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Elemental Characterization of Single-Wall Carbon Nanotube Certified Reference Material by Neutron and Prompt γ Activation Analysis

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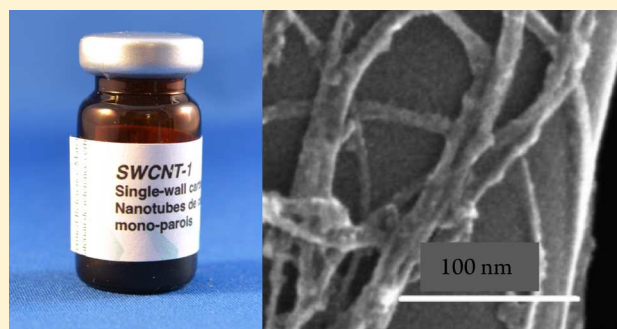
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ABSTRACT: Instrumental neutron activation analysis with both relative and k_0 standardization was used in four experienced laboratories to determine element mass fractions in single-wall carbon nanotube certified reference material (CRM) SWCNT-1. Results obtained were evaluated using the National Institute of Standards and Technology (NIST) “Type B On Bias” approach and yielded consensus values in agreement with National Research Council Canada (NRCC) certified values for Fe, Co, Ni, and Mo and provided mass fraction values for 13 additional elements, namely, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Br, La, W, and Au. In addition, prompt γ neutron activation analysis was employed to determine mass fractions of H, B, Co, Ni, and Mo.

Results of this work provide a basis for the establishment of reference values of element mass fractions in CRM SWCNT-1, thus expanding its usability for more accurate characterization and benchmarking of similar nanotechnology materials.



Nanotechnology refers to a wide range of technologies applied to study, manipulate, or incorporate materials and/or features having at least one dimension sized from 1 to 100 nm to produce new materials, structures, and devices. There is a distinction between naturally occurring nanoparticles and those deliberately “engineered” to have enhanced performance characteristics that can be used for specific purposes.¹ It is anticipated that such manufactured nanomaterials will become a potent driving force for the growth of various industries as they possess properties different from those of their bulk-material counterparts. Nanobased materials have already penetrated many market areas, including those in the medical, material engineering, environmental, optoelectronics, food packaging, energy production, and construction sectors. The rapid expansion of the field of nanotechnology has stimulated interest in and the need for characterization techniques of materials that promise to become ubiquitous products of modern technology.

Accurate characterization of physical and/or chemical properties of nanomaterials is a fundamental requirement for furthering their application in various product lines as well as for understanding and managing potential risks associated with their ultimate release to the environment^{2,3} and assessing their potential impact on human health and safety.⁴ The International Organization for Standardization (ISO) has taken an appropriate lead in this matter, primarily through the work of

the TC229 Nanotechnologies Technical Committee,⁵ in promulgating a number of protocols for this purpose. However, much additional work yet needs to be accomplished, notably in the production of certified reference materials whose property values will serve as benchmarks for quality assurance/quality control (QA/QC) and the development of validated measurement techniques.⁶ Fortunately, other efforts to impart standardization of measurement approaches have recently appeared^{7,8} which, when used in conjunction with available reference materials, will provide for more accurate characterization and benchmarking of these nanomaterials.⁹

Since the discovery of carbon nanotubes by Iijima,¹⁰ these materials have surfaced as one of the first major nanoscale manufactured products to enter the marketplace. Among nanomaterials, single-wall carbon nanotubes (SWCNT) are the most promising, having attracted great attention over the past 20 years as a consequence of their exceptional mechanical, electrical, and thermal properties, making them prime additives for multifunctional composites. Most recently, reference materials for nanotechnology have begun to emerge to support measurement methodologies, e.g., a suite of NIST gold sols of various particle size (NIST RM 8011, 8012, and 8013) as well

