. About 1 to 1.5 mL of serum was placed into a pre-cleaned vial made of synthetic quartz (Suprasil AN, Hereaus). The quartz vial was closed with an acid leached Teflon stopper. All manipulations on blood sampling and handling were performed in the stream of clean air obtained from a mobile filtration unit with ULPA filters (Holten) providing Class 10 environment. Spot samples of urine were collected in acid leached polystyrene vials. All samples were deep-frozen for storage and will be freeze-dried prior to analysis. Hair and nail samples were obtained by clipping with stainless steel scissors. While the IAEA recommended procedure was employed for hair washing (acetone-water-water-water-acetone) [3], the adapted procedure described elsewhere [4] was used for nail cleaning. All collection vials and laboratory ware used for sampling and sample handling (except for Teflon canulas) was pre-cleaned by leaching in dilute sub-boiled nitric acid for 24 hours and washing with deionized water in a clean laboratory providing Class 100 environment.

2.4. Instrumental neutron activation analysis (INAA)

The samples of APM on filters of both types were packed for irradiation in acid leached disk shaped PE capsules of a diameter 15-25 mm made by heat-sealing of PE foils 0.15 mm thick. Synthetic multielement standards were prepared by weighing out 20-50 μL aliquots containing known amounts of elements onto disks of chromatographic paper Whatman, air drying and heat-sealing into PE capsules. Their geometrical parameters (shape and thickness) matched that of the samples.

The samples and standards were irradiated in the Be reflector of active core of a nuclear reactor VVR-15 of the Nuclear Research Institute Rez, plc. at a thermal neutron fluence rate of 1.10^{14} cm^{-2} s^{-1}. Short-time irradiation (1 min.) was carried out with the aid of a pneumatic facility with the transport time of 4 s. The samples and standards were irradiated in PE rabbits individually, together with neutron flux monitors (5 μg of gold prepared as the standards) to check the neutron flux gradient, and were rigidly held in place with polystyrene blocks to ensure the reproducible irradiation geometry. For long-time irradiation (2 hours) in aluminum cans, about 30 samples and standards were placed together in one can to form a column and the neutron flux monitors were inserted between each set of 5 samples and/or standards to check the axial neutron flux gradient.

After irradiation, the PE capsules with the samples and standards were cleaned on their surface with water and ethylalcohol. Short-lived radionuclides were counted using a coaxial HPGe detector (Ortec, rel. efficiency 11 %, FWHM 1.75 keV for the 1332.5 keV photons of ^{60}Co) and associated linear electronics capable of maintaining high count rates. Both decay and counting times were 5 min., the counting geometry was 7 cm. Intermediate and long-lived radionuclides were counted with another coaxial HPGe detector (PGT, rel. efficiency 21 %, FWHM 1.85 keV for the 1332.5 keV photons of ^{60}Co). The Nuclear Data 699 Loss Free counting module according to Westphal was employed in the electronic chain of both detectors to perform the necessary corrections for the variable count rate and dead time. Two counts were performed after long-time irradiation, the first after the decay time of 4 days for 30 min. (counting geometry 1 cm), the second after one month of decay for 2-3 hours in the same counting geometry as in the first count. The Nuclear Data software for NAA was employed for data reduction. Other details of counting equipment and parameters of radionuclides employed have already been given earlier [5].

Although about 40 elements were determined using the above-described procedures the results for Mn, V, Mo, Cr, Ni and Fe are only reported due to their relevance for this study.

2.5. Radiochemical neutron activation analysis (RNAA)

For ultratrace determination of chromium in biological materials the RNAA procedure according to GREENBERG and ZEISLER [6] has been adapted to meet requirements of this study, namely to minimize blank values originating from treatment of irradiated vials after irradiation.

