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Determination of inorganic anions in uranium ore concentrate reference materials

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Abstract

The determination of inorganic anions in uranium ore concentrates (UOCs) is useful to nuclear forensics for establishing the provenance of sample materials. In this collaborative study, quantitation of inorganic anions was carried out on three UOC reference materials from the National Research Council Canada: UCLO-1 (https://doi.org/10.4224/crm.2020.uclo-1), UCHI-1 (https://doi.org/10.4224/crm.2020.uchi-1), and UPER-1 (https://doi.org/10.4224/crm.2020.uper-1). The analytes were extracted into water and characterized by ion chromatography with combined standard uncertainties (u_c) between 1.6 and 11%. The highest contributor to u_c was homogeneity. Sulfate was the most abundant anion (2000–12,000 mg/kg SO_4^{2-}). Other anions were in the 15–500 mg/kg range.

Keywords Inorganic anions · Uranium ore concentrates · Reference materials · Ion chromatography · Laboratory intercomparison · Nuclear forensics

Introduction

Uranium ore concentrates (UOCs), also commonly referred to as yellow cake, are front end nuclear fuel cycle materials employed in the production of nuclear fuels. They are produced after uranium is extracted from uranium ore or obtained as a by-product from mining for other minerals. The treatment process employed to extract uranium depends on the ore mineralogy (uranium mineralogy as well as the gauge mineralogy); acidic ores are treated using acid leaching process (usually sulfuric acid) and alkaline ores are treated with alkaline reagents (usually aqueous solutions containing sodium carbonate and sodium bicarbonate). The resulting uranium solutions are purified (following solid/liquid separation) typically by ion-exchange, solvent extraction, or a combination of both approaches. The UOC products are finally obtained by precipitation using precipitants such as ammonia, $Mg(OH)_2$, H_2O_2 or NaOH, followed by washing, drying and calcination of the precipitate [1]. From a chemical point of view, the UOCs are mixtures of various uranium compounds [1] and their compositional profile can offer valuable information regarding the history and origin of the material. The impurity content of a UOC is influenced by the composition of the original ore as well as impurities added during processing, either intentionally or as contamination. As UOC is an intermediate product of uranium fuel production, these impurities can potentially propagate to nuclear materials at latter stages of the nuclear fuel cycle. In this regard, the characterization of UOCs is relevant in nuclear forensics and helps with the establishment of provenance which can be used to combat nuclear crime and terrorism, including the illicit trafficking of nuclear materials [2].

In order to have a complete origin and history assessment of UOCs and an unambiguous interpretation of measurement results, several parameters usually need to be measured during a nuclear forensic examination. For example, it is common to evaluate the morphology of the UOCs [3, 4] as well as the content and isotopic composition of certain elements, such as uranium [5–7], lead [8–10], strontium

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[9, 11], thorium [12] and samarium [13]. Other parameters commonly measured are trace elements [14–18], Raman spectroscopic properties [19], or $^{228}Th/^{232}Th$ [20] ratio for age dating, and the content of water leachable inorganic anions, typically fluoride, F^-, chloride, Cl^-, bromide, Br^-, nitrate, NO_3^-, phosphate, PO_4^{3-} and sulfate, SO_4^{2-} [1, 16, 21, 22]. Similar to other impurities, the inorganic anion profile in a UOC reflects both the mineralogical makeup of the ore material from which the uranium was mined and the hydrometallurgical process used to recover the uranium, as described above. A high sulfate content in a UOC, for example, most likely indicates that the uranium extraction/purification circuit involved the use of sulfuric acid; the presence of chloride, as another example, might indicate that sodium chlorate was used as an oxidant during the sulfuric acid leaching. Furthermore, other anions can be indicative of the uranium source, for example the presence of phosphates could indicate the uranium concentrate was produced as a by-products of fertilizer production.