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as both a size (length) segregated SWCNT (NIST RM 8281) and a carbon nanotube soot material (NIST SRM 2483). Metallic constituents in SWCNTs typically arise as a consequence of residual catalyst material being incorporated into the product during manufacture [by high-temperature vaporization with laser, plasma, and arc sources on supported and floating chemical vapor deposition (CVD) substrates] as well as from intrinsic impurities present in the starting materials (including synthetic graphite, carbon black, hydrocarbon gases, petrochemical-based carbon, and biochar). NIST SRM 2483 is certified for mass fractions of Ba, Ce, Cl, Co, Dy, Eu, Gd, La, Mo, and Sm with reference values for Al, Mg, Mn, Na, Th, V, and W. All were predominantly determined using instrumental neutron activation analysis (INAA) or prompt γ activation analysis (PGAA), with some of them by inductively coupled plasma mass spectrometry (ICPMS) techniques.¹¹ SWCNTs are extremely refractory, and attempts to oxidatively solubilize them in such a way that standard methods of spectrochemical analysis can be applied lead to difficulties with quantification of metallic impurities as a consequence of incomplete recovery.¹² The National Research Council Canada (NRCC) has recently released a SWCNT certified reference material (SWCNT-1) that was originally certified for mass fractions of a limited number of elements, namely, Co, Ni, Mo, Fe, Pb, and Hg.¹³ The establishment of the certified values using 25 mg test portions has been carried out at NRCC as follows. Three independent sample digestion procedures were utilized, including conventional closed-vessel microwave assisted acid digestion, microwave-induced combustion in combination with the latter, and a dry ashing procedure using $\text{Mg}(\text{NO}_3)_2$ and HNO_3 as ashing aids. Quantification of the element mass fractions was accomplished by ICPMS based on calibration by the method of standard additions for Co and with calibration by isotope dilution for Fe, Ni, Mo, and also Hg and Pb.¹⁴ Some of the digestion steps had to be repeated several times, highlighting the difficulty in achieving complete decomposition of the CRM SWCNT-1 material for subsequent analyses by procedures requiring “wet chemistry”, necessitating extreme care being taken to avoid contamination and/or to achieve low and reproducible blanks (all sample preparation procedures had to be carried out in a class-10 or class-100 clean room). Results of INAA carried out at NIST have also been used in the certification process. In addition to these techniques, solid sampling graphite furnace atomic absorption spectrometry (SS-GFAAS) provided data for Co, Fe, Ni, and Pb.¹⁵ The material will support the validation of procedures and development of methods for the determination of trace metals in carbon nanotubes, or those of a similar matrix, as well as for studies of environmental health and safety and nanotoxicology.

INAA, which has recently been recognized as a primary ratio method of analysis,¹⁶ is ideally suited to the determination of most metallic constituents in SWCNT-1 material. Not only does the method typically possess the needed sensitivity to achieve their quantification, but equally importantly, it does not require any prior treatment of the sample, thereby avoiding the need for dissolution with all of its attendant risks and problems. There are other favorable features of INAA, namely, its inherent potential for accuracy, essentially blank-free nature, and the additional in-built and unique advantage of being able to perform in independent analytical modes or methodological routes. INAA thus provides a means of internally validating or cross-checking the data it generates, a so-called self-validating principle.^{16,17} It is the nuclear physical principle of NAA that

provides the possibility of employing activation of multiple stable isotopes from which more than one radionuclide is formed by different nuclear reactions, e.g., $^{64}\text{Ni}(\text{n},\gamma)^{65}\text{Ni}$ with thermal neutrons and $^{58}\text{Ni}(\text{n,p})^{58}\text{Co}$ with fast neutrons. The multiple radionuclides from one element have different half-lives and emit γ -rays with different energies with accurately known emission probabilities (intensity ratios), e.g., ^{65}Ni , $t_{1/2} = 2.52$ h, $E_\gamma = 1115.5$ keV (15.4% emission probability), $E_\gamma = 1481.8$ keV (23.6%); ^{58}Co , $t_{1/2} = 70.86$ days, $E_\gamma = 511.0$ keV (29.8%), $E_\gamma = 810.8$ keV (99.4%). Thus, if different calibrators and different radionuclides are used for various NAA routes, truly independent measurement results are obtained, increasing the credibility of the analytical results and assessing their accuracy.

