

Determination of Cr in certified reference material HISS-1, marine sediment, by cold plasma isotope dilution ICP-MS and INAA: comparison of microwave *versus* closed (Carius) tube digestion

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The recovery of Cr from National Research Council Canada (NRCC) certified reference material HISS-1 sediment was investigated by non-destructive instrumental neutron activation analysis (INAA) and isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) after two different chemical treatments: (1) microwave dissolution using HNO₃, HF, and HClO₄, followed by reflux with concentrated HClO₄, and (2) a closed system method using sealed Carius tube digestion with HNO₃ and HCl at high temperature (240 °C) and high pressure (1 × 10⁷ Pa, ~100 atm). The first chemical treatment gave recoveries of only ~50% in agreement with observations of Yang *et al.* of NRCC. Samples digested in Carius tubes gave recoveries that ranged from 79 to 110% which may reflect heterogeneity in the samples rather than differing recoveries. This is supported by the excellent agreement of the mean value determined by INAA of 31.4 ± 4.5 µg g⁻¹, and the mean value of 28.1 ± 3.9 µg g⁻¹ by Carius tube digestion and the observation that these standard deviations are essentially equal and much larger than the measurement precisions. The results from this study are also in excellent agreement with the certified value of 30.0 ± 6.8 µg g⁻¹. This preliminary study demonstrates that chemical treatment of this sediment with HNO₃ and HCl acids in closed system Carius tubes is an efficient and capable preparation method for the determination of Cr in silicate materials which typically contain refractory Cr-bearing minerals. This study also demonstrates the unique advantage of using two independent methods for the determination of Cr in a complex matrix which has a high potential for low chemical recovery.

Introduction

The determination of the concentration of chromium in natural materials is a challenging measurement problem. Chromium can form the refractory mineral chromite, FeCr₂O₄, which is very difficult to dissolve and frequently occurs in geologic materials. It can also exhibit volatile behavior in aqueous acids by forming chromyl chloride, CrO₂Cl₂, and the analogous fluoride.¹ Both of these behaviors can result in low recovery which translate to determinations that have a negative bias. It is one of the more difficult transition elements to measure accurately by almost all techniques because of the potential of low recovery in the sample preparation step. The difficulty is illustrated in Table 1 which is a compilation of Cr data on sediments and soils from NIST Standard Reference Material (SRM) certificates.² Note that all the certified values have large uncertainties (expanded uncertainties expressed as a 95% confidence interval) ranging from 3% to 9% relative for the three sediments and from 3% to 15% relative for three soils. It is probable that some of the uncertainty results from the intrinsic heterogeneity of these materials. Round Robin data on the two soil SRMs and the indoor dust show a range from 2 to 3 in concentration and all values were *lower* than the certified value indicating that the chemical treatments give significantly different recoveries. Not surprisingly, the Round Robin data for Cr were always of poorer precision than those for other trace elements. The Cr determination in SRM 2584 is discussed by Yu *et al.*³

Recently, Yang *et al.*⁴ reported low recoveries for Cr in the certified reference material, HISS-1, a sediment from the Hibernia Shelf off the coast of Newfoundland, using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) and closed vessel microwave dissolution with HNO₃

and HF. They obtained a concentration of 11.7 ± 1.1 µg g⁻¹ which is almost a factor of three lower than 31.4 ± 4.5 µg g⁻¹,^{4,5} measured directly in solid samples by instrumental neutron activation analysis (INAA) at NIST. Isotope dilution requires complete mixing of the enriched spike with the element to be measured, but does not require complete recovery after this step whereas all other destructive methods require complete recovery to eliminate a negative bias. INAA, because it does not require sample dissolution, is immune to this potential problem and is a valuable technique particularly for elements that form or are in refractory phases that may be difficult to dissolve.

