



Isotope dilution inductively coupled plasma mass spectrometry to measure the bioaccessible fraction of chromium in sediments



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ABSTRACT

The bioaccessible fraction of chromium in marine sediments is determined first time using isotope dilution Inductively Coupled Plasma Mass Spectrometry (ID-ICPMS). A diluted hydrochloric acid solution enriched with ^{53}Cr was used as extractant to achieve isotope equilibration with the mass fraction of Cr extracted, using ultrasonic probe agitation. The parameters affecting trueness and precision were evaluated and/or corrected to minimize the errors; namely: detector dead time, spectral interferences, mass discrimination factor and selection of the optimum sample/spike ratio. The fraction of Cr measured correlated well with the sum of the certified contents of the 3-step sequential extraction of the Standards, Measurements and Testing Programme, SM&T, when analysing the BCR-701 sediment. The method provided good reproducibility (1.4% RSD) and low detection limit, 16.7 ng g^{-1} . Three additional reference sediments with certified total chromium contents were also analysed as quality control checks. The total uncertainty budget of the procedure was estimated following the EURACHEM Guide propagating together the individual uncertainty components of the isotope dilution, obtaining a satisfactory relative expanded uncertainty of 1.9%. The analysis of sediments from two rias of Galicia (Arousa and Vigo, Northwest Spain) demonstrated the applicability of the proposed methodology.

1. Introduction

Metals are stable and persistent contaminants that tend to accumulate in the environmental compartments because they do not degrade. They are transferred through the aquatic systems, adsorbed quickly on the particulated materials, and subsequently incorporated and accumulated into the sediments, which become a relevant sink for them [1]. In particular, Cr is often found at high levels in contaminated sediments associated to tanneries, smelters and plating activities [2]. The two oxidation states of Cr differ in their mobility and bioavailability. Contrary to Cr(VI) species, in general, Cr(III) compounds are relatively immobile and poorly soluble. Toxicity is also different, being Cr(III) compounds almost innocuous and Cr(VI) compounds explicitly toxic, as they have high oxidizing power and cellular uptake, being potential carcinogens. Despite such relevant issue, current legislation does not state limits for the major forms of this element. With regard to drinking water, the World Health Organization (WHO) limited the concentration of total Cr to $50 \mu\text{g L}^{-1}$ or less [3], as the European Council did [4], whereas the maximum level for total Cr in US is $100 \mu\text{g L}^{-1}$ [5]. On the other hand, Marine Environmental Quality

Standards (EQS) are being developed to control the concentrations of selected substances in the water column, sediments and biota in order to protect human health and the environment. Thus, the Spanish government includes Cr(VI) and Cr(total) as preferential substances in surface waters and set their limits to 5 and $50 \mu\text{g L}^{-1}$, respectively [6].

Establishing maximum limits for Cr species requires sound background studies where their concentrations are measured in a wide range of locations, ecosystems, etc. Unfortunately, to the best of our knowledge, no methodology has been recommended to determine the usually low amounts of Cr species in, for example, natural waters. Therefore, there is room for the development of analytical methods intended to determine Cr and its species and, also important, to determine its (their) bioaccessible fraction(s) in different environmental matrices; in particular, sediments.

A large number of extraction procedures involving different extractants, steps and operational conditions exists to address this last issue [7, 8]. A popular working scheme is the 3-step sequential extraction procedure developed by SM&T (Standards, Measurements and Testing Programme of the European Commission), which determines three metal fractions as acid-extractable, reducible and adsorbed,

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according to the extractant employed [9]. Its main disadvantages are the high workload, time-demand and the possibility of metal redistribution (by readsorption) among phases. These drawbacks led to the use of partial (single) extraction protocols, which provide less specific information but allow the study of the metallic fraction that is easily released from the sediment. A common selection for single extractions is the use of diluted hydrochloric acid as extractant agent, due to its ability to extract environmentally relevant geochemical fractions [10], to dissolve calcareous materials, to attack Fe and Mn oxides (the major sink of metals in oxic sediments) [11] and to decompose organic phases and amorphous sulphides (which control metal bioaccessibility in anoxic sediments [12]); combined to the complexing property of Cl^- (which is a strong ligand [13]). Several authors claimed that the results obtained by diluted HCl extraction can be compared to the sum of the 3-step SM&T sequential extraction procedure [10, 14, 15]. This fraction may be assimilated to what IUPAC defined as bioaccessible fraction (the potential for a substance to come in contact with a living organism and then interact with it) [16]. In this sense, the bioaccessible fractions of Cr have been evaluated using different sequential [17, 18] and single procedures, many of the latter using diluted HCl [19–23], and comparisons among them can be also found elsewhere [15, 22].

Analyte losses can occur during extraction due to evaporation, readsorption, etc. These drawbacks can be overcome using isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) to measure the metal mass fraction extracted. Isotope dilution (ID) involves the isotopic equilibration between the fraction of the natural element, that in this case is released by a partial extraction procedure, and an enriched spike added to the sample, therefore any loss or alteration of the analyte will not affect the overall result [24, 25]. Indeed, this alternative quantitation approach avoids external calibration, compensates for matrix interferences and provides far superior data quality than traditional procedures [26].