Considering the complexity of these measurements and the need for practitioners to validate analytical methods, the availability of well characterized reference materials for UOCs is of high importance [23, 24]. As the samples may be used as evidence in legal proceedings, the measurements must be defensible and typically require the use of recognized reference materials for calibration. However, the availability of such materials is limited. Currently available materials include CUP-2 [25], the seven certified reference materials of the CRM-124 series [26], the four CRMs (named Agaric, Bolet, Chanterelle, and Morille) from the Commission d'Etablissement des Méthodes d'Analyse (CEA, Cetama) [27], and the two reference materials from the International Atomic Energy Agency [17]. These CRMs are certified for limited material characteristics and have decreasing availability over time.

In order to increase the availability of reference materials for UOCs, the National Research Council Canada has recently produced three uranium ore concentrates, UCLO-1 [28], UCHI-1 [29], and UPER-1 [30]. The aim of these new materials is to certify additional parameters which are lacking in the existing materials. The new materials have been certified for uranium content and isotope ratios ($^{234}U/^{238}U$ and $^{235}U/^{238}U$) [7], and for trace elements [18]. In the present work, the characterization of UCLO-1, UCHI-1 and UPER-1 has been further extended to include inorganic anions.

Although many instrumental methodologies, including capillary electrophoresis [31, 32], gas chromatography [33, 34], and sequential injection analysis [35] are available for measurement of inorganic anions, the standard approach for analysis of these analytes in UOC materials is ion chromatography (IC) with suppressed conductivity and/or ultraviolet (UV) detection [36]. Previous work has led to the development of a method for measurement of anions in UOCs: the analytes are extracted in water for 24 h, using a sample-to-water ratio of 1:100 [1, 16], followed by filtration and direct IC analysis of the aqueous solution. The sample-to-water ratio is used to calculate the anion content in the solid UOC sample.

In this collaborative study, the determination of water extractable anions in UCLO-1, UCHI-1, and UPER-1 was carried out by three laboratories: the National Research Council Canada (NRC), ANSTO, and the Joint Research Centre Karlsruhe (JRC) of the European Commission. Good agreement between the results reported by each of the laboratories would allow consensus reference values for inorganic anions to be reached.

Experimental

The measurements of inorganic anions in the UOC samples (UCLO-1 [28], UCHI-1 [29] and UPER-1 [30]) were performed by ion chromatography with conductivity or UV detection by three expert laboratories (NRC, ANSTO and JRC). The methods implemented by the three laboratories were very similar and followed an established approach in the field of UOC analysis [1, 16]. The analytes were extracted in high purity water. For this purpose, a 0.10 ± 0.02 g aliquot of UOC powder sample was dispersed in 10.0 ± 0.1 g of water in a clean, plastic screw-top vial, manually shaken, and maintained static for 24 h at room temperature. NRC performed 9 to 11 independent extractions on each UOC sample and each extract was analyzed 2 times. Both ANSTO and JRC performed 2 independent extractions and each extract was analyzed 2–3 times. The solid UOC sample powder was analyzed 'as-is' (i.e., not dried or further ground). All three laboratories followed this extraction procedure. After 24 h, the slurry was filtered using a filter with a pore size of 0.2 µm (as summarized in Table S1, three different filters were used by the participants). The resulting solution was analyzed directly by ion chromatography or further diluted if required. The operating conditions for the ion chromatography are reported in Table 1. For quantitation, an external calibration approach was employed. For this purpose, the three laboratories were responsible for obtaining and diluting their own SI-traceable primary standards. In all cases, the primary standards were sourced commercially as reported in Table S2. Multi-anion working calibration standards were prepared in-house by gravimetric dilution of the primary standards in water to fit the working range (in this case 0.05 to 20 mg/kg). Quality control samples were also analyzed by all laboratories (Table S3). All reagents employed were of ACS Grade or better and ultrapure water was generated in house to meet or exceed the requirement of ISO 3696 Grade 1 standard (18.2 MΩ cm at 25°C).

