Cobalt determination in the hair of patients after metal-on-metal hip implants by instrumental neutron activation analysis

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Measurements of trace element levels in human hair have been widely used to determine the degree of contamination due to pollutants [1], and in biomedical studies as markers for diseases [2].

Additional hair analyses, carried out after evidence of increased blood and urine levels of Co in patients with metal-on-metal (MoM) hip resurfacing arthroplasties [3], proved a consistency between Co variations in blood and serum with those in hair [4]. Although the outcomes of these studies are encouraging for the use of Co in hair as a biologic marker in periodic check-ups of patients after MoM hip implant, the significance of the results might be questioned due to their strong dependence on the adopted washing protocol.

The currently widely adopted washing procedure was suggested by the International Atomic Energy Agency (IAEA) [1]; it consists of washings performed in three steps: (i) 10 min washing with acetone, (ii) 10 min washing with water repeated three times and (iii) 10 min washing with acetone.

This study assessed the use of the IAEA washing method as a standard protocol in the hair analysis of patients after MoM hip implants; thus, the variation of Co levels in samples following single washing steps was determined by Instrumental Neutron Activation Analysis (INAA). In addition, the effect of neutrons was also investigated by performing hair washing before and after the irradiation. The results were published in the paper [5].

Co determination after washing steps

Hair were collected from two healthy control subjects (C1 and C2) and from three patients after MoM hip implants (P1, P2 and P3).

Weighed aliquots of Co standard solution (1000 mg L^{-1}) pipetted on cellulose filter papers were used as comparators for the application of the relative-INAA method. A single aliquot for each sample and seven aliquots of Co standards were sealed in PE vials and irradiated for 6 h in the central channel of a 250 kW TRIGA Mark II reactor operated by the University of Pavia ($6.11(16) \times 10^{12}$ cm^{-2} s^{-1} thermal neutron flux, 15.6(3) thermal to epithermal neutron flux [6]).

After irradiation, hair samples were removed from their vials and placed in plastic containers for γ-counting. Six γ-spectra per sample were acquired at contact position with a high purity germanium (HPGe) detector (50% relative efficiency). Each γ-counting lasted at least 48 h and followed a washing step according to Table 1. Resulting values of normalized Co mass fraction, $w_{\mathrm{Co,norm}}$, are reported in Figure 1 for the five samples.

Table 1. The number of completed acetone, *a*, and water, *w*, steps, the scheduled washing sequence and the γ-counting number of a hair sample.

Steps	Washing	γ-counting
0	-	1
1	*-a*	2
2	*-w*	3
3	*-a*	4
7	*-w-a-w-a*	5
9	*-w-a*	6

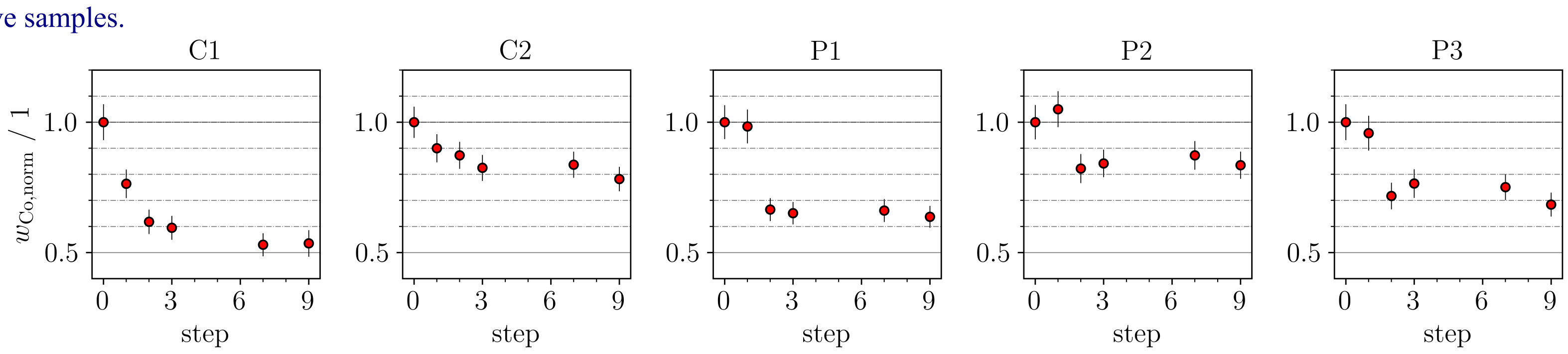

Figure 1. The variation of Co levels in hair of two healthy subjects (C1 and C2) and three patients (P1, P2 and P3) after a 9 steps washing procedure. Measured values for Co mass fraction were normalized to the mass fraction value at step 0 of the corresponding sequence. Error bars indicate the expanded uncertainty (*k*=2)

Moreover, a few strands of C1 sample were selected at steps 0, 1, 2 and 3 to inspect the external hair surface using a scanning electron microscope (SEM); images are reported in Figure 2.

