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INAA and Ion-Beam Analysis of Elemental Admixtures in Carbon-Based Nanomaterials for Battery Electrodes

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Abstract

Six carbon materials with potential application in research and development of battery electrodes were tested for mass fractions of more than 40 elements by instrumental neutron activation analysis and ion-beam methods. The results indicate potential of the methods for characterization of materials with very low content of impurities (carbon black) as well as those with relatively high content of certain transition metals (e.g., single walled carbon nanotubes, SWCNT). A batch-to-batch variability of elemental impurities was found for commercial SWCNT. Quality control was performed by analysis of CRM SWCNT-1, NIST SRM 1633b, NIST SRM 2711, and NIST SRM 1547.

Keywords

carbon nanomaterials, elemental admixtures, instrumental neutron activation analysis, ion-beam analysis

Introduction

The design, synthesis and application of carbon-based nanomaterials (nanocarbons) have had an important role in the physical sciences for the last few decades [1]. These materials exhibit exceptional mechanical, electrical, thermal, and optical properties that make them attractive in various fields of science and technology, including energy storage. Despite the interest in nanocarbons as electrodes for supercapacitors and batteries, additional elements present at variable quantities could influence their electrochemical response. Due to the high chemical resistance of nanocarbons, elemental characterization is a challenging task [2], particularly if total sample decomposition and solubilization is required. For instance in carbon nanotubes, leaching of transition metal catalyst nanoparticles by mineral acids may be prevented by encapsulation of nanoparticles between graphene layers [3]. Absence of information on complete chemical composition is especially bothersome in the case of expensive commercial materials. While routine digestion methods are being developed worldwide, results validation is complicated due to a lack of well-characterized reference materials for many of the known nanocarbons.

Instrumental neutron activation analysis (INAA) is an excellent method to establish reference values of total mass fractions in many types of materials. Recognized as a primary method of chemical analysis [4], INAA has high potential for accuracy, matrix independence, and low limits of detection for many elements. The advantage of the method for nanocarbon characterization is that the material is analyzed without dissolution. Its ability to characterize carbon nanotubes was already demonstrated, e.g., [5-7].

In this work, we examined six different nanocarbon samples by INAA and ion-beam methods that are available at the Nuclear Physics Institute (NPI). The goal was to demonstrate relevance of these radioanalytical methods in quantifying elemental admixtures in nanocarbons. The samples were representatives of carbon materials commonly used in energy storage systems and included carbon black, expandable graphite (purified and non-purified), reduced graphene oxide, and two specimens of single walled carbon nanotubes. The purpose of our study was also to provide

68 benchmarking values for complementary analytical protocols currently being developed
69 at the King Abdullah University of Science and Technology (KAUST).

70 **Experimental**

71 The samples of carbon materials analyzed are summarized in Table 1. These were
72 commercial products, selected to represent various carbon allotropes: carbon black,
73 (expandable) graphite, and single walled carbon nanotube (SWCNT). The last material
74 (CAS No. 308068-56-6) was available in two production batches. In addition, a
75 chemically processed sample of the expandable graphite (hereafter, purified expandable
76 graphite) and a sample of reduced graphene oxide, prepared at the Laboratory for Carbon
77 Nanostructures of KAUST [8], were analyzed. Quality control was performed by analysis
78 of the certified reference material SWCNT-1 (NRC Canada) and the three NIST (USA)
79 standard reference materials SRM 1633b, SRM 2711, and SRM 1547.

80 **Table 1** Analyzed carbon materials with laboratory codes together with quality control
81 samples used in INAA

Sample	Lab code	Producer	Note
Carbon Black	SA1	Alfa Aesar	Acetylene, 99.9+ %, Lot: S20A074
Expandable Graphite	SA2	Asbury Carbons	Grade 3772, Lot: 881201B-3
Purified Expandable Graphite	SA3		Laboratory preparation
Reduced Graphene Oxide	SA4		Laboratory preparation
Single-Walled Carbon Nanotube	SA5	Sigma Aldrich	Lot: MKBW7867
Single-Walled Carbon Nanotube	SA0	Sigma Aldrich	Lot: MKBT4053V
CRM SWCNT-1	SWCNT1	NRC Canada	Single-Wall Carbon Nanotube
NIST SRM 1633b	SRM1633b	U.S. NIST	Constituent Elements in Coal Fly Ash
NIST SRM 2711	SRM2711	U.S. NIST	Montana Soil
NIST SRM 1547	SRM1547	U.S. NIST	Peach Leaves

82 **Instrumental Neutron Activation Analysis**

83 *Samples and calibrators*

84 Typically, 30 mg portions of carbon materials were used, including for the SWCNT-1
85 certified reference material. For the analysis of the purified expandable graphite, test

portions with lower mass (about 20 mg) were used due to a low specific mass of this material. About 50 mg and 150 mg test portions of SRM 1633b and SRM 1547, respectively, were used for short time irradiation mode. Long-time irradiation mode was performed with 150 mg portions for all three NIST SRMs. The samples were heat-sealed into irradiation capsules made from two polyethylene (PE) discs with 25 mm diameter and 0.15 mm thickness. The PE discs were leached with diluted sub-boiled nitric acid (1+5) and deionized water prior to their use. Empty capsules were prepared in the same way and irradiated with the samples for determination of the blank contribution. A set of synthetic multi-element standards (MES) were used as calibrators for quantification. They were prepared according to procedures described earlier [9-11].