This study was undertaken to use the performance of independent INAA laboratories for the determination of mass fractions of more metallic and other constituents in a stable, sufficiently homogeneous CRM SWCNT-1. PGAA¹⁸ was used to quantify elements that cannot be determined by INAA, e.g., H and B. The results obtained with INAA and PGAA are compared with those obtained by other techniques, where available.

■ EXPERIMENTAL SECTION

SWCNT-1 Preparation.¹³ Renewable carbon from the pyrolysis of hardwood biomass was sieved to pass a 300 μm particle size, blended with 0.6 atom % each of Co and Ni metal powders, mixed with GrafTech graphite adhesive, cured at 850 $^\circ\text{C}$ for 8 h in Ar, and pressed into cylinders. These were mounted onto a Mo support stub in a resistance furnace heated to 1200 $^\circ\text{C}$ and flushed with a blended flow of Ar and CO .^{19,20} The briquettes were subjected to laser vaporization from a pulsed source 1064 nm primary laser beam in combination with a 1064 nm continuous wave output from a second laser. The ablated material was flushed from the reaction chamber and collected on a filter. A master batch was synthesized from 52.1 g production sequences over the course of 2 months. The material was then placed in a large stirred drum, slurried with 16 L of ethanol, and homogenized for 2 days. Following decantation of supernatant solvent, the slurry was transferred to individual bottles, centrifuged, and washed multiple times in a sequence with acetone, toluene, dimethylformamide, and finally with acetone to help remove non-SWCNT amorphous material such as soot and fullerene synthesis byproducts. After air drying and crushing of agglomerates, the material was sieved to pass a 400 μm filter. The combined mass was placed in a quartz cylinder within a resistance oven for final desorption of residual solvents and a brief annealing. This was accomplished by ramping the temperature from 150 to 1000 $^\circ\text{C}$ over 1 h, holding for 1 h, and then cooling. Heating was performed in a flow of clean Ar which had been first passed over moisture and oxygen traps as well as over heated “sacrificial” carbon black to prevent oxidation of the SWCNT-1. The dry SWCNT was passed through a 200 μm screen and homogenized by rolling the sample in a clean bottle for 48 h. Following an initial homogeneity check using random subsamples based on results from Raman spectroscopy as well as thermogravimetric analysis, the material was packaged under dry Ar into pre-cleaned amber vials and sealed with a full aluminum crimp cap containing a septum coated with both Teflon and silicone. SWCNT-1 was then γ -sterilized by irradiation with a minimum dose of 15 kGy at the Canadian Irradiation Centre, Laval, Quebec. Individual bottles were then packaged under Ar into

heat sealed trilaminate foil bags to which a silica drying pouch had been added.

Analytical Procedures. The SWCNT-1 test samples were distributed in three vials, each containing 100 mg of the material, to NAA laboratories at the Australian Nuclear Science and Technology Organisation (ANSTO), Nuclear Energy Center for Agriculture of the University of São Paulo (CENA), U.S. National Institute of Standards and Technology (NIST), and the Nuclear Physics Institute, Academy of Sciences of the Czech Republic (NPI).

INAA with either relative calibration (r-INAA) or the k_0 -method of standardization (k_0 -INAA) was used in the individual laboratories, and both standardization methods were employed by NPI. The nuclear reactions used and parameters for the radionuclides employed are listed in Table 1. NIST also used PGAA. Experimental conditions in the individual laboratories are summarized in Table 2.