Table 1 Operating conditions for the ion chromatography measurements

	NRC	ANSTO	JRC
Instrument	Dionex ICS-5000+	Dionex ICS 2100	Metrohm Advanced Compact IC 861
Mode	Isocratic	Gradient	Isocratic
Guard column	Dionex AG23 (4×50 mm)	Dionex AG19 (4×50 mm)	METROSEP anion dual 1 (4.6×50 mm)
Column	Dionex IonPack AS23 (4×250 mm)	Dionex IonPack AS19 (4×250 mm)	METROSEP A supp 5 (4×150 mm)
Eluent	4.5 mM Na_2CO_3, 0.8 mM $NaHCO_3$	10 to 50 mM KOH	1.0 mM Na_2CO_3, 3.2 mM $NaHCO_3$
Flow rate	1.0 mL/min	1.0 mL/min	0.7 mL/min
Injection volume	25 µL	100 µL	20 µL
Separation temperature	30 °C	30 °C	30 °C
Suppressor current	25 mA	125 mA	n/a
Suppressor regeneration	Self-regeneration	Self-regeneration	50 mM H_2SO_4
Detector(s)	Conductivity and UV at 210 nm	Conductivity	Conductivity
Run time	30 min	35 min	25 min

Results and discussion

This section is devoted to the description of the analytical method used by the three laboratories (i.e. NRC, ANSTO, and JRC) for the determination of inorganic anions in UCLO-1, UCHI-1, and UPER-1 CRMs along with the consensus values and their uncertainties obtained within this collaborative study.

Some of the methodological information summarized in the "Experimental" section will be reiterated here and further discussed for validation purposes.

Measurement method: analyte extraction

As reported by Badaut et al. [1] and by Keegan et al. [16], the screening of inorganic anions in UOC samples is based on the aqueous extraction of the analytes from the matrix. In particular, 0.1 g of sample is dispersed in high purity water at a ratio of 1:100 and kept at room temperature for 24 h. It was shown that longer extraction periods (up to 48 h) and/or higher temperatures (up to 80 °C) did not increase extraction efficiency [16]. The anion measurements performed in this study adhere to this specific leaching approach.

After 24 h extraction, the aqueous extracts were filtered (0.2 µm) to remove solid particulates and then analyzed (as-is or further diluted) by ion chromatography. As reported in Table S1, three types of filters were used by the participant laboratories (nylon, polyethersulfone, and cellulose acetate). Furthermore, ANSTO measured the uranium content of the water solution by ICP-MS and found that some U was also extracted during the anions extraction procedure. The average concentrations of U in the aqueous extracts were: 525 ± 90 mg/kg for UCLO-1, 370 ± 20 mg/kg for UCHI-1 and 285 ± 10 mg/kg for UPER-1 ($n = 2$).

Example chromatograms recorded for UCLO-1, UCHI-1 and UPER-1 are shown in Figs. S1, S2 and 1. With the exception of fluoride, which eluted close to unknown interfering peaks, all other anions were baseline separated and could be quantified by conductivity detection (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) or by UV detection at 210 nm (Br^-, NO_3^-).

Measurement method: quantitation

Ion chromatography is a suitable technique for quantitation of inorganic anions in aqueous solution at the low mg/kg levels. Chromatograms obtained from anion mixtures at 0.1 mg/kg and 1 mg/kg are shown in Fig. S3 and S4 respectively. Detection limits, estimated as 3 times the standard deviation of the baseline, are given in Table 2.

For all anions and detection modes, a response curve was produced in the 0.05 to 20 mg/kg working range. As shown in Figs. S5 to S12 (and Tables S4 to S11), both conductivity and UV detection exhibit nonlinear response which is evident from the graphs of the residuals.