Irradiation and counting

The INAA procedures developed and routinely employed at the NPI laboratory [10, 12] were used with minor modifications. Quantification was carried out by the comparator method. Irradiations were performed in the experimental reactor LVR-15 of the Research Centre Řež.

Short time irradiation was performed for 1 min at thermal, epithermal, and fast neutron fluence rates of $3.2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, $1.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, and $1.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, respectively, with the aid of a pneumatic facility with a transport time of 3.5 s. The samples and standards were irradiated separately in a PE rabbit. A set of monitors (Au+Mn+Rb) was used to check neutron fluence rate stability during the irradiation period of the whole batch of samples and calibrators. The samples, calibrators and monitors were counted for 10 min after a 10 min decay using an HPGe coaxial detector with relative efficiency of 21 % and FWHM resolution of 1.75 keV (both for the 1.33 MeV photons of ^{60}Co).

For long time irradiation (2 h), the samples and calibrators were packed to form a column that was inserted into an aluminum irradiation can. Iron monitors were inserted between each set of 5 to 6 samples and/or calibrators to determine the axial neutron flux gradient. Irradiation was performed in the above mentioned experimental reactor with thermal,

epithermal, and fast neutron fluence rates of $2.6 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, $3.9 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, and $2.9 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. Counting was performed with coaxial HPGe detectors (relative efficiency 50 to 80 %, FWHM resolution of 1.8-1.9 keV, both for the 1.33 MeV photons of ^{60}Co) after decay time of about 5, 25, and 40 days.

The HPGe detectors were interfaced to a Canberra Genie 2000 gamma-spectroscopy computer controlled analyzer through a chain of associated linear electronics. A Canberra 599 Loss Free Counting module was used to correct variable count-rate and dead time. The measured gamma-ray spectra were evaluated with the use of Canberra Genie 2000 software.

SA0 sample was analyzed in five replicates, the other samples were analyzed in duplicates. The uncertainties of INAA results are combined uncertainties that include error from net peak area evaluation for the sample and calibrator and an estimated contribution from differences of sample and calibrator dimensions on irradiation and counting at the level of 1.5 % of the mass fraction determined.

Ion-beam analysis

The targets for ion beam analysis were prepared by depositing sample on a polypropylene (PP) foil (Fluxana, thickness 4 μm) which was glued over a 10 mm hole in the centre of an acrylic glass holder. Due to the variable physical and chemical properties of the samples, two procedures for deposition were used.

1) For SA1, SA3 and SA4 materials, a suspension of 2 mg of sample and 0.3 mL of deionized water was prepared in a PP vial. The suspension was transferred by a micropipette on the foil and dried at elevated temperature (approximately 50 $^{\circ}\text{C}$) in several portions. Different layer thicknesses were obtained because the variable amount of material was lost during the transfer (adhesion on the walls of the vial and pipette). A blank sample was prepared by evaporation of the same volume of water on the foil. The thickness of the layer prepared was 0.3, 1.9, and 2.3 mg cm^{-2} for SA1, SA3, and SA4 materials, respectively, as determined by Rutherford Backscattering Spectrometry (RBS).

2) An undiluted solution of polyvinylalcohol – PVA (Film release agent PVA, R@G GmbH) was used to glue SA2 and SA5 materials on the foil. The PVA was mixed with $\text{Y}(\text{NO}_3)_3$ so that the dried polymer contained approximately 1 mg g^{-1} of Y as a tracer. For fixing of the material on the foil, 25 μL and 50 μL of PVA solution with Y was used in the case of SA2 and SA5 materials, respectively (25 μL of PVA solution contained about 2.5 mg of material after drying).

The prepared targets were analyzed in a multipurpose target chamber for simultaneous analysis by Particle Induced X-ray Spectrometry (PIXE), RBS, Proton Elastic Scattering Analysis (PESA), and Particle Induced Gamma-Ray Spectrometry (PIGE). The targets were irradiated with the 2.9 MeV proton beam with the rectangular size of $3 \text{ mm} \times 3 \text{ mm}$ that was produced by a Tandetron 4130 MC accelerator (High Voltage Engineering Europa B.V., the Netherlands). The beam current used for targets made from SA1, SA3, and SA4 was about 15 nA with typical irradiation time of 900 s. For targets prepared with PVA (SA2 and SA5), the irradiation time was between 200 and 500 s and the beam current used was lower (varied from 2 to 7 nA) to limit polymer degradation.

