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# Chromium in rivers impacted by tannery WASTES DETERMINED by high performance liquid chromatography – inductively coupled plasma mass spectrometry

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**Abstract.** The total chromium concentrations by ICP-MS and HPLC-ICP-MS and the redox chromium species have been determined in rivers impacted by untreated wastes from tanneries at Fès (Morocco).
The results obtained by two ICP-MS analysis methods showed significantly different chromium values at *m/z* 53. The higher values obtained with external calibration, can be attributed to matrix effects, especially $^{37}Cl^{16}O^+$ at *m/z* 53. This is confirmed on the chromatograms by the presence of a peak at 100s with the anomalous $^{52}Cr/^{53}Cr$ isotopic ratio. The hexavalent chromium was not detected. Two trivalent chromium monomer species, $Cr(OH)(H_2O)_5^{2+}$ and $Cr(H_2O)_6^{3+}$, were present in low concentrations. We suppose that the major part of chromium occurred as Cr(III) polymeric species which were not retained on the column. These Cr(III) forms are usually complexed with $Cl^-$ or/and $SO_4^{2-}$, used as tanning agents.

## 1. INTRODUCTION

The separation and identification of different oxidation states of chromium is essential for evaluation of potential toxicity of this contaminant. At low concentration Cr(III) is an essential trace nutrient and becomes toxic only at high concentration; whereas Cr(VI) is known to be carcinogenic and mutagenic. Trivalent chromium is the most commonly used tanning agent and is found in large quantities in tannery wastewater. Basic chromium sulfate $[Cr_4(SO_4)_5(OH)_2]$ solutions at different concentrations and pH are used as tanning baths for the stabilization of skin and against the degradation of leather.

Since untreated tannery wastewaters are characterized by high organic carbon and salt contents [1]; matrix interferences, especially from carbon, chloride [2] and sulfate [3] can make quantification of chromium very problematic.

The present study was carried out on two rivers heavily impacted by tannery wastes (Oued Sébou and Oued Fès in Morocco). We determined the total content of chromium by ICP-MS and HPLC-ICP-MS in order to compare total chromium measurements in a very complex matrix. Furthermore, we found the trivalent and but no hexavalent chromium in the water impacted by untreated tannery wastes.

## 2. EXPERIMENTAL

### 2.1 Instruments and reagents

The ICP-MS was an 4500 HP with Babington nebulizer. When coupled to HPLC, the cross flow nebulizer was used. The HPLC system consisted of GP50 gradient pump (Dionex), IonPac CG5A guard column (4*50mm) and CS5A analytical column (4*250 mm).

Cr(III) and Cr(VI) solutions were prepared daily by an appropriate dilution of the stock solution (Fluka, 1 $g.l^{-1}$ $Cr(NO_3)_3$ and $K_2CrO_4$) using suprapur water (18MΩ). $HNO_3$ 0.5N and 1N were used as mobile phases.

### 2.2 Sample collection and analysis

Surface water samples were filtered in the field through a 1.2µm PP cartridge using a peristaltic pump. Filtered samples were stored frozen (–20°C) after acidification at 1% with $HNO_3$ for ICP-MS or without acidification for HPLC-ICP-MS.

The chloride and sulfate contents were analyzed by ionic chromatography (IC) at the University of Lausanne (Centre d'Analyses Minérales, CAM).

Due to interference of carbon at mass 52 (organic carbon up to 90 ppm in our samples), the isotope at mass 53 (relative abundance 9.5%) was used for the determination of total chromium concentration with ICP-MS using two methods: standard calibration technique (SCT) and the analyte addition technique (AAT). The limit of detection of the methods (Table 1) were calculated from the equation: $LOD = 3 * S_{bl}$ where $S_{bl}$ is the standard deviation of blank.

Separation of Cr(VI) and Cr(III) was preformed according to the protocol [4]. However, in order to eliminate carbon spectral interference on the chromium peak at m/z 52 and 53, the elution time for re-equilibration was ten minutes instead of three minutes. Data acquisition in "Time Resolved Analysis" mode was used and the concentrations were calculated from peak area. The calibration blank was examined for each analysis, to verify the memory effect. The correlation coefficients for the calibration were 0.9945 and 0.9968 at *m/z* 52 and *m/z* 53, respectively. The limit of detection was 0.47 µg $l^{-1}$ for $^{52}Cr$(III) and 0.58 µg $l^{-1}$for $^{53}Cr$(III) for HPLC method, and the isotopic ratio $^{52}Cr/^{53}Cr$ [5] have been evaluated to detect matrix effects.