Table 1. Nuclear Reactions and Parameters of Radionuclides Employed in INAA^a

element	nuclear reaction	product half-life	main γ -ray energy, keV (intensity, %)
Na	$^{23}\text{Na}(n,\gamma)^{24}\text{Na}$	14.997 h	1368.63 (99.99), 2754.01 (99.86)
Mg	$^{26}\text{Mg}(n,\gamma)^{27}\text{Mg}$	9.458 min	843.76 (71.8), 1014.43 (28.2)
Al	$^{27}\text{Al}(n,\gamma)^{28}\text{Al}$	2.2406 min	1778.99 (100)
K	$^{41}\text{K}(n,\gamma)^{42}\text{K}$	12.321 h	1524.6 (18.08)
Ca	$^{48}\text{Ca}(n,\gamma)^{49}\text{Ca}$	8.718 min	3084.4 (90.72)
Ti	$^{50}\text{Ti}(n,\gamma)^{51}\text{Ti}$	5.76 min	320.08 (93.1)
V	$^{51}\text{V}(n,\gamma)^{52}\text{V}$	3.743 min	1434.06 (100)
Cr	$^{50}\text{Cr}(n,\gamma)^{51}\text{Cr}$	27.702 days	320.08 (9.91)
Mn	$^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$	2.5789 h	846.76 (98.85), 1810.73 (26.9)
Fe	$^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$	44.495 days	1099.24 (56.5), 1291.59 (43.2)
Co	$^{59}\text{Co}(n,\gamma)^{60\text{m}}\text{Co}$	10.467 min	58.60 (2.01)
	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	5.271 years	1173.23 (99.85), 1332.49 (99.98)
Ni	$^{64}\text{Ni}(n,\gamma)^{65}\text{Ni}$	2.518 h	1115.53 (15.43), 1481.84 (23.59)
	$^{58}\text{Ni}(n,p)^{58}\text{Co}$	70.86 days	810.76 (99.45)
Br	$^{81}\text{Br}(n,\gamma)^{82}\text{Br}$	35.282 h	554.35 (71.1), 776.52 (83.4)
Mo	$^{100}\text{Mo}(n,\gamma)^{101}\text{Mo}$	14.61 min	191.92 (18.21), 590.10 (19.2)
	$^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}-^{99\text{m}}\text{Tc}$	65.976 h	140.51 (89), 739.50 (12.26)
La	$^{139}\text{La}(n,\gamma)^{140}\text{La}$	1.679 days	487.02 (45.5), 1596.21 (95.40)
W	$^{186}\text{W}(n,\gamma)^{187}\text{W}$	24.00 h	479.53 (26.6), 685.81 (33.2)
Au	$^{197}\text{Au}(n,\gamma)^{198}\text{Au}$	2.695 days	411.80 (95.62)

^aRef 21.

ANSTO k_0 -INAA Procedure. Test portions of 30–50 mg mass (and one of 17 mg) were weighed into high-purity high-density polyethylene (HDPE) vials. Six samples underwent short-time irradiations in the OPAL nuclear research reactor and 5–11 samples were submitted to long-time irradiations in a highly thermalized position ($f > 3000$). Coaxial P-type high-purity germanium γ -ray detectors (HPGe, relative efficiency 25–30% for the 1332.5 keV γ -line of ^{60}Co) coupled to digital spectrometers were used to accumulate γ -ray spectra. The k_0 -

method of standardization was employed using IRMM-530R Al-0.1% Au wire (for all long- and three short-irradiations) or aliquots of NIST SRM 3121 Gold Standard Solution on filter paper (for the final three short-irradiations) as k_0 comparators. HyperLab software was used for deconvolution of γ -ray spectra, while Kayzero for Windows software²² was used for element quantification and detector calibrations. The self-validation principle was used for the Co and Mo determination using different (n, γ) nuclear reactions (Table 1).

CENA k_0 -INAA Procedure. Six test portions having sample mass in the range of 38–48 mg were weighed into high-purity PE vials and irradiated in the IEA-R1m nuclear research reactor of the IPEN/CNEN, São Paulo. The γ -ray spectrometry was carried out using HPGe detectors with relative efficiency of 50–55% for the 1332.5 keV γ -line of ^{60}Co . The k_0 -method of standardization was based on k_0 values according to De Corte and Simonits;²³ detector efficiency calibration was carried out according to Bacchi et al.,²⁴ and Ni–Cr wires of well-known content of Cr ($19.62\% \pm 0.07\%$)²⁵ were used as the k_0 comparator. Each vial was sandwiched between two comparators. For quality control purposes, the following materials were coanalyzed with the samples: one empty PE vial (blank), a graphite sample (internal control), BCR CRMs 320R Channel Sediment and 143R Sewage Sludge Amended Soil, NIST SRM 2781 Domestic Sludge, and IAEA RM Soil-7.