Yang *et al.* were able to obtain higher values by extensive chemical treatment of the samples permitting the Cr in HISS-1 to be certified subsequently at 30.0 ± 6.8 µg g⁻¹,⁶ which is in excellent agreement with the INAA value. They investigated a variety of dissolution procedures and concluded that complete dissolution of Cr in marine sediment samples can only be achieved through high temperature refluxing with a mixture of H₂SO₄ and HClO₄. The use of these acids is cumbersome, complicated, and time consuming and frequently results in the precipitation of metal sulfates and perchlorates. In addition, they are well known to be difficult to purify and thus typically contain relatively high concentrations of trace metals. The HISS-1 certificate contains a paragraph specifically addressing the low recovery issue and states that HISS-1 contains "...a significant fraction of Cr that is not easily solubilized. The certified value of 30 mg kg⁻¹ was obtained using solid sampling techniques or prolonged digestion with hydrofluoric, sulfuric and perchloric acids. *Less vigorous acid dissolution techniques (including microwave heating using closed vessels at high pressure) result in Cr values between 10 and 13 mg kg⁻¹*" (emphasis added).

Table 1 Cr concentrations in SRM sediments and soils

SRM	Material	Cr/ $\mu\text{g g}^{-1}$	Relative uncertainty (%)	Round Robin data ^a	
				Mean	Range
Sediments					
1646a	Estuarine sediment	40.9 \pm 1.9	4.6		
8704	Buffalo River sediment	121 \pm 3.8	3.1		
1944	NY/NJ waterway sediment	266 \pm 24	9.0		
Soils					
2586	Trace elements in soil	301 \pm 45	15	114	57–156
2587	Trace elements in soil	92 \pm 11	12	34	21–53
2709	San Joaquin soil	130 \pm 4	3.1		
2710	Montana soil	39 ^b			
Dust					
2584	Trace elements in indoor dust	135.0 \pm 9.1	6.7	70.3	47–108

^aThe number of Round Robin participants was 23 and 22 for SRMs 2586 and 2587 and 14 for SRM 2584. ^bMontana soil Cr value is not certified.

In this note two methods were investigated for the dissolution of Cr in HISS-1: (1) microwave dissolution using HNO₃, HF, and HClO₄, followed by reflux with concentrated HClO₄, and (2) sealed Carius tube digestion using HNO₃ and HCl at high temperature and high pressure. Using Method 1 verified the incomplete recoveries observed by Yang *et al.*⁴ The Carius tube technique, which is much simpler, gave good recoveries for HISS-1 samples. Carius tubes have been used for the determination of sulfur⁷ and mercury,⁸ two other elements that can exhibit volatile behavior, in coal fly ash, which is a refractory silicate material.

Experimental

Instrumentation

Microwave dissolution was performed using a model MLS 1200 Mega microwave system equipped with a 6-vessel model HPR 1000 rotor from Milestone Laboratory Systems, Monroe, CT, USA[†]. The 50 mL TFM Teflon vessels are sealed by the action of a calibrated torque wrench on a thick plastic pressure release spring designed to withstand a pressure of 1×10^7 Pa.

ICP-MS measurements were made using a VG PlasmaQuad 3[†] (Thermo Elemental, Winsford, Cheshire, England). The instrument was operated with the plasma screen and S-option pump under low-power conditions. Operating parameters are listed in Table 2. The sample solution was pumped at a rate of 0.6 mL min⁻¹ and was introduced to the plasma *via* a concentric nebulizer and impact bead spray chamber with water cooled to 4 °C. The auxiliary gas flow rate and torch position had a significant effect on the intensity of the background plasma-based molecular ions, and these parameters were optimized to achieve the best signal-to-background ratio. The mass calibration and lens voltages were optimized to yield maximum sensitivity.

Reagents

Concentrated high-purity nitric and hydrochloric acids (Optima grade) were obtained from Fisher Scientific, Pittsburgh, PA, USA. Concentrated perchloric and hydrofluoric acids and de-ionized water were purified in-house by sub-boiling distillation. Enriched ⁵³Cr was obtained from Oak Ridge National Laboratory, Oak Ridge, TN, USA. The concentration of the ⁵³Cr spike solution was determined by calibration against two primary standard solutions: (1) Cr metal of high chemical purity (99.996%) was used to prepare

[†]Any mention of commercial products within this paper is for information only; it does not imply recommendation or endorsement by NIST.

