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MONITORING OF EXPOSURE TO SELECTED METALS IN WORKERS OF A FERROALLOY PRODUCTION PLANT USING NAA AND PIXE

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ABSTRACT

Advantages and pitfalls of direct and biological monitoring of occupational exposure are briefly mentioned and a project aimed at evaluating exposure to chromium (and possibly manganese) in workers of a ferro-alloy production plant using both the above approaches is outlined. Facilities for NAA and PIXE at the Nuclear Physics Institute at Rez to be used in the project are described. Results of quality assurance of INAA method for analysis of workplace air born particulate matter and blood sampling are presented. Results from previous work relating to this Co-ordinated Research Programme - studying exposure of workers of a vanadium pentoxide production plant are also briefly reviewed.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

In connection with the prevention of the adverse health effects of harmful substances in occupational and environmental settings, there is a growing need to harmonize activities in the field of toxicological methodology and approaches to risk assessment [1]. The results of direct monitoring, i.e. the assessment of exposure from a concentration in air, water, food, workplace, etc., may be misleading, if various mechanisms of intake and/or absorption lead to a different burden of the organism, if multiple mechanisms of intake are to be considered, and especially if short- and long-term effects are to be distinguished [2]. Therefore, in the assessment of health risk arising from environmental, occupational and accidental exposure to toxic metals and other substances, the use of biological monitoring is steadily increasing [3-5]. This approach is facilitated if reliable biological indicators of exposure, such as changes of a concentration of the substance of interest, its metabolites, and other specific species in indicator or target tissues, are well established.

Both approaches will be used to study exposure in workers of a ferro-alloy production plant in Slovakia (at Istebné, the Orava region) where alloying compounds for the steel industry, such as ferrochromium, ferromanganese, ferrosilicon, etc. are produced. Exposure to chromium will be of the main concern owing to allergic and carcinogenic effects of the element in the Cr^{VI} form. Toxicity of chromium is mainly due to Cr^{VI} that can be absorbed mainly by the respiratory tract. Chromium compounds are also easily absorbed through the skin. Besides direct monitoring of exposure by determining a chromium concentration in the workplace air, the element concentration in serum, erythrocytes, urine, hair and nails will be studied in exposed and control persons. In serum chromium occurs as Cr^{III} and is bound to serum proteins, especially transferring and albumin. The hexavalent chromium absorbed during inhalation rapidly penetrates the erythrocyte membrane, is then reduced to Cr^{III} and binds predominantly to haemoglobin [6]. Thus, a ratio of chromium concentrations in serum and erythrocytes in exposed persons may provide useful information about dynamic changes of the element concentrations during exposure. Chromium in urine measurements appear the most suitable indicator for biological monitoring [6], while the element content in hair and nails may provide additional information about the chromium exposure.

Exposure to manganese, which has adverse effects on the central nervous systems and the lungs, may be studied in a similar manner as well. This will depend on availability of a facility for short-time irradiation for NAA which is presently being reconstructed.

2. METHODS

2.1 Sampling and sample handling

A respirable portion of air particulate matter (APM) in the workplace air will be collected in two size fractions with the aid of personal samplers (SKC, USA) with PM10 and PM2.5 inlets.

Analytical requirements for measurement of both elements in blood and urine are very stringent, because there is a high risk of contamination on sampling and sample handling. A stainless steel needle cannot be used for blood collection. Therefore, needles siliconized on the inside from two producers (SARSTEDT, BECTON DICKINSON) that are recommended for trace element analysis were tested, as well as collection vials from both producers, i.e. plastic S-Monovette® vials and siliconized glass Vacutainer® vials, respectively. The test were performed by simulating blood collection from acid-washed polyethylene (PE) vials which contained serum obtained by reconstitution of Versieck's 2nd Generation Biological Reference Material (uncontaminated freeze-dried human serum) [7] with certified concentrations of chromium and manganese. The serum was reconstituted with demineralized water in an acid-cleaned polyethylene (PE) vial and warmed up to 37^0C. Then, blood sampling was simulated by puncturing the PE vial with the needle and by collecting 5 mL of the reconstituted serum which was subsequently left in the collection vial for 1 hour. Chromium and manganese contents in the serum were determined by ET-AAS at the Institute of Analytical Chemistry, Trace Element Laboratory, Prague, in Class 100 environment, because the Rez nuclear reactor was out of operation for a considerable part of 1997.