Results and discussion

Quality control of INAA was accomplished by analysis of NIST SRM 1633b Coal Fly Ash and NRC CRM SWCNT-1 Single-Wall Carbon Nanotube. The latter material has similar matrix to samples SA0 and SA5. Additionally, NIST SRM 2711 and SRM 1547 were analyzed in some batches of INAA. Tables 2 summarizes the mass fractions determined, or the limits of detection (LOD), for quality control samples. The results for NIST materials are given on a dry mass basis. The moisture in CRM SWCNT-1 was not determined in the study and the mass fractions listed are thus related to the as-received state, similarly as the materials tested (this could result in systematic underestimation for all elements in a given material). Previously, the moisture was determined in at that time candidate CRM SWCNT-1 by Karl Fisher titration and by drying in a desiccators, resulting in values in the range of 0.5–0.7 % (traditional oven drying was not recommended for this material) [17].

With some exceptions, the mass fractions results were in agreement with the certified values within uncertainty margins. The Na mass fraction in SRM 1547 was much higher than the certified value in both short-time (ST) and long-time (LT) irradiation modes (Na was determined by both modes of INAA employing the same nuclear reaction but different calibrators). We proved previously [18] that the SRM 1547 (containing a low Na mass fraction) became contaminated via the corrosion of the sodium-rich glass bottle provided by the producer. For the other materials, the Na results from both irradiation modes are some 10 % underestimated. Similar bias was indicated also for the K mass fractions in the control samples. It is not clear if this systematic deviation was due to the calibrators used (several calibrators were used in two different modes) or some unknown issue. The discrepancy of the determined Cl mass fraction with its certified value for SRM 1547 has been previously observed in our laboratory (unpublished results). By contrast, good agreement is normally obtained for other control materials with certified Cl values (e.g., SRM1566b Oyster tissue [19]). For all other elements determined, the systematic bias in control samples was not observed thus confirming the accuracy of our INAA results.

The INAA of CRM SWCNT-1 revealed that the Mg mass fraction is below LOD ($<800 \text{ mg kg}^{-1}$). It was in disagreement with the former reference value $4180 \pm 380 \text{ mg kg}^{-1}$ [20] that was recently removed from the certificate [13]. The old reference value was based on a single INAA result [7, 20]. Apparently, the gamma-line of ^{101}Mo with energy of 1012.5 keV (intensity 13.0 %), well visible in the gamma-ray spectrum due to a high concentration of Mo in the CRM SWCNT-1, was incorrectly assigned to the 1014.5 keV gamma-line (intensity 28.2 %) of ^{27}Mg that is typically used for Mg evaluation in INAA.

Table 2 here (separate file, landscape mode, reformatted according to Reviewer request)

The results for nanocarbon samples are listed in Tables 3 and 4. The mass fractions determined are complemented with LOD for elements that could not be quantified. Substantial variance of the replicates in INAA (indicated also if estimated standard deviation was much larger than the uncertainty of single determination) was found in four cases – Al (SA2), Cr (SA2 and SA3), and Fe (SA2). This might be due to the

inhomogeneous distribution of particular elements in the test portion mass used. However, this could only be confirmed by analysis of a higher number of test portions.

Table 3 and **Table 4** here (separate file, landscape mode, reformatted according to Reviewer request)

Several procedures for target preparation for ion-beam analysis were tested. The goal was to minimize the risk of sample contamination. Preparation of a thin pellet using a hydraulic laboratory press in a stainless steel die was applicable for SA1 and SA3 materials only. Nevertheless, the pellets were brittle and it was difficult to remove PE foils that were used in the press to avoid contamination of the pellet from the stainless steel die. The method used for preparation of targets from SA1, SA3, and SA4 was based on deposition of the material from water suspension on a thin PP foil. The contribution of the foil and water evaporates (blank) was on an acceptable level so that it was possible to correct that if necessary.

The above method was not applicable for flakes of SA2 and conglomerates of SA5. A hair spray was tested to fix these two materials on a PP foil, however, the layer was mechanically unstable. Finally, PVA polymer was found as an acceptable glue for these two materials. The layer would be more homogeneous if the materials had been pulverized prior target preparation. This was avoided as it would create a risk of contamination or partial loss of volatile elements. The final targets were still acceptable and allowed quantification of several elements.

For many elements the results from both INAA and ion-beam analysis are in agreement. We suspect that the disagreement observed for Fe (SA2 and SA4) and Cr (SA4) values might originate from inhomogeneity. The reason for the deviation between results from the two methods for SA4 material (Ca, Cr, Zn) and SA5 material (As, Mo) has not been identified.