In order to account for the nonlinear effects, the NRC approach was to reduce the working range of the calibration to an interval suitable for quantitation of the analyte, using a nonlinear model to fit the calibration data (second-order polynomial, $y = a_0 + a_1x + a_2x^2$). Details of these calculations can be found in the SI. Similarly, the JRC used a four-point calibration plus one blank and a nonlinear model was fitted to the data ($y = a_1x + a_2x^2$). Finally, ANSTO used a linear model ($y = a_0 + a_1x$) in conjunction with a point-to-point

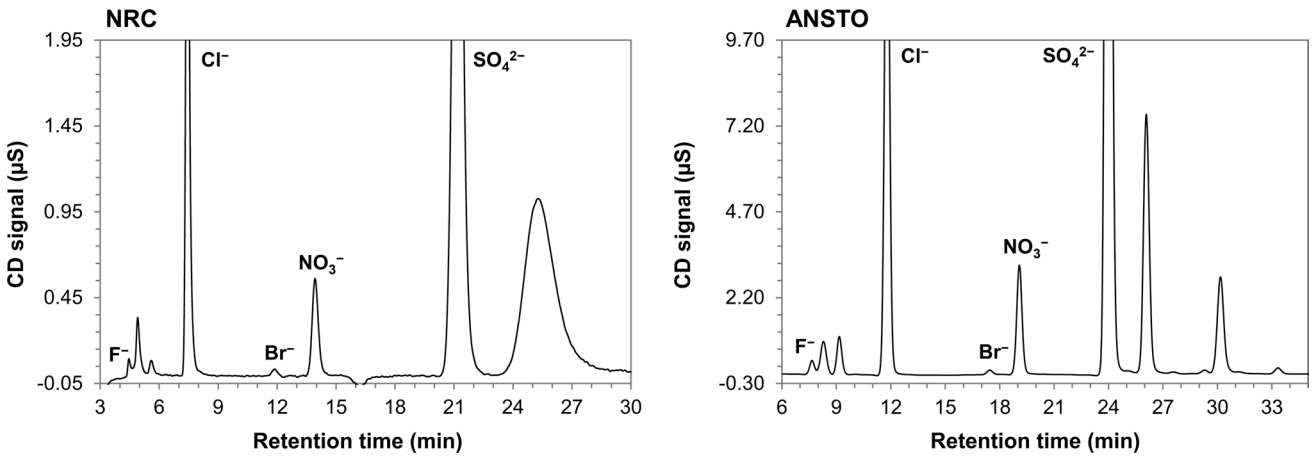

Fig. 1 Ion chromatogram of UPER-1 CRM (suppressed conductivity). Left: chromatogram observed at NRC. Right: chromatogram observed at ANSTO. The chromatogram observed at JRC was similar to that observed at NRC. The retention times and CD signal differences between NRC and ANSTO were due to the different experimental conditions (Table 1). Peaks eluting after sulfate were not identified

calibration approach by bracketing the response of the sample between the response of two standards.

The procedural blanks were free of most analytes. Some small unknown peaks were observed near the retention time of fluoride (NRC and JRC chromatograms), and high procedural blanks for nitrate were observed by the JRC. For chloride and nitrate quantitation, minor blank correction was performed by the NRC (see SI).

As detailed in the "Experimental" section, all three laboratories employed an external calibration approach by preparing multi-anion calibration standards in water. Although the matrix of the calibration standards was not perfectly matched to the UOC aqueous extracts, no matrix effects were observed; the response generated by the standards prepared in water was comparable with the response of those prepared in the UOC aqueous extracts (Tables S12 to S14), therefore, the external calibration approach with standards prepared in water was suitable for this quantitation. As reported in Table S3, all laboratories used at least one quality control (QC) sample. For ANSTO and JRC, the quality control materials were certified aqueous solutions of anions which were used to demonstrate the accuracy of the calibration curve. For the NRC, the quality control material was a soil matrix reference material (Sigma Aldrich SQC013, Lot LRAC0708) used to demonstrate recoveries obtained by aqueous leaching (Table 3). With the exception of phosphate, for which recovery was only 75%, all other anions were fully recovered and the results were comparable to the reported reference values (i.e., result in Table 3 passed the conformity test ISO 10576-1 and the Wald test).