Real sampling and sample handling prior to analysis will be performed in class 10 environment provided by prefilters and ULPA filters contained in a transportable module for air filtration (Holten, Denmark). Prior to collection of venous blood, cleaning of the skin will be performed with deionized water and ethylalcohol, because both chromium and manganese are excreted by sweat in concentrations that exceed those found in serum of normal persons several times [6]. After separation of serum and erythrocytes, both blood components will be freeze-dried prior to analysis.

Spot samples of urine will be collected in acid-washed PE vials and freeze-dried as well.

Hair and nail samples will be cut with scissors and/or a clipper and external contamination will be removed by the IAEA standardized procedure [20] and by an adapted IAEA procedure, respectively, which has been described elsewhere [2].

2.2. Analytical methods

2.2.1. Neutron activation analysis

Instrumental neutron activation analysis (INAA) and proton induced X-ray emission (PIXE) will be used for analysis of APM samples, while radiochemical neutron activation analysis (RNAA) will be employed for low level determination of Cr (and possibly Mn) in biological samples.

For INAA and RNAA, facilities for both short- and long-time irradiations are available at the LWR-15 nuclear research reactor of the Nuclear Research Institute Rez, plc. in which a thermal neutron fluence rate of 8×10^{13} cm^{-2} s^{-1} is available. Gamma-ray spectrometric measurements are performed using several HPGe detectors with relative efficiency ranging from 11 to 52% and a FWHM resolution of 1.75 to 1.85 keV (both for the 1332.4 keV photons of ^{60}Co) and a well-type HPGe detector with an active volume of 125 cm^3 and the FWHM resolution of 1.95 keV. Several software packages for gamma-ray spectra evaluation (NUCLEAR DATA software, DEIMOS [8], HYPERMET for PC [9]) and calculation of the final results (ND software, KAYZERO/SOLCOI [10]). INAA procedures will be used similar to those validated for analysis of APM samples in ambient air that have already been described earlier [11]. For low level determination of chromium, a

RNAA procedure developed by Greenberg and Zeisler [12] is presently being adapted, while another RNAA procedure for low level determination of manganese in biological samples has been developed in our laboratory earlier [13].

2.2.2. PIXE

The following PIXE experimental set-up is available at the NPI. A beam of protons with the energy of 1.31 MeV and 2.35 MeV is obtained from a Van de Graaff accelerator. The lower energy is more suitable for the excitation of elements with lower atomic numbers (up to Mn), whereas the higher energy is favourable for determination of elements with higher atomic numbers. The beam collimated to a diameter of 5 mm enters a vacuum target chamber after passing through a thin Al diffusion foil which is used as part of a monitoring system and simultaneously, to improve the homogeneity of the beam. In this arrangement, a relatively high irradiation current can be used and the influence of the possible sample micro-homogeneity is reduced. The bombardment is performed to achieve a collected charge of 10 μC and 50 μC for the lower and higher energy of protons, respectively. The chamber is equipped with a sample changer for 7 samples fixed in standard polyframes. Characteristic X-rays induced by protons are allowed to leave the chamber through a thin exit window formed by a 10 μm mylar foil and are measured employing a Si(Li) detector (active area 80 mm^2) with a Be window coupled to a Canberra ACCUSPEC PC-based analyser through the standard associated electronics. A sample-to-detector distance is 30 mm, the FWHM energy resolution of the system amounts to 180-190 eV for the 5.9 keV X-rays of Fe. Outside the chamber, between the exit window and the detector, a suitable X-ray attenuation filter can be inserted. Determination of a proton dose is carried out by measuring a number of protons scattered from the Al foil using a surface barrier Si(Au) detector connected to a separate counter. For the X-ray spectra evaluation, a programme package PIXE-NPI developed at the NPI is available.

3. RESULTS

3.1. Quality assurance of the present study

Great care is devoted to quality assurance of both sampling and analytical stages of the project to be able to arrive at valid results. Quality assurance of air pollution studies is hampered by lack of suitable certified reference materials, i.e. air particulate matter (APM) on a filter. In our previous INAA studies we have been using small 0.5 mg to 15 mg aliquots of NIST SRM 1648 Urban Particulate matter. Our results for chromium and many other elements agreed well with the NIST certified or information values [14]. This demonstrates excellent homogeneity of NIST SRM 1648 for much smaller masses than 100 mg which is a minimum given in the certificate and also very good stability of our analytical system. However, for manganese (and vanadium) our values have been by about 10% lower compared to the NIST information (certified) values, but in agreement with those compiled from the literature by Gladney et al. [15]. Therefore, we decided to elucidate these discrepancies in detail by optimizing the irradiation and counting conditions for determining these two elements and to perform simultaneous analysis of other NIST SRMs and BCR CRMs of environmental and biological origin with contents of the investigated elements of the same order of magnitude as in NIST SRM-1648. Experimental details have already been given elsewhere [14]. Results of Mn determination in the samples investigated are summarized in Table 1 where the mean values and their combined uncertainties are given.