As expected, SA1 sample (Carbon Black) contained a minimum of elemental impurities. Only the elements Cl and Br were determined in both portions with Cl mass fraction about 70 times higher compared to Br. The values of Ca, Sc, Cr determined in one of two

portions and the value of Na above LOD in one of four portions (from both irradiation modes) may either be due to inhomogeneous distribution of the elements in the materials or due to contamination prior to measurement, especially in the case of Na.

In total, 13 elements were determined in SA2 samples (Expandable Graphite). High S content indicates some sulfur compound is intercalated between graphene layers to allow material expansion after heating. Mass fractions of Na, Mn, Fe, and Hf are also relatively high. These elements probably originate from the preparation procedure. The Cl to Br ratio in SA2 is about 170.

The SA3 specimen was prepared by expansion and purification of SA2. Naturally, S was dramatically eliminated during the SA2 expansion due to formation of sulfur oxides gases. Mass fractions of Na, Mn, and Fe are substantially lower in SA3 in comparison to SA2 confirming the effectiveness of the purification procedure. However, contents of some trace elements (Al, Si, Sc, Cr, Co, Hf) are the same or higher in SA3 product. The Cl to Br ratio was <30 (Cl mass fraction was below LOD) indicating that Cl was eliminated more effectively by purification procedure than Br.

The reduced graphene oxide specimen (SA4) was characteristic with relatively high mass fractions of Al, K, Mn, Br, and W. Similarly to SA1, one test portion exhibited a higher Na mass fraction than the others. Unlike SA1, however, the Cl mass fraction was also higher in the same portion (Cl analyzed in two portions only). This might be result of a contamination and result for these two elements should be used carefully. Nevertheless, a source of possible contamination in our INAA laboratory was not discovered.

Two different specimens, SA0 and SA5, of a commercially available SWCNT sample were analyzed (same supplier, two different production batches). The material is characterized by a high content of Co and Mo. The two metals play important role in the production of carbon nanotubes and are incorporated in the nanotubes structure [3]. In addition, relatively high mass fractions of F, Si and As are also present in the SA5 specimen. Using the self-verification principle of INAA [22,23], Co and Mo in SWCNT materials were determined from two independent nuclear reactions; cobalt via $^{59}\text{Co}(n,\gamma)^{60\text{m}}\text{Co}$ ($T_{1/2} = 10.47$ min) and $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$ ($T_{1/2} = 1925.28$ d); molybdenum via

255 $^{100}\text{Mo}(n,\gamma)^{101}\text{Mo}$ ($T_{1/2} = 14.61$ min) and $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ ($T_{1/2} = 65.976$ h). The mass
256 fractions determined agree within the uncertainty margins (for $k=2$), thus increasing
257 credibility of the results obtained.

258 The high content of Co and Mo in the analyzed SWCNT materials notably deteriorated
259 LOD of other elements by INAA (compare LOD for SA5 and SA4 in Table 4). The
260 radionuclides formed by activation of Co and Mo nuclides increased background in
261 gamma-ray spectra (due to the Compton scattering effect), in which the analytical
262 gamma-lines of other radionuclides formed were masked. Moreover, the high activity of
263 the activated test portion dictated counting at a large distance from the HPGe detector,
264 which also impaired LOD of many elements compared to “clean” carbon material. Still,
265 at least 10 additional elements were determined in both SA0 and SA5 materials. Notably
266 high mass fractions were found for Cl, Cr, As, Br, I, and W. The Cl to Br ratio was about
267 5 and 10 for SA5 and SA0, respectively.

268 The comparison of SA5 and SA0 results gives an interesting picture about the batch-to-
269 batch variability in terms of elemental admixtures. It appears that only Co, Mo, and W
270 are at a similar level in the two batches. The analysis identified four elements with a
271 higher content in SA5 compared to SA0 (V, Cr, Mn, As). By contrast, SA0 exhibits
272 higher mass fractions for Na, Al, Ca, halogens and lanthanoids. The difference is
273 remarkable especially in the case of Ca and lanthanoids. It seems that different
274 procedures or chemicals were used in production of the two batches. This finding shows
275 the importance of analytical control of materials in applications where chemical purity
276 can have an impact on various properties of the product.

277 Two elements, Cl and Br, were determined in almost all samples. The Cl to Br mass
278 fractions ratio was high for SA2, medium for SA1 and low for the other materials. It can
279 be another useful parameter for evaluation of the purification procedure (difference
280 between SA2 and SA3) and batch-to-batch variability (SA5 and SA0).

281 **Conclusions**

The applicability of INAA and ion-beam methods for analysis of carbon materials was demonstrated. Comparing the results determined for the different samples highlights how their composition can vary, even when sold as (or presumed to be) “pure” carbon materials. In the set of samples analyzed, the mass fractions of some elements span from sub- $\mu\text{g g}^{-1}$ to units of percent. Moreover, a non-negligible batch-to-batch concentration variability for the same element was observed for the SWCNT commercial material.