## 3. RESULTS AND DISCUSSION

### 3.1 Total chromium concentration with ICP-MS

The results of the total chromium content are presented in Table1.

Statistical differences between results obtained by the two methods were found using paired t-test and F-test (P=0.05). This indicates that there was an influence of the matrix, most probably, the interference of $^{37}Cl^{16}O^{+}$ [8], at *m/z* 53. The Cr concentrations obtained by the AAT are lower than theses obtained by the SCT, except for sample 3MF, due to the highest chromium content in this latter sample. Since the AAT allows to correct the interference signal, the obtained results are coherent.

### 3.2 Total chromium and redox chromium species with HPLC-ICP-MS

Figures 1a, 1b and 2 show the chromatograms typical[1].

No peak of Cr(VI) was detected in any sample, whereas a peak of Cr(III) was always observed at a retention time around 410s.

At low concentrations (1MF, 5MF and 6MF), a peak was observed at *m/z* 53 at about 100s, whereas this peak was not observed at *m/z* 52. On the contrary, for high concentrations (2MF, 3MF and 4MF) this peak was also observed also at *m/z* 52. Moreover, for samples 3MF and 4MF, a second peak of Cr(III) appeared around 360s.

[1] The samples 1MF and 6MF have spectral shape equivalent to 5MF, likewise 4 MF to 3MF.

**Table 1:** Total chromium concentrations and standard deviations (SD) obtained by two ICP-MS methods. Chloride and sulfate concentrations and their standard deviations obtained by IC.

| Sample | $[Cr]^a$ (µg $l^{-1}$) | SD | $[Cr]^b$ (µg $l^{-1}$) | SD | $[Cl^-]$ (mg $l^{-1}$) | SD | $[SO_4^{2-}]$ (mg $l^{-1}$) | SD |
|---|---|---|---|---|---|---|---|---|
| 1MF | 1.18 | 0.06 | 0.58 | 0.01 | 166.37 | 0.01 | 19.37 | 0.01 |
| 2MF | 8.93 | 0.12 | 8.27 | 0.03 | 198.20 | 0.02 | 33.65 | 0.01 |
| 3MF | 213.65 | 4.70 | 226.50 | 0.22 | 218.57 | 0.01 | 81.03 | 0.01 |
| 4MF | 74.55 | 0.83 | 69.77 | 0.07 | n.d | n.d | 44.12 | 0.01 |
| 5MF | 0.78 | 0.01 | 0.51 | 0.02 | 144.77 | 0.01 | 106.93 | 0.01 |
| 6MF | 0.80 | 0.02 | 0.69 | 0.02 | 148.40 | 0.01 | 107.49 | 0.01 |

[a] SCT method; LOD =0.098 µg $l^{-1}$,
[b] AAT method; LOD =0.03 for samples 1MF and 2MF, 0.02 for the others samples
n.d : Not determined

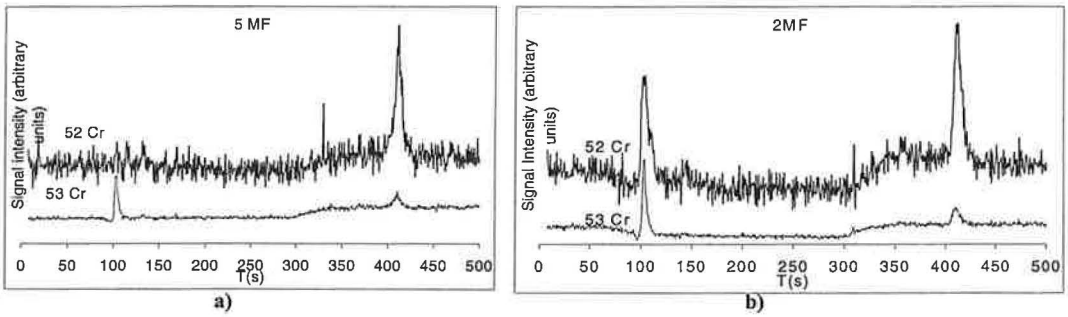


**Figure 1:** Chromatograms at *m/z* 52 and *m/z* 53 of samples: **a )** 5MF and **b)** 2MF

**Table 2** Total chromium concentration at m/z 52. Isotopic ratio $^{52}Cr/^{53}Cr$ from peak at 100s. and their standard deviations.