Table 2 ICP-MS operating conditions

Forward power/W	630
Gas flows/L min ⁻¹	
Coolant flow	13
Auxiliary flow	1.1
Nebulizer flow	0.99
Len voltages/V	
Extraction	-75
Collector	0.0
Lens 2	1.4
Lens 3	-4.1
Lens 4	-147.7
Pole Bias	-4.5
Data collection	
Mode	Peak jump
Points per peak	1
Dwell times/ms	
Mass 52	20
Mass 53	10
Measurement time/s	60
Replicates per sample	5

one primary standard solution, and (2) NIST SRM 3112a, Cr Spectrometric Solution, was used to prepare the other. Bottles of HISS-1 were obtained from the National Research Council of Canada (Ottawa, Ontario).

Carius tubes

Carius tubes were fabricated in our glass shop from Pyrex glass. A diagram of the tube and the dimensions are given in previous papers.^{9,10} The internal volume is \approx 25 mL. The tubes were cleaned with reagent grade nitric acid at \approx 80 °C for 24 h, rinsed three times with high purity water, and then dried in a laboratory oven. Tubes were used only once and then discarded. Horvat *et al.*¹¹ used sealed Pyrex tubes for Hg determinations and discuss in detail the advantages of this system for Hg determinations in coal fly ash. Carius tube digestion is particularly suited to these types of samples because of their very low carbon content (less than 10%); therefore, after combustion the tubes have very little excess pressure. Nevertheless, the safety precautions discussed in the next section should be strictly followed.

Safety considerations

Carius tube digestion involves the reaction of nitric and hydrochloric acids at 240 °C and the generation of internal pressures in excess of 1×10^7 Pa (100 atm). Under these conditions all forms of carbon are oxidized to CO₂, which generates additional pressure in the tubes. Extreme care should be used in the handling and venting of pressurized tubes. Tubes

having any defects or small holes should not be used as they represent a severe explosion hazard from pressurized CO₂. The venting process should be conducted behind an appropriate explosion-resistant safety shield by appropriately trained personnel. A discussion of Carius tube design for minimizing losses and hazards by explosion has been provided by Gordon *et al.*⁹ and references therein to their two previous papers as well as more recent work.^{7,8}

Sample preparation

Instrumental neutron activation analysis. Approximately 250 mg portions from six different bottles of HISS-1 were transferred to polyethylene foil bags and heat sealed. Additional samples were taken simultaneously for moisture determinations. Moisture was determined by drying the samples at 105 °C for 2 h. The mass loss averaged 0.102% ± 0.007%. Samples were irradiated for 30 min at a thermal flux of 3 × 10¹³ neutrons cm² s⁻¹ and were not removed from the bags before counting because of the extremely fine particle size of the sample. The uncertainty in the blank correction was 0.01%. The ⁵¹Cr peak at 320.1 keV was used to determine the Cr concentration. The interference from the ¹⁴⁷Nd peak at 319.4 keV was less than 0.5% and was corrected using the clean 531.0 keV peak of ¹⁴⁷Nd. The mean value for Cr is 31.4 µg g⁻¹ with an expanded uncertainty¹² of 3.8 µg g⁻¹ (*k* = 2). The standard used for these determinations were weighed amounts of the pure element.

Inductively coupled plasma mass spectrometry analysis. Two samples from two different bottles of HISS-1 were subjected to Carius tube digestion. Two additional samples, one from each bottle, were subjected to high-pressure microwave digestion followed by wet ashing with HClO₄. For method validation and proof of control, two sub-samples from a single bottle of SRM 1648, Urban Particulate Matter, were also digested using the above microwave procedure. The dry masses of the different bottles of the CRMs were determined on separate samples using the procedure recommended for each material. They were initially dried for 3 h and weighed and then dried an additional 2 h and weighed again. There was no change in mass between the first and second weighings. The dry mass correction for the sediment samples averaged 0.111%. Two samples from each bottle were also dried at 107 °C in a dynamic high-purity nitrogen atmosphere for 5 h.¹³ The average mass loss by this procedure was 0.11%. Accurately weighed samples of approximately 0.25 g were added to Carius tubes and the Teflon vessels that came with the microwave system. The samples were spiked with an appropriate amount of enriched ⁵³Cr solution prior to digestion. The ⁵³Cr solution was calibrated concurrent with the samples by reverse isotope dilution.