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361

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- 1 **Table 2** INAA results in mg kg⁻¹ (unless otherwise stated) for CRM SWCNT-1 (NRC Canada), SRM 1633b, SRM 2711, and
- 2 SRM 1547 (all three from U.S. NIST) quality control materials. The average (X), estimated expanded uncertainty of single
- 3 determination (U, coverage factor k=2), and number of portions analyzed (N) are given

	NRC CRM SWCNT-1				NIST SRM 1633b			NIST SRM 2711				NIST SRM 1547		
	X ± U	N	NRC [13] ^a		X ± U	N	NIST [14] ^a	X ± U	N	NIST [15] ^a		X ± U	N	NIST [16] ^a
Na ^b	139±6	3	(167±7)	Na ^b , %	0.183±0.006	5	0.201±0.003	1.05±0.03	2	1.14±0.03	Na ^b	33.9±1.2	2	23.8±1.6
Na ^c	153±18	4	(167±7)	Na ^c , %	0.185±0.009	4	0.201±0.003	NA	—	—	Na ^c	35.5±3.2	1	23.8±1.6
Mg	<800	—	—	Mg, %	0.36±0.14	4	0.482±0.008	NA	—	—	Mg	4320±160	1	4320±150
Al	475±23	4	(494±94)	Al, %	15.3±0.5	4	15.05±0.27	NA	—	—	Al	248±8	1	248.9±6.5
Cl	38±9	4	—	Cl	33±12	3	—	NA	—	—	Cl	299±10	1	361±14
K	2800±350	4	(3220±200)	K, %	1.80±0.08	4	1.95±0.03	2.31±0.10	2	2.45±0.08	K	22100±800	2	24330±380
Ca	2430±250	4	(2650±300)	Ca, %	1.39±0.08	4	1.51±0.06	NA	—	—	Ca	15000±600	1	15590±160
Sc	<0.23	—	—	Sc	41.1±1.2	4	(41)	9.3±0.3	2	(9)	Sc	0.042±0.002	1	(0.04)
Ti	170±60	3	(193±22)	Ti, %	0.78±0.03	4	0.791±0.014	NA	—	—	Ti	27±6	1	—
V	4.20±0.35	4	(4.37±0.31)	V	300±10	4	295.7±3.6	NA	—	—	V	0.34±0.05	1	0.367±0.038
Cr	266±16	3	(285±26)	Cr	201±8	4	198.2±4.7	44.8±1.8	2	(47)	Cr	1.14±0.20	2	(1)
Mn	133±5	4	(135.8±1.8)	Mn	133±5	4	131.8±1.7	NA	—	—	Mn	92±3	1	97.8±1.8
Fe, g kg ⁻¹	2.9±1.2	3	2.2±0.2	Fe, %	7.52±0.24	5	7.78±0.23	2.89±0.10	2	2.89±0.06	Fe	205±12	2	219.8±6.8
Co ^b , g kg ⁻¹	14.3±0.5	4	15.9±1.0	Co ^b	48.0±1.8	5	(50)	9.6±0.3	2	(10)	Co ^b	0.068±0.008	2	(0.07)
Co ^c , g kg ⁻¹	15.1±0.6	4	15.9±1.0	Co ^c	39±3	4	(50)	—	—	—	Co ^c	—	—	—
Ni, g kg ⁻¹	12.2±0.6	4	14.4±0.8	Ni	110±60	2	120.6±1.8	<50	—	20.6±1.1	Ni	<6	—	0.689±0.095
Zn	<130	—	—	Zn	209±8	5	(210)	333±10	2	350.4±4.8	Zn	16.4±1.0	2	17.97±0.53
As	<10	—	—	As	130±6	5	136.2±2.6	102±4	2	105±8	As	<0.4	—	—
Br	<3	—	—	Br	2.7±0.4	5	(2.9)	4.20±0.18	2	(5)	Br	9.6±0.3	2	(11)
Rb	<100	—	—	Rb	137±10	5	(140)	113±6	2	(110)	Rb	18.1±1.2	2	19.65±0.89
Sr	<200	—	—	Sr	980±100	4	1041±14	261±22	2	245.3±0.7	Sr	39±8	2	53.0±5.0
Mo ^b , g kg ⁻¹	6.77±0.24	4	7.3±1.1	Mo ^b	29.8±2.0	3	—	<40	—	(1.6)	Mo ^b	<8	—	0.0603±0.0068
Mo ^c , g kg ⁻¹	6.65±0.24	4	7.3±1.1	Mo ^c	<150	—	—	—	—	—	Mo ^c	—	—	—
Ag	<9	—	—	Ag	<1.2	—	—	4.7±0.6	2	4.63±0.39	Ag	<0.06	—	—
Sb	<5	—	—	Sb	4.49±0.30	3	(6)	18.8±0.6	2	19.4±1.8	Sb	<0.03	—	(0.02)
I	<4	—	—	I	<5	—	—	NA	—	—	I	<0.3	—	(0.3)
Cs	<3	—	—	Cs	10.60±0.4	5	(11)	6.61±0.22	2	(6.1)	Cs	0.074±0.020	2	—