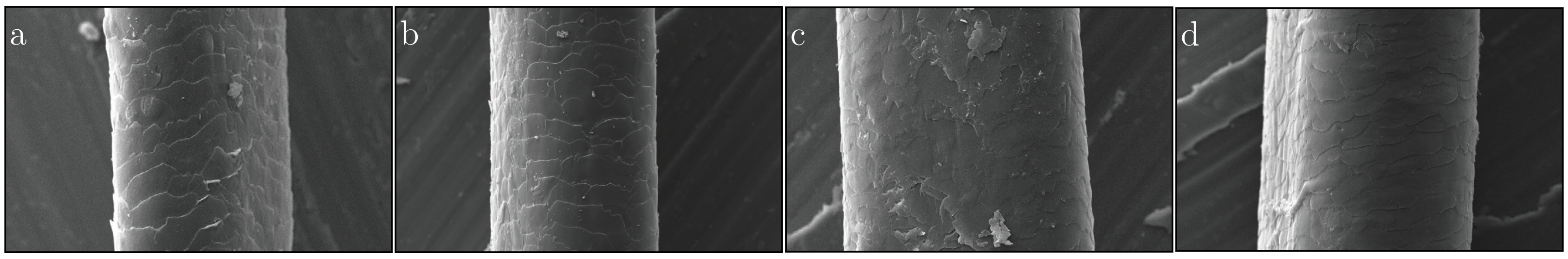

Figure 2. SEM images of hair selected from sample C1 recorded after washing steps 0, 1, 2 and 3 and recalled with letters a, b, c and d, respectively.

Effect of neutron irradiation on Co determination

Hair collected from C2 were used in a second experiment to test whether the neutron irradiation affects the Co concentration. In particular, two samples were irradiated for 6 h in the central channel of the TRIGA Mark II reactor of Pavia: the first one underwent a complete, i.e. 9 steps, washing procedure before the irradiation while the latter a complete washing procedure after the irradiation.

Samples and the co-irradiated standards obtained from the Co solution were counted on a HPGe detector (35% relative efficiency). A single γ-counting was performed for the sample washed before irradiation while six γ-spectra were sequentially acquired during the post-irradiation washing procedure of the second sample as in Table 1.

Results for Co mass fraction, w_{Co}, at step 9 for the two washing procedures didn't show appreciable differences as shown in Figure 3.

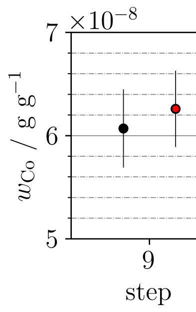

Figure 3. Values of Co mass fractions, w_{Co}, measured for the samples washed before (black circle) and after (red circle) neutron irradiation. In both cases the complete washing procedure (9 steps) was performed. Error bars indicate the expanded uncertainty (*k*=2).

Conclusions

This study investigated the application of the IAEA washing procedure for the measurement of Co in hair of patients after MoM hip implants via INAA.

The data showed that the step 3 of the washing protocol removes amounts of Co close to a plateau. Moreover, the agreement between the Co levels measured in samples washed pre- and post-irradiation demonstrated that the irradiation exposure does not affect the behavior of hair samples (at least up to 6 h in a TRIGA Mark II reactor).

In conclusion, the higher measured Co levels in hairs of P1 and P2 patients with respect to P3 (Figure 4) confirmed the outcome of the analysis previously performed in blood; thus, the adoption of the IAEA washing sequence to determine the Co level is recommended in clinical follow-up of patients after MoM hip resurfacing arthroplasties.

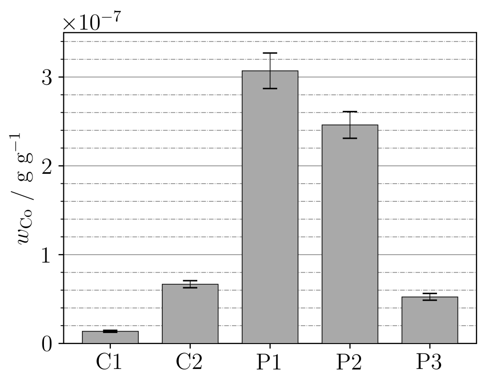

Figure 4. Values of Co mass fractions, w_{Co}, measured at washing step 9 in hair of healthy subjects (C1 and C2), patients requiring revision hip surgery (P1 and P2) and a patient requiring only monitoring (P3). Error bars indicate the expanded uncertainty (*k*=2).

References

[1] Ryabukhin; 1978, *IAEA/RL/5 report*
[2] Wozniak; 2016, *Biometals*, 29: 81-93
[3] Iavicoli; 2006, *J. Trace Elem. Med. Biol.* 20: 25-31
[4] de la Flor; 2013, *J. Orthop. Res.* 31: 2025-2031
[5] D'Agostino; 2019, *Metrologia* 56: 014001
[6] Di Luzio; 2017, *J. Radioanal. Nucl. Chem.* 312: 75-80