An accurate determination of Cr by ID-ICPMS requires avoiding or minimizing the isobaric and polyatomic interferences that affect the isotope masses of this metal. Chromium has four naturally occurring isotopes - ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr – being isotopes 52 and 53 free of isobaric interferences. Meanwhile ^{50}Cr and ^{54}Cr overlap with ^{50}Ti , ^{50}V and ^{54}Fe , which require mathematical correction. Polyatomic ion interferences from carbon, chloride or oxide (e.g. $^{36}\text{Ar}^{16}\text{O}^+$, $^{37}\text{Cl}^{16}\text{O}^+$, $^{35}\text{Cl}^{16}\text{O}^{16}\text{H}^+$, $^{40}\text{Ar}^{12}\text{C}^+$, etc.) can enhance significantly the signals of ^{52}Cr and ^{53}Cr . In these cases, traditional mathematical corrections [27] have been replaced by the use of high resolution ICPMS instruments or collision/reaction cells in quadrupoles, as demonstrated when determining chromium in honey [28], seawater [29] or silicates [30]. Other alternatives are based on effective matrix separations [29, 31, 32].

ID-ICPMS has been frequently applied to determine the total content of Cr and their species in a wide range of matrices; e.g., polycarbonate [33], plastics [34], honey [28], drinking water [35, 36], seawater [29], silicate materials [31, 37] and soils [38]. However, scarce references were found dealing with sediment analysis. McLaren et al. [39] applied first time ID to determine 11 trace elements, including Cr. No reports were found applying ID to determine partial fractions of Cr (nor other metals) from solid samples, including extractable or bioaccessible metal fractions from sediments.

In the present work, isotope dilution (ID) was applied to determine the bioaccessible fraction of Cr in marine sediments by ICP-MS, for which, as it was mentioned above, no references were found in literature. A diluted HCl solution enriched with ^{53}Cr isotope was used as extractant to achieve isotope equilibration with the mass fraction of Cr extracted, using ultrasonic probe agitation. The parameters affecting trueness and precision were evaluated and/or corrected to minimize the errors; namely: detector dead time, spectral interferences, mass discrimination factor and selection of the optimum sample/spike ratio. The mass fraction of Cr calculated using this methodology was compared with the sum of the 3-step sequential SM&T extraction procedure

using the BCR-701 sediment to validate the method. Furthermore, additional assays were performed adding the enriched spike to the acid extract obtained after the extraction step to study the performance of the extraction procedure and point out the advantages of isotope dilution analysis in partial extractions. Three reference sediments with certified total chromium contents were analysed as quality control checking. The total uncertainty budget of the procedure was estimated following the EURACHEM Guide propagating the individual uncertainty components of the isotope dilution equation. The analysis of sediments from two environmentally and economically important areas of Galicia (rias of Arousa and Vigo, Northwest of Spain) was done to demonstrate the applicability of the proposed methodology.

2. Materials and methods

2.1. Instrumentation

The extractions were performed using a VC50-1 ultrasonic probe (50 W, 20 KHz) equipped with a CV18 titanium probe (Sonic Materials, Newtown, CT, USA). The digestions were accomplished with a microwave oven (Anton Paar Multiwave, Graz, Austria) equipped with a built-in magnetic stirrer, temperature and pressure sensors, a basic six-position extraction rotor and high pressure Teflon vessels.

A XSERIES 2 Quadrupole ICP-MS (Thermo Scientific, Bremen, Germany) was utilized to measure isotope ratios, which included a collision/kinetic energy discrimination cell, and was equipped with standard Ni-cones, a Meinhard nebulizer and a Scott double pass spray chamber refrigerated at 4 °C. An ASX-520 autosampler (CETAC Technologies, USA) was employed. The instrumental settings are summarised in Table 1. The nebulizer gas flow rate, torch position and ion lens settings were optimized for high sensitivity and minimal values for CeO^+/Ce (< 1.5%), monitoring a $10\ \mu\text{g L}^{-1}$ standard solution of Be, In and U in 1% (v/v) HNO_3 .

2.2. Chemicals and materials

High-purity water, 18.2 M Ω -cm resistivity, was obtained from a Milli-Q® Direct purification device (Millipore Co., Bedford, MA, USA). Hydrochloric (37%) and nitric (65%) acids were of suprapur quality (J.T. Baker, Phillipsburg, NJ, USA). Stock standard solutions of Cr, Fe and Ti ($1000\ \text{mg L}^{-1}$) for ICP analysis (SCP Science) were used to prepare working solutions to study the detector dead time, mass discrimination factor (referred to as “K factor”) and spectral interferences. The natural isotopic composition for Cr was assumed to agree with IUPAC data in all samples and solutions [40].

The enriched ^{53}Cr standard (as oxide, 97.7%) was obtained from Cambridge Isotope Laboratories (USA). The solid spike was dissolved following the 6800 EPA method [41], adding 8 mL of concentrated

Table 1
Instrumental operating conditions and acquisition parameters used in ICPMS.

ICP operation conditions	
Rf power	1.35 kW
Nebulizer gas flow	0.75 L min ⁻¹
Auxiliary gas flow	1.00 L min ⁻¹
Cooling gas flow	14 L min ⁻¹
He-KED	4.00 mL min ⁻¹
Acquisition parameters	
Acquisition mode	Pulse counting
Measurement mode	Scan
Number of sweeps	100
Dwell time (ms)	10
Isotope masses	$^{50}, ^{52}, ^{53}, ^{54}\text{Cr}$ - ^{48}Ti - ^{56}Fe

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