Ba	<50	–	–	Ba	670±60	4	709±27	730±60	2	726±38	Ba	113±10	2	123.7±5.5
La	0.93±0.08	3	(0.96±0.27)	La	85±3	5	(94)	37.0±1.2	2	(40)	La	9.3±0.3	2	(9)
Ce	<8	–	–	Ce	178±6	5	(190)	70.0±2.2	2	(69)	Ce	9.9±0.4	2	(10)
Pr	<12	–	–	Pr	16±5	5	–	<9	–	–	Pr	1.8±0.6	2	–
Nd	<30	–	–	Nd	83±4	5	(85)	28.9±1.4	2	(31)	Nd	6.8±0.7	2	(7)
Sm	<0.05	–	–	Sm	17.0±0.6	5	(20)	4.99±0.16	2	(5.9)	Sm	1.11±0.03	2	(1)
Eu	<1.0	–	–	Eu	3.85±0.14	5	(4.1)	1.06±0.04	2	(1.1)	Eu	0.180±0.009	2	(0.17)
Tb	<0.7	–	–	Tb	2.57±0.12	4	(2.6)	0.79±0.03	2	–	Tb	0.107±0.007	2	(0.1)
Dy	<0.3	–	–	Dy	16.6±0.6	5	(17)	NA	–	–	Dy	0.62±0.03	1	–
Tm	<1.4	–	–	Tm	1.41±0.14	5	(2.1)	0.56±0.04	2	–	Tm	<0.03	–	–
Yb	<0.5	–	–	Yb	7.5±0.4	5	(7.6)	2.95±0.16	2	(2.7)	Yb	0.16±0.03	2	(0.2)
Lu	<0.6	–	–	Lu	1.12±0.14	5	(1.2)	0.47±0.04	2	–	Lu	0.019±0.005	2	–
Hf	<1.5	–	–	Hf	6.9±0.3	5	(6.8)	7.9±0.3	2	(7.3)	Hf	0.074±0.008	2	–
Ta	<2	–	–	Ta	1.72±0.08	5	(1.8)	1.25±0.06	2	–	Ta	<0.010	–	–
W	<2	–	–	W	5.0±0.4	5	(5.6)	2.56±0.22	2	(3)	W	<0.08	–	–

^a – Reference and non-certified values are given in parenthesis

^b – Determined using long-time irradiation mode

^c – Determined using short-time irradiation mode

NA – Not analyzed

Table 3 Results for SA1, SA2 and SA3 carbon-materials in mg kg⁻¹ unless otherwise stated. X₁ and X₂ are duplicates INAA results with combined uncertainties or the LOD. If the element was determined in both test portions, standard deviation estimated from the range was calculated (SD)

	SA1				SA2				SA3			
	INAA			Ion Beam	INAA			Ion Beam	INAA			Ion Beam
	X ₁	X ₂	SD ^a		X ₁	X ₂	SD ^a		X ₁	X ₂	SD ^a	
F	NA	NA	–	<10	NA	NA	–	66±15	NA	NA	–	8±2
Na ^b	<0.13	<0.13	–	NA	1660±30	1645±25	13	NA	313±5	317±5	4	NA
Na ^c	<0.8	7.4±1.0	–	NA	1810±30	1820±30	9	NA	322±8	348±8	23	NA
Mg	<60	<60	–	NA	<220	<210	–	<100	<160	<140	–	NA
Al	<0.6	<0.6	–	<30	79±5	56±5	20	<250	70±3	75±3	4	130±30
Si	NA	NA	–	<30	NA	NA	–	<150	NA	NA	–	980±140
P	NA	NA	–	<20	NA	NA	–	<100	NA	NA	–	<20
S, %	NA	NA	–	<0.0015	NA	NA	–	2.45±0.25	NA	NA	–	0.105±0.015
Cl	15.8±1.6	10.9±1.5	4.3	NA	89±6	105±5	14	NA	<8	<7	–	NA
K	<11	<11	–	<5	240±40	240±40	0	211±22	<50	<50	–	50±8
Ca	62±8	<30	–	<4	240±30	250±40	9	241±25	108±20	<60	–	40±6
Sc, µg kg ⁻¹	4.7±0.7	<1.5	–	NA	9.9±1.2	10.0±0.9	0.09	NA	16.3±1.2	17.8±1.2	1.3	NA
Ti	<5	<5	–	<1	<50	<50	–	<10	<40	<30	–	7.2±1.4
V	<0.019	<0.018	–	NA	<0.25	<0.3	–	NA	<0.19	0.33±0.06	–	NA
Cr	<0.21	0.56±0.09	–	<1	11.2±0.3	12.5±0.3	1.2	10±2	17.1±0.4	19.9±0.5	2.5	20±3
Mn	<0.05	<0.04	–	<2	1186±20	1191±20	4	1030±100	352±6	361±6	8	300±40
Fe	<13	<12	–	<2	870±30	485±19	340	109±11	166±13	177±14	10	150±30
Co ^b , µg kg ⁻¹	<19	<20	–	NA	204±14	171±13	30	<10000	117±14	125±12	7	NA
Ni	<6	<5	–	<3	<9	<9	–	<5	<9	<11	–	<5
Cu	NA	NA	–	<3	NA	NA	–	<5	NA	NA	–	<3
Zn	<0.8	<0.8	–	<2	<1.1	0.96±0.19	–	<5	2.0±0.3	1.33±0.24	0.6	<2
As	<0.18	<0.16	–	NA	<1.2	<1.1	–	<10	<0.7	<0.7	–	NA
Br, µg kg ⁻¹	176±16	226±16	44	NA	590±30	550±30	40	NA	227±23	255±24	25	NA
Rb	<0.7	<0.7	–	NA	<1.0	<1.1	–	NA	<1.2	<1.2	–	NA