Table 1. Manganese contents in biological and environmental reference materials

Reference material	Mn content, mg kg^{-1} (dry weight)			
	This work	Previous NPI results	Certified or information value[b]	Literature value [15]
	Mean ± unc. [a] (N)	Mean ± SD (N)		
NIST SRM-1648[c]	768 ± 18 (4)	770 ± 46 (27)	860	822 ± 45 (19)
NIST SRM-1648[d]	768 ± 23 (4)			
NIST SRM-1648[e]	795, 791 (2)			
NIST SRM-1633a	185 ± 17 (4)	-	179 ± 8	188 ± 20 (43)
NIST SRM-2704	570 ± 17 (4)	566 ± 46 (6)	555 ± 17	550 ± 50 (9)
BCR CRM 038	479 ± 7 (4)	-	479 ± 16	-
BCR CRM 101	908 ± 20	-	915 ± 11	-
BCR CRM 143	930 ± 27	-	904 ± 13	-

[a] - combined uncertainty
[b] - certified values are those associated with uncertainties
[c] - about 5 mg aliquots from bottle A
[d] - about 5 mg aliquots from bottle B
[e] - two aliquots of about 100 mg from bottles A and B

Obviously, excellent agreement was obtained between our previous results in small aliquots of NIST SRM-1648 and values obtained in this study, including the results for about 100 mg-aliquots of this material. The precision of Mn determination was significantly improved. Excellent homogeneity of this material for sample masses of about 5 mg was again confirmed. Our results also compared well within the uncertainty margins with certified and/or information values for other NIST SRMs and BCR CRMs studied. Therefore, two conclusions can be derived from results of this study. First, agreement of our results with certified and/or information values in the NIST SRMs and BCR CRMs analyzed, except for NIST SRM-1648, suggests that these values are mutually traceable, because INAA is known as an analytical technique without the measurable matrix dependence for many matrices. On the other hand, the previously found discrepancies between our results and the NIST values for manganese and vanadium in SRM-1648 were confirmed for both 5 mg and 100 mg sample masses which suggests that the NIST values are positively biased by about 10% and a similar bias has also been found for vanadium [14]. The same conclusion can also be derived from a comparison of the NIST values with those compiled from the literature by Gladney et al. [15] and with those determined by INAA by Greenberg [16]. Finally, it can be mentioned that besides very well known advantages of neutron activation analysis for certification of element contents in reference materials, a special capability of INAA for establishing the mutual traceability of certified element values in reference materials with different matrices has been demonstrated.

In case of chromium and manganese determination in human blood and urine, it is not only a problem of quality assurance of analysis, but also quality assurance of sampling and sample handling, i.e. preventing contamination, which makes the accurate determination of very low levels of the elements a challenging analytical task. Therefore, the blood sampling devices produced by SARDSTET and BECTON DICKINSON companies, i.e. disposable steel needles siliconized on the inside surface and collection vials designated for "trace metal analysis", were tested for extraneous additions of both elements. It has been obvious from the producer data that the possible maximum amounts of elements that are guaranteed by both producers would prevent determination of normal levels of both chromium and manganese in blood and its derivatives. This is demonstrated in Table 2 where the maximum amounts of elements possibly released from the collection devices are given and compared with those in serum of occupationally unexposed persons provided that 5 mL of blood are

collected. Moreover, the maximum extraneous additions for the Vacutainer® tubes and needles may be underestimated, because a higher contamination is to be expected on blood sampling than this caused by "water extractable" concentrations, due to complexing properties of blood aminoacids and peptides.