NIST INAA Procedure. Three test portions taken from each of three different bottles of SWCNT-1 test samples were pelletized in a KBr press at 1 tonne. Their mass was in the range of 12.35–17.50 mg. The pellets were sealed in polypropylene film (XRF film, 6.3 μm thick) or in linear PE film for irradiation. All sample handling and sample preparation, except the weighing of the final sample pellets, was performed in a laminar flow hood certified for use with nanomaterials. INAA with relative calibration was employed. Two sets of irradiations were carried out. For short-time activation, each sample was individually irradiated in the RT-2 pneumatic facility of the NIST research reactor at a reactor power of 20 MW together with one pipetted standard (calibrator) or one metal foil or a micropellet of a pure compound and a titanium neutron flux monitor foil. For long-time activation, one set consisting of one sample from each vial and standard pellets were packaged in an irradiation capsule and irradiated in the same channel of the reactor. The standards had been verified in previous certification analyses. The use of multiple standards of similar preparation as well as of a common element with different standard preparation provided data for estimation of the reproducibility of the standard preparation and the neutron flux variations during irradiation. The γ -ray spectrometry was conducted using HPGe detectors (relative efficiency 27.0% and 33.6%) coupled through a chain of associated electronics with a computer-based multichannel analyzer. For dead-time and pile-up corrections, Canberra 599 loss-free counting modules were used. For quality control purposes, NIST SRM 2483 Single-Wall Carbon Nanotubes (Raw Soot) was employed.

NIST PGAA Procedure. Three test portions taken from each of three different bottles of SWCNT-1 test samples were pelletized using a 5 mm stainless steel die and a hydraulic press. Each pellet was weighed into a bag of FEP Teflon and heat-sealed. The pellet mass ranged from 65 to 90 mg. Metal foils, 13 mm in diameter, were used as standards for Co (37 mg), Mo (135 mg), and Ni (117.5 mg). In order to evaluate the effects of geometry and matrix on element sensitivities, additional nickel

Table 2. Irradiation and Counting Conditions in INAA

laboratory	thermal neutron fluence rate ($\text{cm}^{-2} \text{s}^{-1}$)	irradiation time	decay/counting time
ANSTO	2.0×10^{13}	45–120 s ^a	3 min/3 min; 18 min/12 min
	$2.3\text{--}2.7 \times 10^{12}$	9 h	>4 days/>30 min; >14 days/>8 h
CENA	1.25×10^{13}	4 h	4 days/45 min; 7 days/1 h; 18 days/2 h
NIST–INAA	3.2×10^{13}	1 min	5 min/5 min; 1 h/30 min; 2 h/30 min
	3.2×10^{13}	30 min + 30 min ^b	5 days/2 h; >14 days/16 h
NIST–PGAA ^c	8×10^8	~24 h	not applicable/~24 h
NPI	3.0×10^{13}	1 min	12 min/15 min; 1 h/15 min
	3.6×10^{13}	2 h	3 days/45 min; 1 month/3 h

^aDepending on sample size. ^b180° inversion of the irradiation capsule after the first 30 min to ensure flux homogeneity. ^cThermal equivalent neutron flux at the cold neutron PGAA beam.