Sr	<12	<11	–	NA	<14	<13	–	NA	<17	<16	–	NA
Mo ^b	<5	<5	–	NA	<30	<30	–	NA	<17	<17	–	NA
Ag	<0.07	<0.07	–	NA	<0.12	<0.11	–	NA	<0.12	<0.11	–	NA
Sb	<0.06	<0.05	–	NA	<0.07	<0.09	–	NA	<0.11	<0.10	–	NA
I	<0.18	<0.18	–	NA	<1.9	<1.4	–	NA	<1.3	<1.2	–	NA
Cs, µg kg ⁻¹	<30	<24	–	NA	<40	<40	–	NA	<40	<40	–	NA
Ba	<9	<8	–	NA	<10	<10	–	NA	<11	<12	–	NA
La, µg kg ⁻¹	<17	<10	–	NA	<50	<50	–	NA	89±12	<30	–	NA
Ce	<0.15	<0.14	–	NA	<0.23	<0.23	–	NA	<0.20	<0.23	–	NA
Pr	<0.5	<0.4	–	NA	<3	<3	–	NA	<1.8	<1.9	–	NA
Nd	<0.4	<0.4	–	NA	<0.9	<0.9	–	NA	<0.7	<0.7	–	NA
Sm, µg kg ⁻¹	<1.4	<1.4	–	NA	<8	<8	–	NA	<4	<5	–	NA
Eu, µg kg ⁻¹	<9	<8	–	NA	<7	<9	–	NA	<10	<11	–	NA
Tb, µg kg ⁻¹	<9	<8	–	NA	<13	<12	–	NA	<14	<14	–	NA
Dy, µg kg ⁻¹	<12	<12	–	NA	<120	<120	–	NA	<80	<80	–	NA
Tm, µg kg ⁻¹	<21	<20	–	NA	<50	<50	–	NA	<40	<30	–	NA
Yb, µg kg ⁻¹	<18	<17	–	NA	<100	<100	–	NA	<60	<60	–	NA
Lu, µg kg ⁻¹	<6	<6	–	NA	<10	<10	–	NA	<10	<11	–	NA
Hf, µg kg ⁻¹	<16	<16	–	NA	241±14	232±13	8	NA	319±16	269±17	40	NA
Ta, µg kg ⁻¹	<19	<13	–	NA	<21	<21	–	NA	<30	<30	–	NA
W, µg kg ⁻¹	<30	<30	–	NA	<230	<240	–	NA	230±40	<150	–	NA

^a – Range multiplied by factor 0.8862 (for N=2) [21]

^b – INAA results determined using long-time irradiation mode

^c – INAA results determined using short-time irradiation mode

NA – not analyzed

19 **Table 4** Results for SA4, SA5 and SA0 carbon-materials in mg kg⁻¹ unless otherwise stated. X₁ and X₂ are duplicates INAA results
20 with combined uncertainties or the LOD. For SA0, the average (X) and uncertainty of single determination (U) from INAA (5
21 replicates) are given. If the element was determined in 2 or more test portions, standard deviation estimated from the range was
22 calculated (SD)