The lower recovery of phosphate was likely due to low water solubility of phosphate salts present in the sample. However, since no aqueous leachable phosphates were

Table 2 Limits of detection (LODs) by ion chromatography estimated on the analysis of aqueous standards (conductivity detection)

Analyte	LOD in mg/kg (NRC and JRC)	LOD in mg/L (ANSTO)
Fluoride	0.017	0.01
Chloride	0.031	0.01
Bromide	0.10	0.01
Nitrate	0.094	0.05
Phosphate	0.29	0.1
Sulfate	0.12	0.05

To convert these detection limits to the solid sample material, the dilution factor needs to be considered

Table 3 NRC analysis: recoveries of inorganic anions in soil reference material SQC013 (Sigma Aldrich, Lot LRAC0708)

Analyte	Certified value (mg/kg)		Measured at NRC (mg/kg)	
	Value	SD	Value	SD
F^-	263	26	253	21
Cl^-	753	75	802	47
Br^-	33.5	3.4	34.8	2.0
NO_3^-	988	99	1039	58
PO_4^{3-}	1040	104	788	47
SO_4^{2-}	632	63	696	35

These values are referred to as the mass fraction of analyte in the solid sample. Aqueous leaching could only solubilize 75% of available phosphates, whereas all other analytes were fully recovered

detected in the UOC materials, the lower recoveries for this analyte were not a concern for this project. The chromatogram obtained on the soil QC sample is given in Fig. S13 and shows that the analytical signals were fully resolved.

In order to assess the uncertainty of individual measurements, a Monte Carlo approach [37] was used by the NRC whereas repeatability standard deviation was used by ANSTO and JRC. The Monte Carlo method used by NRC is described in Paragraph S1 and detailed calculations are shown in the Excel supporting file. The input variables (*x*-axis: mass fraction, *y*-axis: signal) were assumed to be normally distributed and an estimate of their uncertainty was obtained by repeated measurements (uncertainty on *y*-axis) or by error propagation (uncertainty on *x*-axis). The Monte Carlo simulation consisted of 10^4 draws from the distribution of the input variables, followed by calculation of the corresponding output variable (i.e., the mass fraction of the analyte in the sample). The uncertainty on the single measurement was then estimated from the standard deviation of the 10^4 simulated results. As reported in Table S15 the relative standard uncertainty for single measurements was between 1.1 and 2.3% for all analytes with the exception of bromide (4.7%).

Homogeneity and stability

A homogeneity study was performed on 0.1 g samples and the uncertainty due to homogeneity was estimated using the DerSimonian–Laird random effects model [38]. For this purpose, 9 to 11 aliquots of UOC were sampled across each batch and analyzed by ion chromatography at the NRC. Each UOC aliquot was extracted in water and injected into the IC system two times. A calibration and uncertainty evaluation on each single measurement was obtained as described in the previous paragraph and detailed in the supporting Excel file. The DerSimonian–Laird calculation was performed using the dsl function (R software, version 4.0.2; metRology package, version 0.9-28-1) and the estimate of the heterogeneity of the sample (i.e., homogeneity uncertainty, u_{hom}) was the excess variance from the DerSimonian–Laird calculation (Paragraph S2). As reported in Table 4, for the UOC materials studied herein, the u_{hom} was the major source of uncertainty contributing to the reported combined standard uncertainty.