About 2 ml vials made of high-purity synthetic quartz (Suprasil AN, Hereaus) were cleaned prior to irradiation by leaching in subboiled dilute nitric acid, steamed out with demineralized water and dried in a laboratory providing Class 100 environment. The ampoules were sealed using a glassblower torch made of quartz and irradiated for 20 hours at the above given fluence rate. Since a high pressure is created by irradiation of biological samples in our experimental conditions, it is necessary to cool down the ampoules with samples in liquid nitrogen, to open the ampoule by crashing, and to process the quartz splinters together with the sample. This gives rise to a blank value of chromium from the processing the quartz splinters, even when the high-purity quartz ampoules are used. Therefore, several decomposition procedures prior to radiochemical separation were tested to find conditions yielding the lowest blank value. This was achieved by leaching the splinters in fuming nitric acid in the presence of 4 mg of inactive Cr carrier for 1 hour. During this time the majority of biological samples are solubilized (as was tested with serum which belongs to one the most difficult samples to decompose), so that the quartz splinters can be filtered off and the procedure can be continued as follows. To the sample solution 3 mL of conc. sulphuric acid are added and the mixture is heated in a Kjehldal flask using a strong gas burner until the sample starts to char. Then 4 x 1 mL of conc. nitric acid is carefully added, fumed off, and after cooling 1 mL of conc. perchlorid acid is added. The solution is then heated until white fumes appear and the solution becomes orange due to Cr oxidation to Cr(VI). After cooling, 5 mL of water and 1 mL of a $KMnO_4$ solution (10 mg mL^{-1}) are added, the solution is heated to about 150^{O}C, cooled down and transferred to a 50 mL separation funnel to which 25 mL of a 2.5 mol L^{-1} HCl solution are added. The solution is extracted with 2 x 10 mL of a 5 % solution of tribenzoyl amine in chloroform and the organic phases are combined. The combined organic phase is washed with 5 mL of water for 30 s to strip the activity of ^{65}Zn that is partially co-extracted with ^{51}Cr and would increase background for gamma-ray spectroscopy measurement of low activities of ^{51}Cr. The ^{51}Cr activity is stripped from the organic phase for counting with a solution of 3 % NH_4OH, and 5 mL of the water phase are taken for counting with the aid of a well-type HPGe detector. The separation yield of chromium amounts to 89 to 91 % as found in tracer experiments. The chromium blank value using this procedure is well reproducible and a reasonably low (0.050 ± 0.002 ng per ampoule weighing about 1.45 g) to allow sufficiently accurate determination of chromium in serum. Obviously, long counting times are required, at least 10 hours even in a 125 cm^3 well-type HPGe detector, as used in our experiments, to be able to measure such low chromium concentrations.

For ultratrace determination of manganese and nickel in biological materials, RNAA procedures have already been developed earlier [7,8]. No problems are expected regarding a blank value for manganese, because no significant pressure is created on short-time irradiation, which is carried out in PE vials, so that the sample can easily separated from the irradiation container. In case of blank problems in nickel determination, the original decomposition procedure can be adapted as for the chromium RNAA procedure.

3.1. Quality assurance

3.1.1. Quality control of personal sampling of APM

The mass difference of matched-weight SKC filters for personal samplers is guaranteed by the producer to be within 50 μg. To check this, seven cassettes were dismounted and both filters (later on used for determination of element blank values) were weighed using a microbalance (Sartorius) with readability of 1 μg. The mass differences in the range of 8 μg to 50 μg (mean 18 μg) were found in agreement with the producer specification. The mass of APM collected in the described conditions amounted to 0.240 to 6.950 mg (mean 1.291 mg). Thus, for the mean mass of APM the error due to the mean mass difference of the filters is only 1.4 % (when element concentration is given as mass fraction), while for the lowest mass of APM collected this error is 7.6 %. Thus, it seems that the expression of element concentrations in mass per volume may provide more accurate data, because the flow rate through the sampler can be checked several times during the sampling period and the possible deviations from the preset flow rate can be accounted for.

The elemental composition of APM deposited on the backing SKC filter (after passing the upper filter) was also measured in 8 randomly selected matched-weight pairs of filters. The relative values of element contents found on the backing filter are given in Table I.