Carius tube samples were digested using a mixture of 6 g of HNO₃ and 2 g of HCl. After the addition of sample, spike, and acids the Carius tubes were flame sealed, encased in a steel shell along with 20 g of solid CO₂ for external pressurization, and heated to 240 °C in a conventional laboratory oven for 15 h. A noticeable amount of precipitate remained presumably due to undissolved silicates. Samples were centrifuged and the supernatant transferred to glass beakers and taken to dryness. Residues were dissolved in 2% HNO₃ (v/v) to form a clear solution.

Microwave samples were decomposed using 0.5 g HF, 2 g HClO₄, and 4 g HNO₃. Samples were heated in a Milestone microwave for 45 min at powers ranging from 250 W to 500 W. The maximum external target temperature was set at 90 °C. The temperature monitored on the external surface of the vessel ranged from 80 °C to 90 °C. Based on an approximate conversion factor of 2.4, the internal temperature was estimated to be 200 °C, which is below the maximum safe

operating temperature of 240 °C. A noticeable amount of precipitate remained, and the samples were heated again on a hot plate. Solution was evaporated until fumes of HClO₄ were observed. The samples were cooled, and an additional 1 g of HF and 1 g of HNO₃ were added. Samples were refluxed for 1 h. The solution was again evaporated until fumes of HClO₄ were observed, and the samples were allowed to reflux in concentrated HClO₄ for 5 h. Samples were taken to near dryness twice, and the residue was redissolved in 2% HNO₃ (v/v). Solutions were clear, but a small amount of undissolved crystalline residue was observed at the bottom of the vessels.

All samples were diluted to approximately 3 ng g⁻¹ of the spike isotope in 2% HNO₃ (v/v) for analysis by cold plasma ICP-MS. Use of cold plasma conditions, low power and use of the torch shield, lowered the plasma-induced molecular ion interferences from 10⁵ cps to less than 700 cps at mass 52. The sensitivity was 7 × 10⁴ cps per ng g⁻¹. Matrix-induced interferences were assessed by measuring the natural ⁵²Cr/⁵³Cr ratio in an unspiked HISS-1 sample. The measured ratio differed from the ratio measured in a pure Cr solution by less than 0.5%. Mass bias corrections were applied externally, and the drift was assessed every three samples. Repeatability and reproducibility of the measured ⁵²Cr/⁵³Cr ratios was better than 0.2% in all cases. Blank corrections were less than 0.5% for all samples.

Results and discussion

The Cr concentration, the measurement uncertainty, and recoveries determined for all HISS-1 samples are presented in Table 3. The recoveries were calculated relative to the certified value. The top third of the table gives the summary of the INAA results. The middle of the table gives the results for both HISS-1 and SRM 1648 samples obtained by digestion using the microwave/HClO₄-wet ashing procedure. The lower third of the table gives the same information for HISS-1 samples that were digested in the closed system Carius tubes using a mixture of nitric and hydrochloric acids.

The uncertainties for the INAA results are counting statistics

Table 3 Cr concentration and percent recovery for CRM HISS-1 and SRM 1648

Non-destructive instrumental neutron activation analysis ^a			
Sample	Cr/µg g ⁻¹	Uncertainty ^{b/} µg g ⁻¹	Recovery ^c (%)
HISS-1 (A)	33.8	0.07	113
HISS-1 (B)	37.7	0.04	126
HISS-1 (C)	29.6	0.06	99
HISS-1 (D)	25.4	0.05	85
HISS-1 (E)	33.6	0.07	112
HISS-1 (F)	28.2	0.09	94
Mean	31.4	^d 4.5	105 ± 15
Microwave/hot plate digestion ^e			
HISS-1-A	16.4	0.51	55
HISS-1-B	15.1	0.49	50
SRM 1648-1	398.2	3.5	99
SRM 1648-2	389.2	3.5	97
Carius tube digestion ^e			
HISS-1 (A1)	27.1	0.35	91
HISS-1 (A2)	33.1	0.37	110
HISS-1 (E1)	28.3	0.39	94
HISS-1 (E2)	23.7	0.34	79
Mean	28.1	^d 3.9	94 ± 13 (1 s)