Since the UOC materials have marginal residual water levels (the water content is 0.005 g/g for UCLO-1, 0.003 g/g for UCHI-1 and 0.022 g/g for UPER-1), no concerns about the stability of inorganic anions, such as their eventual

Table 4 Reference values and uncertainty components for inorganic anions in the UOC materials

Material	Analyte	Value mg/kg	u_c mg/kg	u_c Relative	u_{hom} mg/kg	u_{char} mg/kg
UCLO-1	F^-	< 3	–	–	–	–
	Cl^-	< 4	–	–	–	–
	Br^-	< 4	–	–	–	–
	NO_3^-	< 15	–	–	–	–
	PO_4^{3-}	< 8	–	–	–	–
	SO_4^{2-}	8170	450	5.5%	410	180
UCHI-1	F^-	< 3	–	–	–	–
	Cl^-	< 4	–	–	–	–
	Br^-	< 4	–	–	–	–
	NO_3^-	< 15	–	–	–	–
	PO_4^{3-}	< 7	–	–	–	–
	SO_4^{2-}	11,600	1300	11%	1200	300
UPER-1	F^-	< 7	–	–	–	–
	Cl^-	462	23	5.0%	21	9.4
	Br^-	16.1	0.73	4.5%	0.00	0.73
	NO_3^-	202.8	4.6	2.3%	4.4	1.5
	PO_4^{3-}	< 8	–	–	–	–
	SO_4^{2-}	2168	35	1.6%	31	16

Value = consensus value NRC, ANSTO and JRC. u_c is the combined standard uncertainty. $u^2_c = u^2_{hom} + u^2_{char}$, where u_{hom} is the uncertainty component due to homogeneity, and u_{char} is the uncertainty component due to characterization. The uncertainties are reported with two significant digits. Individual data from all laboratories along with the calculation of the consensus can be found in the Excel supporting file

degradation, are expected in the long and short term, therefore a zero stability uncertainty was assigned. However, these materials tend to be hygroscopic and should be stored in a dry environment to avoid moisture adsorption after opening.

Calculation of consensus value and characterization uncertainty

As discussed, characterization data were obtained from a collaborative study which saw the participation of NRC, ANSTO and JRC. The NRC performed 9 to 11 independent aqueous extractions on each sample and each extract was analyzed by ion chromatography two times (reported in SI). Nitrate was measured with both a UV and conductivity detector, bromide was measured only by UV while all other analytes were measured only by conductivity. Similarly, both ANSTO and JRC performed two independent aqueous extractions of each reference material followed by 2 to 3 analyses with ion chromatography (conductivity detection). For each independent extraction, one result was reported along with its uncertainty. For those analytes which could be quantified, agreement between the results reported by each of the three laboratories was found (Figs. 2 and 3).

For the calculation of the consensus values and its characterization uncertainty (u_{char}), the DerSimonian–Laird approach was used similar to that presented previously for the estimation of u_{hom}. Table 4 summarizes the consensus values obtained for inorganic anions in UCLO-1, UCHI-1 and UPER-1, the average results presented by the three participating laboratories are given in Tables S16 to S18, and detailed calculation can be found in the Excel supporting file. The nitrate results returned by JRC were not used for the consensus value calculation on UPER-1 as the data carried a critical blank correction of nearly 40%. The higher variability in the uncertainty of chloride measurements reported by the three laboratories was also due to the variations in the procedural blanks (Fig. 3).

For all three materials, the most abundant inorganic anion was sulfate which most likely indicates that their hydrometallurgical processing involved sulfuric acid leaching and possibly the use of sulfuric acid during purification (e.g. by solvent extraction). Although minerals containing sulfur are likely to be present in the ore material, the high concentration of sulfur present as a result of sulfuric acid leaching will obscure any original 'ore provenance' signature. Furthermore, there was a substantial agreement between the amount of sulfate recovered by aqueous extraction and the total sulfur [28–30] measured by ICP-MS (recovery = 87–100%, Table S19). This indicates that aqueous leaching can be sufficient to recover sulfur. The sulfur can also be used for other characterization techniques such as sulfur isotope ratio measurements [39]. Other than sulfate, the ion chromatograms of UCLO-1 and UCHI-1 looked clean: fluoride could be detected in UCHI-1 but not UCLO-1 while the peaks