TABLE I. ELEMENT CONTENT IN THE BACKING FILTER OF MATCHED-WEIGHT PAIRS OF SKC FILTERS (RELATIVE TO THE UPPER FILTER)

Element	Cr	Fe	Mn	Mo	Ni	V
Range (%)	0.45 – 4.65	0.43 – 4.69	0.12 – 1.35	0.23 – 3.59	0.42 – 6.15	< 0.3 – 1. 33
Mean (%)	2.00 ± 1.28	1.86 ± 1.28	0.53 ± 0.40	1.27 ± 1.24	1.97 ± 1.76	-

The highest values were always found in the same filter, indicating that the quality of the filters is obviously responsible for the differences in the amount of a particular element (and the amount of APM) passing through the upper filter.

3.1.2. Quality control of elemental analysis of APM by INAA

The quality control of INAA was pursued by co-analyzing about 4 mg aliquots of NIST SRM 1648 Urban Particulate Matter with the loaded filters. The results obtained are compared with NIST and/or literature values in Table II. It is obvious that our results agree very well with NIST values for Cr, Fe and Ni within the uncertainty margins. Significantly lower values were found for V and Mn compared with NIST certified and information, respectively. However, our results for these elements are in excellent agreement with those we have been finding for several years in our laboratory, and which were also obtained in a separate study which demonstrated that NIST values are positively biased by about 10 % [9]. Also the mean value found for Mo in this work agree well with the literature value [10] and with our previous results [9].

TABLE II. RESULTS FOR ABOUT 4 MG ALIQUOTS OF NIST SRM-1648 URBAN PARTICULATE MATTER (MG KG^{-1} UNLESS OTHERWISE INDICATED)

Element	Cr	Fe*	Mn	Mo	Ni	V
This work (Mean ± SD; N=6-8)	399 ± 22	3.915 ± 0.094	779 ± 16	20.5 ± 2.1	79 ± 4	125 ± 3
NIST value**	403 ± 12	3.91 ± 0.10	860	-	82 ± 3	140 ± 3
Lit. value [9,10]			768–791	18.2 ± 1.9		126-128

* - content in %

** - certified values are those associated with uncertainties

Another quality control exercise consisted in taking part in an intercomparison run on welding fumes loaded on filters, which was organized within this CRP. The results obtained for Cr, Fe, Mn, Ti, and other elements were submitted to the co-ordinator (Dr. J.M. Christensen) for evaluation and their quality will be reported separately.

3.2. INAA results of APM collected using personal and stationary samplers

The workers of the plant manufacturing stainless steel vessels were not assigned fixed working activities during the sampling, which took one week. It seems that, at least part of the workers is changing their activities regularly. Although each subject was sampled twice during the week, no attempt was made to evaluate exposure of a particular worker, because the results would not be comparable for those who changed their activities. Evaluation of personal exposure will be done in a later stage when results of biomonitoring are available. Then, correlation between the results of the direct monitoring and biomonitoring may be studied. In the present evaluation, the workers studied were rather considered as independent subjects and were grouped for evaluation according to the prevailing working activity into 3 categories: welding (W), polishing (P) and other activities, such as cutting stainless steel sheets, drilling, assembling of the vessels (O). Results of exposure to the studied elements within these groups using personal samplers are given in Table III. Since most of the results were not normally distributed (as can be inferred from a comparison of the arithmetic and geometric means and the median), the median value appears to be the most appropriate for comparing exposure among the studied groups. It follows from Table III that the highest concentrations were found in the breathing zone of welders for Cr, Mn and Mo, while for Fe and Ni the highest concentrations were found in the group of workers dealing mostly with polishing (part of their activities was also welding). About the same values for V vanadium were found in these groups, although this element is not contained in the type of steel manufactured in a high concentration. The lowest values for all elements were found in the group of workers dealing with drilling and assembling of the stainless steel vessels as was expected. If we compare the median values in the individual groups with those for welders, i.e. W/W, P/W, O/W we obtain the following ratios; for Cr 1, 0.97, 0.26; for Fe 1, 1.24, 0.42, for Mn 1, 0.45, 0.24; for Mo 1, 0.57, 0.22; for Ni 1, 1.36, 0.28; for V 1, 1.04, 0.30.

