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SIMULTANEOUS DETECTION OF CHROMIUM SPECIES WITH HPLC-ICP-MS TECHNIQUE

Cristina Dinu, Anda-Gabriela Tenea, Alexandru-Paul Rus, Gabriela-Geanina Vasile

National Research and Development Institute for Industrial Ecology – ECOIND Bucharest, 57-73 Drumul Podul Dambovitei Street, district 6, 060652, Bucharest, anda.tenea@incdecoind.ro, Romania

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Introduction

Chromium is one of the most abundant metals in the earth's crust; the presence of this element in the environment is due to both natural processes (rocks, volcanic eruptions, soil erosion) and industrial activities. Recent studies on this subject show that contamination with chromium (especially Cr VI) in groundwater is mainly due to geogenic sources, chromium being naturally leached into water from rocks with high fractions of chromium (chromite ($FeOCr_2O_3$), crocoite ($PbOCrO_3$) or chromic oxide (Cr_2O_3)). Mn V oxides, which are present in chromium-containing minerals, are responsible for oxidizing Cr III into Cr VI.

The mobility, bioavailability and toxicity of the two-oxidation states differ greatly. Compounds with Cr III are generally immobile and slightly soluble compared to compounds with Cr VI, which have high mobility, solubility and bioavailability.

Cr III is considered essential for insulin regulation and glucose metabolism, while Cr VI is toxic, being known to be carcinogenic by inhalation. Cr III is an essential trace element in mammals, while Cr VI has great mutagenic and genotoxic effects on biological systems.

Materials and methods

A HPLC Agilent 1260 Infinity II couplet with an ICP-MS Agilent 7850 equipment was used. For chromiun speciation was used an Agilent G3268-80001 column, 4.6mm x 30mm i.d. For ICP-MS was used collision/reaction cell operated in helium mode in order to eliminate the multiple interferences, such as ArC and ClO. Operation in helium mode eliminates polyatomic interferences due to the matrix from both isotopes of chromium (52, 53).

Separation of Cr III from Cr VI in chromatographic column was perform using a mobile phase of 5 mM EDTA(2Na)/5mM NaH_2PO_4/15mM Na_2SO_4 mixture at 7 pH, because Cr III is binding by EDTA.

For Cr III was used a Certified Reference Material (CRM) of 1000 mg/L in 2% HNO_3 (CPA Chem., Bulgaria) and for Cr VI a CRM of 1000 mg/L in water from Sigma Aldrich, Germany was used.

A stock solution of 10 mg/L from both species was prepared using 10 mM EDTA. From this solution, an intermediate solution of 1 mg/L (Cr III and Cr VI) was prepared using same EDTA solution. The calibration standards were 10 µg/L, 30 µg/L, 50 µg/L, 80 µg/L, 100 µg/L. 10 mM EDTA were used for all standards.

Results and conclusions

The calibration curve was performed in the range of 10-100 µg/L (Figure 1), the curves indicated R^2 values higher than 0.998 for both species and both isotopes.

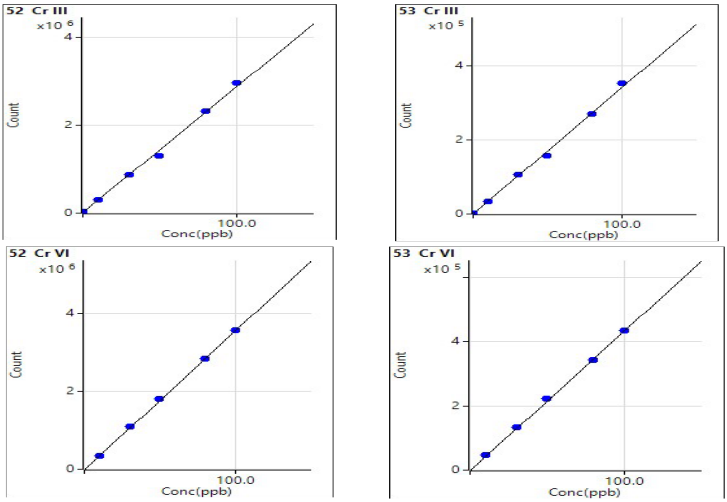

Figure 1. Linear regression curves for Cr III and Cr VI , for both isotopes (52, 53)

In the validation protocol were evaluated the following parameters: quantification limits (LOQ), precision, recovery, uncertainty measurement (Uex) and also liniarity of the calibration curves.

The experimental data were performed for both species and both isotopes in order to control the interferences of other mineral elements from the real samples that compete for the binding sites in the column, which leads to changes in the recovery and retention time. The abundance of isotope 52 is 9 times higher than that of isotope 53, so the change in this ratio indicates interference due to the analysed matrix. The values of some parameters are presented in Table 1.

Table 1. The performance parameters obtained for the monitored Cr species

Element	LOQ, µg/L	Liniarity, R^2	Uex, %
$52Cr^{3+}$	5.3	0.9980	16.3
$53Cr^{3+}$	7.8	0.9981	15.7
$52Cr^{6+}$	3.0	0.9999	16.9
$53Cr^{6+}$	2.0	0.9998	17.5

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