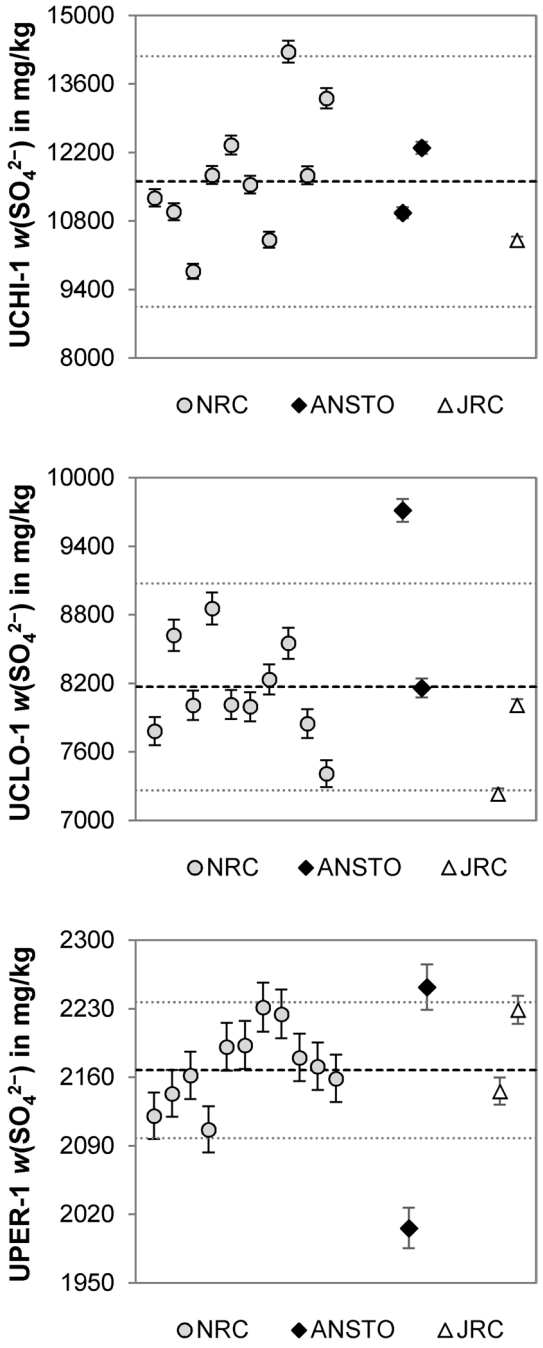

Fig. 2 Determination of sulfate in UCLO-1, UCHI-1 and UPER-1: results from the collaborative study. NRC data: gray circles, ANSTO data: black diamonds, JRC data: white triangles, consensus value: dashed black line, combined expanded uncertainty ($k = 2$): area between the two dotted gray lines. The error bars refer to the standard uncertainty reported on the single measurements ($k = 1$)