In the specification of the employed personal samplers no information has been found regarding the particle size distribution of APM collected. Therefore, it has been considered important to measure the elemental composition of APM collected in two size categories using the Gent stacked filter unit, i.e. the particles with EAD 2-10 μm and < 2 μm, which was positioned in the centre of the assembling hall where all welding, polishing and other activities take place. The results obtained in four whole-shift sampling campaigns are shown in Table IV.

TABLE III. EVALUATION OF EXPOSURE TO SELECTED METALS USING PERSONAL SAMPLERS (ELEMENT CONCENTRATIONS IN μG M^{-3})

Element	Cr	Fe	Mn	Mo	Ni	V
Working category W (N=15)						
Range	19.5-169	60.3-595	4.5-109	0.27-9.7	5.0-39.9	0.10-0.68
Arith. Mean	63.2	214	29.4	2.25	19.0	0.26
Geom. Mean	49.1	176	19.1	1.28	15.6	0.21
Median	56.4	170	18.1	1.45	17.7	0.23
Working category P (N=9)						
Range	2.6-260	17.9-1017	1.6-81.3	0.03-4.2	1.1-118	0.021-0.79
Arith. Mean	95.5	345	17.3	1.86	38.5	0.31
Geom. Mean	53.3	208	9.6	0.99	21.5	0.22
Median	54.5	211	8.1	0.82	24.0	0.24
Working category O (N=15)						
Range	7.6-35.8	32.5-240	3.2-10.5	0.14-0.60	2.7-14.5	0.041-0.17
Arith. Mean	17.8	89.3	5.3	0.34	6.7	0.085
Geom. Mean	16.1	78.0	5.0	0.31	5.8	0.078
Median	14.4	71.1	4.3	0.32	4.9	0.069

TABLE IV. ELEMENTAL COMPOSITION OF SIZE FRACTIONATED APM IN THE WORKPLACE AIR (ELEMENT CONCENTRATIONS IN μG M^{-3})

Element	Cr	Fe	Mn	Mo	Ni	V
"Coarse" fraction (EAD 2 –10 μm)						
Range	5.49-15.2	31.7-46.4	2.60-5.86	0.015-0.087	1.81-4.81	0.029-0.072
Median	9.23	44.3	3.16	0.034	3.57	0.042
"Fine" fraction (EAD < 2 μm)						
Range	1.32-2.48	3.34-6.17	0.73-1.51	0.093-0.54	0.35-0.53	0.005-0.007
Median	1.36	3.58	1.16	0.15	0.39	0.0069

The results obtained using both types of samplers are difficult to interpret, especially from the point of view of their location (the breathing zone of workers versus the common workplace air in the assembling hall). Nevertheless, the results for the size fractionated APM show that the element concentrations in the respirable "fine" fraction are much lower compared with those in the "coarse" fraction. This seems to indicate that the values measured using the personal samplers may be misleading for the assessment of health risks, because they do not provide information on the element amount that may be inhaled.

4. PLANS FOR FUTURE WORK

In the next period, the study will be completed by elemental analysis of the biological material collected. The elements Cr, Fe, Mn, Mo, Ni and V will be determined in hair and nails in subjects of the exposed and control groups by INAA, while the elements Cr, Mn and Ni will be determined by RNAA in urine, Mn in whole blood and Cr in serum of subjects of both groups. The results for both groups will be compared, correlations between the data obtained by direct and biological monitoring of the occupationally exposed workers will be examined, and the results of the genotoxicity and immunological testing will be taken into account for the assessment of health risks associated with the described occupational exposure.

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