| Sample | [Cr] (µg $l^{-1}$) | SD | $^{52}Cr/^{53}Cr$ | SD |
|---|---|---|---|---|
| 1MF | 1.65 | 0.40 | - | - |
| 2MF | 4.51 | 0.33 | 2.48 | 0.01 |
| 3MF | 46.02 | 3.79 | 8.59 | 0.72 |
| 4MF | 17.89 | 1.27 | 5.59 | 1.77 |
| 5MF | 1.55 | 0.36 | - | - |
| 6MF | 1.01 | 1.4 | - | - |

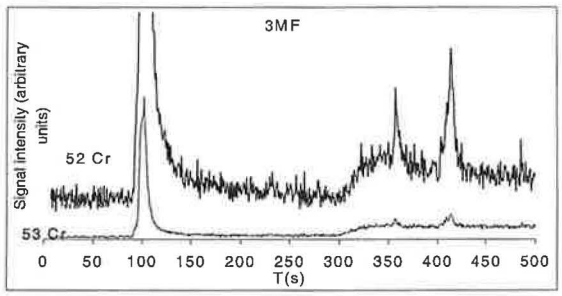


**Figure 2:** Chromatograms of 3MF sample at m/z 52 and m/z 53

For samples 1MF-5MF-6MF, the peak at 100s is clearly an interference peak, since it was observed at *m/z* 53 but not at *m/z* 52 (relative abundance 9.50% and 83.79%, respectively). Moreover, for all but one sample, the $^{52}Cr/^{53}Cr$ ratio (Table 2) is lower than the expected ratio of 8.82. This confirms that the apparent higher Cr concentration at *m/z* 53 from the ICP-MS using the SCT could be caused by the presence of $^{37}Cl^{16}O^+$ ion, except for 3MF which is less sensitive for interference, due to the very high chromium concentration in this sample.

The chromatogram at *m/z* $^{34}S$ was also monitored (not shown). The peak at this *m/z* appeared with retention time at 100s. Consequently, $^{36}S^{16}O^+$ ion could influence the $^{52}Cr$ content. However no peak was observed at *m/z* 52 (Figure 1a,) for samples 5MF and 6MF, although they have a high sulfate content (Table 1). Thus this ion does not interfere with chromium 52 in HPLC-ICP-MS measurements. Finally, with regard to the first peak at 100s, we suppose that a major part of Cr(III) is present as chromium sulfate complex and/or with other complexing agents, such as $Cl^-$ [9]. Indeed, such complexes can cross link with collagen originating from the leather treatment [10, 11].

At 360s and 410s, the redox chromium species could be $Cr(OH)(H_2O)_5^{2+}$ and $Cr(H_2O)_6^{3+}$, respectively [4]. These species were reported to be stable in natural water due to the complexation reactions, for example with humic acids [12].

To obtain an accurate chromium concentration by HPLC-ICP-MS technique, the isotope $^{52}Cr$ was chosen and the signals of all peaks summed up (Table 2).

For samples 1MF, 5MF and 6MF, the Cr concentrations by ICP-MS agree reasonably with these obtained by HPLC-ICP-MS, though they are close to the LOD of the latter technique. On the contrary, for chromium concentration higher than 2 $\mu g\ l^{-1}$, the values obtained with HPLC-ICP-MS were lower than these measured with of ICP-MS. The losses could be due to the conservation of samples without acidification, but this observation calls for a more detailed examination.

## 4. CONCLUSION

The presented results demonstrate the difficulties of a reliable determination of Cr concentration with ICP-MS in a complex matrix. The results obtained with HPLC-ICP-MS confirm the influence of the matrix, notably $^{37}Cl^{16}O^+$ ion on the results of total chromium concentration at *m/z* 53 by ICP-MS. This is shown by the presence of a peak at 100s only at *m/z* = 53 or the anomalous isotopic ratio $^{52}Cr/^{53}Cr$.
The hexavalent peak was not detected by HPLC-ICPMS. Only the trivalent chromium species $Cr(OH)^{2+}$ and $Cr^{3+}$ could be identified in our samples. We suppose that, at a high total Cr concentration, an important part of Cr(III) is present as polymeric chromium complex. This complex, either negatively charged or with no charge, was not retained on the column.

In future work, high resolution ICP-MS will be used to separate the interferences from a chromium signal and to verify the total Cr concentration in our samples.
Samples will be spiked with Cr(VI) and analyzed after equilibration in order to confirm the absence of Cr(VI).

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