Table 2. Comparison of the possible extraneous element additions on blood sampling using S-Monovette® for metal analysis, SARSTEDT, and Vacutainer® for trace element analysis, BECTON DICKINSON, with the normal levels in serum

Element	Max. extraneous addition according to the producers leaflets (µg/L)		Resulting value in serum[b] (µg/L)		Normal serum value (µg/L) [6, 17]
	Monovette®[a]	Vacutainer®[b]	Monovette®[c]	Vacutainer®	
Al	40	-	8.0	-	1.3 -1.6
Cd	1.5	0.6	0.3	0.6	0.1 - 0.2[d]
Cr	5.0	0.9	1.0	0.9	0.1 - 0.2
Cu	70	8.0	14	8.0	0.8 - 1.4
Fe	50	60.0	10	60.0	750 - 1500
Hg	10	-	2.0	-	0.5
Mn	10	1.6	2.0	1.6	0.5
Ni	8.0	-	1.6	-	< 0.3
Pb	5	2.5	1.0	2.5	29 - 73[e]
Sb	-	0.8	-	0.8	-
Se	10	-	2.0	-	0.04 - 0.16
Tl	2.5	-	0.5	-	-
Zn	70	40.0	14	40.0	1000

a - ng per S-Monovette
b - maximum levels of water extractable trace elements
c - provided that 5 mL of blood are collected
d - in blood of non-smokers
e - in blood in Sweden and China in 1992

Results of the simulated blood collection (using the reconstituted Versieck's 2nd Gen. Biological Reference Material - uncontaminated human serum)) are summarized in Table 3.

Table 3. Chromium and manganese values in reconstituted Versieck's human serum "collected" with SARSTEDT's and BECTON DICKINSON's collection devices for "trace metal (element) analysis"

Sample/Collection device	Cr (µg/L)	Mn (µg/L)
Reconstituted Versieck's serum	< 1.5	1.0
Versieck's mean value (95% CI)[a] [7]	0.069 (0.061-0.079)	0.70 (0.67-0.73)
Monovette®, SARSTEDT	4.4	5.0
Monovette®, SARSTEDT	5.4	3.6
Vacutainer®, BECTON DICKINSON	5.0	4.4
Vacutainer®, BECTON DICKINSON	5.3	4.3

a - dry weight values in ng/g converted to ng/mL of original serum by dividing the former values by 11

Table 3 shows that even higher contamination with chromium and manganese was observed that could be expected from data in Table 2. This clearly demonstrates that the extraneous additions of chromium and manganese from the collection devices exceed several times the element levels in uncontaminated human serum and therefore these devices cannot be used for studying levels of these (and other elements - Cf. Table 2) in human blood and its components. Therefore, our sampling campaign has to be delayed until non-contaminating sampling devices will be obtained.

3.2. Results from previous work relating to this CRP

Exposure to vanadium was studied in occupationally exposed workers of a plant producing vanadium pentoxide from a vanadium rich-slag by a hydrometallurgical process. The production involves several processes that are associated with a release of vanadium-rich dust that presents a risk of occupational exposure, especially if workers do not permanently use their protection respirators.

APM samples were collected mostly at several supervision workplaces of the plant that were considered to be the most significant pollution sources. Hair, nails, blood and urine was collected from both exposed and control persons. The APM, hair, and nail samples were analyzed by INAA, while low level determination of vanadium in blood and urine was performed by a RNAA method with proven accuracy even at the ultratrace vanadium level by analysis of suitable reference materials. Cystine in hair and nails was also measured to elucidate the existing discrepancies about suitability of this test to indicate occupational exposure to vanadium.

Determination of vanadium levels in hair, fingernails, blood and urine in both exposed and non-exposed persons made it possible to evaluate the sensitivity of biological monitoring of exposure to vanadium. This was done in two possible ways: i) by comparing the maximum value of the exposed group to the median of the control group C-2 (criterion 1); ii) by comparing the median of the exposed group to the median of the control group C-2 (criterion 2). These comparisons are presented in Table 4.

Evaluation of sensitivity of the tests studied suggests that the vanadium determination in hair and fingernails might be considered the most sensitive bioindicator of occupational exposure to vanadium. About the same sensitivity of both tests also resulted in significant correlation of vanadium content in both tissues. Owing to the known growth rate of both tissues, these tests should provide information on long-term body burden with vanadium. On the other hand, significance of these tests should not be overestimated, due to the problems with complete removal of external contamination of the tissues. Obviously, by using various cleaning procedures, different results could be obtained and therefore the results of vanadium determination in both fingernails and hair should be interpreted with a caution.