^aSample size ranged from 0.21 to 0.26 g. ^bUncertainties are 1 s for a single determination. ^cRecoveries were calculated using the certified values for HISS-1 (30.0 µg g⁻¹⁸) and SRM 1648 (403 µg g⁻¹⁴). Uncertainties for the means are 1 s. ^dUncertainties for the means are 1 s. ^eSample sizes ranged from 0.24 to 0.28 g for HISS-1. For SRM 1648 they were 0.098 and 0.025 for samples 1 and 2.

only. The uncertainties given for all the individual ICPMS determinations are estimates of the total uncertainty expressed as a 95% confidence interval. It includes the standard deviation of the mean of five, 1 min ratio measurements, the spike calibration, the correction for blank, and type B uncertainty estimates for calibrant assay, drying of the samples, dead time correction, mass bias, and possible spectral interferences. The uncertainty for sample recovery and sample heterogeneity are not included since these are the variables that we wish to determine by these experiments. The important point is that the precision of the measurements is about 1% or better which is much less than differences among samples.

The recoveries for two HISS-1 samples processed in the microwave followed by wet ashing with HClO₄ were only 55% and 50% whereas complete recovery of Cr was attained in SRM 1648. The very low recoveries for HISS-1 are similar to those reported by Yang *et al.*⁴ Neither a closed vessel microwave procedure nor wet ashing with HClO₄ is sufficient to recover Cr completely in the HISS-1 sediment despite quantitation by isotope dilution. This indicates clearly that the spike atoms of ⁵³Cr did not completely mix with all the Cr atoms in the sediment. This probably is a result of incomplete dissolution of Cr-bearing phases in the sediment.

The four samples processed in Carius tubes had much higher recoveries ranging from 79% to 110% and all concentration values are within the uncertainty range of the certified value. The mean value for the four determinations was 28.1 μg g⁻¹ ± 3.9 μg g⁻¹ which is in excellent agreement with the mean INAA value of 31.4 μg g⁻¹ ± 4.5 μg g⁻¹. Furthermore, the range of the six determinations by INAA was 25 μg g⁻¹ to 38 μg g⁻¹, which is almost identical to the range observed by Carius tube digestion. It is important to note that the relative counting precision of the INAA procedure was 0.3% or better for each of the six determinations. The excellent agreement between these two totally independent techniques suggest that the variation in recoveries (79% to 110%) reflect intrinsic sample heterogeneity rather than loss of Cr or poor blank control.

The cause for low recovery of Cr after wet ashing with HClO₄ could result from lack of dissolution of a refractory Cr phase because of insufficient heating or lack of solubility of a refractory phase in the acids used. The ion intensities indicate that there was no loss of the added ⁵³Cr spike isotope. This observation suggests that the low recoveries result from incomplete dissolution of natural Cr in the sample.

Conclusions

The use of two independent (no common systematic errors) techniques to determine Cr recovery helps to ensure accurate Cr certification of sediment samples. Instrumental neutron activation analysis of Cr would be the technique of choice for

comparative purposes, because no chemical treatment of the sample is required.

The Carius tube digestion of sediment with HNO₃ and HCl appears to give complete recovery of Cr and to be a promising alternative to the use of H₂SO₄ and HClO₄ acids. The higher digestion temperatures and pressures that can be attained in the Carius tube (a closed system in the thermodynamic sense—no matter can enter or exit the system) are significant advantages compared to existing methods. All the experiments in this study were carried out at 240 °C, but the tubes could be heated to as much as 400 °C. The digestion time for Carius tubes is typically 12 h to 15 h, but the tubes are normally placed in the oven at the end of the day and heated overnight and then removed the next morning; therefore, a batch of 12 samples takes only about 2 h of actual preparation time. This is much less time, and it is much simpler than the microwave procedure.

If the microwave experiments were performed at the maximum allowable temperature of 240 °C using nitric and hydrochloric acids, it is possible that the recoveries could equal those of the Carius tube procedure.

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