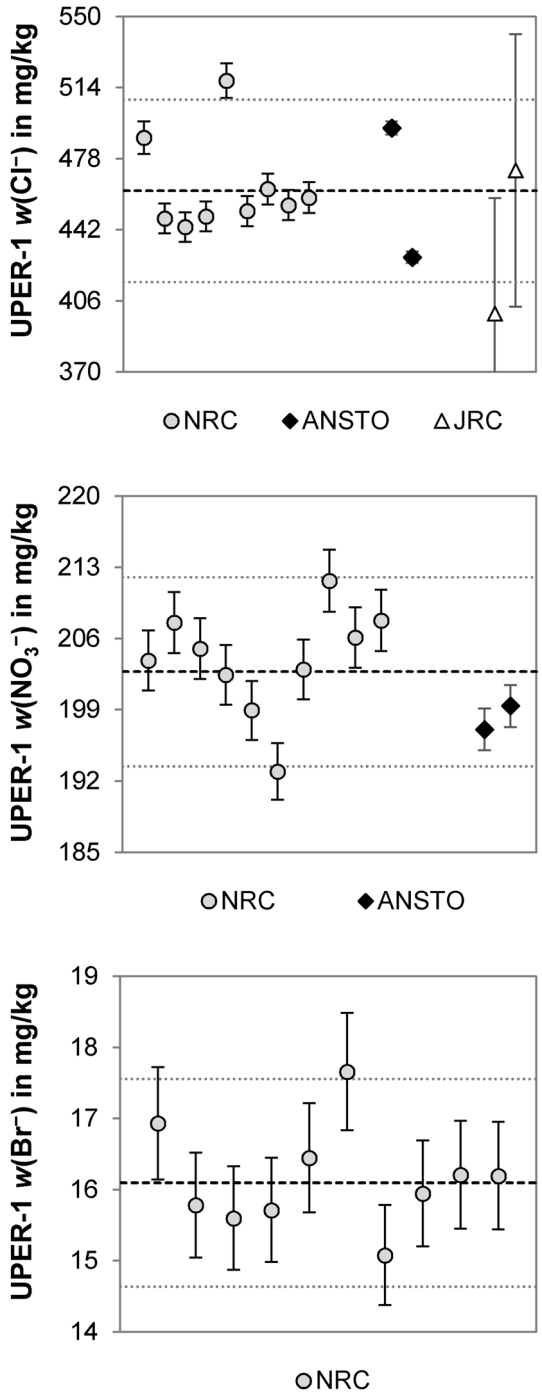

Fig. 3 Determination of chloride, nitrate, and bromide in UPER-1: results from the collaborative study. NRC data: gray circles, ANSTO data: black diamonds, JRC data: white triangles, consensus value: dashed black line, combined expanded uncertainty ($k=2$): area between the two dotted gray lines. The error bars refer to the standard uncertainty reported on the single measurements ($k=1$)

of chloride and nitrate were similar to those observed in the procedural blank (Figs. S1 and S2). On the other hand, UPER-1 showed a more complex anions profile (Fig. 1; Table 4) with a detectable amount of fluoride, and quantifiable amounts of Cl^-, Br^- and NO_3^-.

Phosphate was not detected in any of the aqueous extracts. For UCLO-1 and UCHI-1 this result was consistent with the measurement of total phosphorous in the UOC samples by ICP-MS; in fact, *P* was undetected in UCLO-1 and only 5.8 ± 2.8 mg/kg was detected in UCHI-1. However, this amount is below the detection capability of ion chromatography with conductivity detection. Conversely, 282 ± 23 mg/kg total phosphorus was measured in UPER-1 by ICP-MS. Assuming this phosphorous was in the form of PO_4^{3-}, one would expect 865 ± 71 mg/kg PO_4^{3-} in the UOC samples, which should be detectable by ion chromatography despite the 1:100 dilution introduced by the aqueous extraction method (0.1 g sample in 10 g water). However, no PO_4^{3-} peak was observed (Fig. 1; Table 4). It is likely that the phosphate was either inaccessible to the water extraction (many phosphates salts are water insoluble or poorly soluble in water) and/or the phosphorous was present as insoluble chemical species other than phosphates.

Conclusion

In this study, value assignment for the content of inorganic anions in uranium ore concentrate reference materials (UCLO-1, UCHI-1 and UPER-1) was carried out within an international collaborative study involving the National Research Council Canada, ANSTO, and the Joint Research Centre Karlsruhe of the European Commission. Following common practice in this field, the analytes were extracted from the uranium matrix using a simple water leaching procedure. The results herein were generated by strictly following this method of analysis which should be followed when these results need to be replicated. The characterization uncertainty was small in comparison to the homogeneity uncertainty which, for most analytes, was the main contribution to the combined uncertainty. Considering the low combined uncertainty obtained for all measurable analytes ($u_c = 1.6–11\%$, $k=1$), these three reference materials will be a valuable tool for practitioners in the nuclear forensic field for the validation and proof of methods for anions quantitation in uranium ore concentrates.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10967-023-08837-0.

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Declarations

Conflict of interest All authors declare that they have no conflict of interest.

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