	SA4				SA5				SA0		
	INAA			Ion Beam	INAA			Ion Beam	INAA		
	X ₁	X ₂	SD ^a		X ₁	X ₂	SD ^a		X	U	SD ^a
F	NA	NA	–	10±3	NA	NA	–	11800±1200	NA	–	–
Na ^b	21.3±0.5	20.5±0.5	0.7	NA	28.3±1.2	22.6±1.4	5	NA	183	4	4
Na ^c	<7	39.6±2.3	–	NA	25.0±2.3	29±3	4	NA	189	11	8
Mg	<180	<170	–	NA	<1000	<1000	–	<300	<1200	–	–
Al	426±8	418±8	6	550±80	39±3	45±3	5	<600	225	9	16
Si	NA	NA	–	2400±300	NA	NA	–	1950±200	NA	–	–
P	NA	NA	–	150±30	NA	NA	–	<200	NA	–	–
S	NA	NA	–	3400±500	NA	NA	–	<300	NA	–	–
Cl	<9	50±4	–	NA	358±12	369±12	10	NA	1450	30	9
K	516±22	518±22	1	580±80	<400	<400	–	<100	<300	–	–
Ca	<70	<70	–	380±60	<70	<40	–	<150	2920	140	180
Sc, µg kg ⁻¹	82±3	84±3	1.8	NA	<100	<100	–	NA	<120	–	–
Ti	<40	<40	–	90±13	<80	<80	–	<10	<110	–	–
V	7.97±0.18	7.79±0.17	0.16	NA	2.35±0.15	2.26±0.14	0.08	NA	0.86	0.09	0.09
Cr	2.05±0.17	1.59±0.16	0.4	7.0±1.2	318±6	333±6	13	440±50	46	4	6
Mn	830±14	788±13	37	800±110	18.6±0.6	18.3±0.6	0.3	<20	3.5	0.5	0.4
Fe	52±10	<30	–	96±14	<800	<800	–	590±60	<1300	–	–
Co ^b	0.094±0.008	<0.04	–	NA	5870±90	5820±90	44	6600±700	6360	100	90
Co ^c	NA	NA	–	NA	6070±170	6140±180	66	NA	6450	110	50
Ni	<11	<10	–	<3	<400	<400	–	330±40	<300	–	–
Cu	NA	NA	–	<3	NA	NA	–	<30	NA	–	–
Zn	<1.6	<1.3	–	11.3±1.7	<50	<50	–	<20	<60	–	–

As	<0.4	<0.4	–	NA	1318±23	1351±24	29	2250±300	471	10	5
Br	4.17±0.08	4.35±0.08	0.16	NA	76.5±1.2	75.0±1.2	1.3	NA	160	3	2
Rb	<1.4	<1.3	–	NA	<60	<60	–	NA	<70	–	–
Sr	<19	<19	–	NA	<400	<400	–	NA	<120	–	–
Mo ^b	73±3	75±3	1.8	NA	42700±700	42100±700	530	52200±5200	37600	600	430
Mo ^c	NA		–	NA	40100±800	39900±800	180	NA	37800	600	340
Ag	<0.10	<0.15	–	NA	<4	<4	–	NA	<4	–	–
Sb	6.73±0.17	6.56±0.18	0.15	NA	<3	<3	–	NA	<1.3	–	–
I	<1.6	<1.6	–	NA	101.3±2.5	99.7±2.4	1.4	NA	244	5	5
Cs	<0.04	<0.05	–	NA	<1.5	<1.5	–	NA	<1.5	–	–
Ba	<16	<15	–	NA	<300	<300	–	NA	<90	–	–
La	0.041±0.007	<0.011	–	NA	<0.10	<0.11	–	NA	12.8	0.2	0.8
Ce	<0.21	<0.23	–	NA	<3	<3	–	NA	21.2	2.4	5
Pr	<0.8	<0.8	–	NA	<9	<9	–	NA	<7	–	–
Nd	<0.8	<0.9	–	NA	<12	<12	–	NA	<21	–	–
Sm	<0.005	0.012±0.002	–	NA	<0.07	<0.08	–	NA	1.53	0.03	0.03
Eu	<0.011	<0.016	–	NA	<0.4	<0.4	–	NA	<0.3	–	–
Tb	<0.015	<0.017	–	NA	<0.3	<0.3	–	NA	<0.8	–	–
Dy	<0.10	<0.10	–	NA	<0.3	<0.3	–	NA	1.25	0.16	0.21
Tm	<0.03	<0.04	–	NA	<0.7	<0.7	–	NA	<0.9	–	–
Yb	<0.05	<0.06	–	NA	<0.5	<0.5	–	NA	<1.2	–	–
Lu	<0.013	<0.013	–	NA	<0.21	<0.22	–	NA	<0.5	–	–
Hf	<0.04	<0.04	–	NA	<0.7	<0.8	–	NA	<1	–	–
Ta	<0.03	<0.03	–	NA	<1.1	<1.1	–	NA	<0.7	–	–
W	10.11±0.18	10.19±0.18	0.07	NA	8.0±0.5	6.6±0.4	1.2	NA	6.3	0.6	0.6

^a – Range multiplied by factor 0.8862 or 0.4299 for 2 or 5 test portions, respectively [21]

^b – Determined using long-time irradiation mode

^c – Determined using short-time irradiation mode

NA – not analyzed