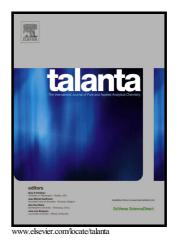
## Author's Accepted Manuscript

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## Study of Chromium Species Release from Metal Implants in Blood and Joint Effusion: Utilization of HPLC-ICP-MS

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Abstract:

The objective of this study was to develop and validate a novel analytical procedure for determination of total chromium and Cr(III) and Cr(VI) species released from metal implants into whole blood and joint effusion. Firstly, the ion-pair chromatographic method employing reversed-phase high-performance liquid chromatography inductively coupled plasma mass spektrometry (ICP-MS)for analysis of species was developed. Secondly, all samples and protein and low molecular fractions were analyzed for their total chromium content using ICP-MS. This new measurement procedure was validated by the following parameters: limit of detection (0.13  $\mu$ g L-1 for Cr(III), 0.14  $\mu$ g L-1 for Cr(VI)), linearity of calibration, trueness (recovery 84 - 92 %), intermediate precision (RSD < 5 %). We determined statistically significantly higher chromium levels in joint effusion samples obtained from patients in comparison with a control group. On the other hand, no relevant difference among the concentrations of both species and total chromium in blood was observed. Our results show that the majority of chromium is present in the trivalent form and bound to proteins. This speciation study is rare in the field of speciation analysis in clinical samples. It is characterized by very fast and simple sample preparation without changes in distribution or stability of both Cr forms and efficient simultaneous analysis of Cr species.

Keywords: speciation analysis, chromium, blood, joint effusion, liquid chromatography, ICP-MS

## **1. Introduction**

Using metal implants in orthopaedics has increased enormously during the last decades and can be considered as a routine surgery nowadays. Nevertheless, metal ion release from all metallic materials is becoming a major cause of concern. When pure metal and alloy-based implants are inserted into a corrosive and complex physiological environment such as human body, the surface oxide film could be affected and is exposed to release a large amount of metal ions resulting in increased metal concentration in biological fluids and surrounding tissues as well as the deep organs. As a result, released metal ions can cause various deleterious phenomena, inciting allergies and potentially promoting granuloma formation and

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