Table 4. Evaluation of sensitivity of biomonitoring tests of exposure to vanadium

Tissue	Criterion 1 $\frac{Max_{(exp)}}{\%_{(C-2)}}$	Criterion 2 $\frac{\%_{(exp)}}{\%_{(C-2)}}$
Hair	11,278	1167
Fingernails	17,056	553
Blood	3,875	239
Urine	3,594	145

Vanadium levels in blood and urine are undoubtedly more unambiguous and straightforward indicators of occupational exposure to vanadium, although sensitivity of these tests is 3 to 5 times and 2.5 to 8 times lower for the first and second criterion, respectively, compared to the hair and fingernail tests. Due to the quick excretion of vanadium via the kidneys observed in this work and

also by other authors, vanadium determination in urine should be considered as a test of a very recent exposure (sensitivity of this test will decrease with the time elapsed from the end of exposure). On the other hand, vanadium determination in blood appears to be the best indicator of the long-term body burden with vanadium.

It has also been proved that exposure to vanadium has no effect on cystine levels in fingernails, nor in hair.

The determination of vanadium in hair and fingernails yielded the highest sensitivity for detecting occupational exposure, because up to four orders of magnitude higher values were found in the exposed workers compared to controls. However, the interpretation of these tests may be difficult due to known problems with cleaning these tissues prior to analysis to completely remove external contamination (vanadium rich dust from the factory), without influencing the endogenous element content. Moreover, if another cleaning of hair is employed than the IAEA recommended procedure used in this work, somewhat different results and output of the tests may be expected. This problem appears to be even more severe for fingernails.

For these reasons, blood and urinary vanadium levels should be considered the most reliable indicators of occupational exposure to vanadium. These tests exhibited up to one order of magnitude lower sensitivity compared to hair and fingernail analysis. However, the interpretation of these tests appears to be unambiguous and straightforward provided that no contamination occurred on sampling and analysis, because the mechanisms of excretion of the inhaled vanadium via these body fluids seems to be reasonably well established. None of these tests should be valued over the other, because they may be regarded as having a complementary role. Urinary vanadium appears to be the best indicator of very recent exposure, because this parameter increases within few hours after the onset of exposure and also drops quickly after its cessation. The latter is explained by the rapid excretion of vanadium via the kidneys with a half-life between 12 to 18 hours as was found in one exposed worker in the present work. After excretion of the major part of the inhaled vanadium, increased urinary vanadium was still found. However, no time changes of this elevated level could be studied. Our knowledge about the time response of blood vanadium in humans after the start of exposure is still lacking. However, due to known mechanism of slow remobilization of the absorbed vanadium from the bones after several days following the end of exposure, blood vanadium levels may be regarded as the most suitable indicator of the long-term body burden.

The reliable assay of vanadium in these body fluids in occupationally non-exposed persons is a difficult analytical task. Until now, only well elaborated procedures of RNAA, GF-AAS, preferably with preseparation, and high-resolution ICP-MS proved to be capable of accurate vanadium determination. The RNAA method should be considered superior for this purpose. From the analytical point of view, the reliable vanadium determination in urine is somewhat easier to achieve than in blood, because about 3 to 4 times higher element levels in the former fluid of both normal and exposed persons may be expected. This may be a reason why the determination of vanadium in urine might be preferred. If the above mentioned analytical techniques that are best suited for vanadium determination at the ultratrace level in biological samples are not available, it may be proposed that biomonitoring of vanadium exposure by blood and urine analysis is performed in the following way. The elevated vanadium levels can usually be reliably determined by commonly available GF-AAS methods, provided that appropriate quality assurance procedures on sampling and analysis are pursued. Then, the recently published critically evaluated normal vanadium concentrations in human blood, serum and urine [18,19] may be used for a comparison.

More experimental and other details about this work can be found in Ref. [2].

4. PLANS FOR FUTURE WORK

- Validation of the radiochemical neutron activation analysis (RNAA) method developed for low level determination of Cr (Mn) in human serum and urine by analysis of 2nd Generation Biological Reference Material (uncontaminated freeze-dried human serum)

- Collection of the workplace air born particulate matter in a ferro-alloy production plant and its analysis by the validated INAA and PIXE methods

- Contamination-free collection of blood, urine, hair, and nails from a 15-20 member group of occupationally exposed workers in the ferro-alloy production plant and determination of Cr (Mn) in these tissues by the validated RNAA procedures.

- Evaluation and interpretation of the results obtained.

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