standards were prepared to approximate the thickness, diameter, and hydrogen and carbon content of the samples. The additional standards were prepared by mixing nickel powder, urea, and graphite in a Spex mixer mill for 20 min. The mixture was then pressed into three 5 mm pellets spanning the thickness range of the samples. The preparation of boron standards from a mixture of boric acid, graphite, and silicon dioxide has been described previously.²⁶ Because element sensitivities vary greatly as a function of hydrogen content, it is not easy to measure hydrogen sensitivity directly in a homogeneous material. Hydrogen sensitivity was determined by first measuring the H/Ti sensitivity ratio from a pellet prepared from a mixture of titanium powder, graphite, and urea (composition 12.55% Ti, 3.171% H) and then the H sensitivity was determined by measuring the Ti sensitivity from irradiation of a high-purity Ti foil. Measurements were performed using the cold neutron PGAA spectrometer at the NIST Center for Neutron Research.²⁷ Samples were irradiated in a magnesium alloy sample chamber under air; standards were irradiated for sufficient time to obtain $\leq 1\%$ RSD based on counting statistics. A 12.7 mm diameter titanium foil was irradiated at regular intervals to monitor any changes in the neutron fluence rate. An empty Teflon bag was irradiated for approximately 24 h under air to serve as a background measurement. The γ -ray peaks were integrated using the SUM code²⁸ and also using a commercial peak search algorithm. Results from peak search and SUM were used to evaluate peak integration uncertainties. Energies of peaks integrated for the element of interest are given in Table 3. For quality control purposes, NIST SRM 2483 was analyzed.

NPI INAA Procedures. Four approximately 45 mg test portions from two different bottles of SWCNT-1 test samples were sealed into acid-cleaned PE disk-shaped capsules for irradiation. Irradiations were carried out in nuclear reactor LVR-15 of the Research Centre Řež, Ltd. within the CANAM

Table 3. γ -Ray Energies, Interference and Background Corrections Employed in PGAA

element	γ -ray energy, keV	interference and background corrections
H	2223	Co, H background
B	478	Co, Mo
Co	447, 1515, 1830	none
	8998	none
Ni	8998	none
Mo	777	Co (NRCC samples), Co, Gd, Cl, Sm (NIST SRM 2483) ^a

^aCorrections for Gd, Cl, and Sm were estimated from previous data.

infrastructure (MŠMT project no. LM2011019). The samples were irradiated simultaneously with multielement standards for relative standardization and with neutron flux monitors for k_0 standardization. The multielement standards containing known amounts of elements were prepared by weighing out aliquots of certified standard solutions, such as those from NIST, Analytika Ltd. (Czech Republic), or from solutions prepared by dissolution of high-purity metals or well-defined chemical compounds as described earlier.²⁹ The newly proposed monitor set for the determination of neutron flux parameters in short-time k_0 -NAA,³⁰ which contained the elements Au, Mn, and Rb, was used, while for long-time irradiation the monitor set was IRMM-530R Al-0.1% Au wire plus Zr foil.³¹ The γ -ray spectra of samples and monitors after short-time irradiation were measured using a coaxial HPGe detector with relative efficiency 20.3%, whereas those after long-time irradiation were measured using a coaxial HPGe detector with relative efficiency of 77.8%. Measurement of monitors in k_0 -NAA was carried out considering the methodology of determination of neutron flux parameters f and α using the bare triple-monitor method.³¹ For quality control purposes, three aliquots with masses of about 10 mg of NIST SRM 1648 Urban Particulate Matter and three aliquots with masses of about 100 mg of NIST SRM 2711 Montana II Soil were coanalyzed with the test samples.

RESULTS AND DISCUSSION

For the element mass fractions determined in this study by both standardization methods of INAA in individual laboratories, the number of laboratory means, N_j (including those obtained by the self-validation principle), the number of individual results, n_i , and the range of laboratory means of element mass fractions obtained are listed in Table 4. In addition to these elements, hydrogen and boron were determined from three replicate analyses by PGAA at NIST.

The NAA laboratories at ANSTO, CENA, and NPI validated their data through concurrent analyses of quality control samples (SRM, CRM, RM) and/or by participation in international proficiency testing. At NIST, there is vast experience and expertise in the certification of element mass fractions in various SRMs by NAA and PGAA, including a material with matrix similar to SWCNT-1, namely, NIST SRM 2483 Single-Wall Carbon Nanotubes (Raw Soot). Although well-experienced laboratories took part in the elemental characterization of SWCNT-1, ranges of laboratory means determined by more than two participating laboratories exceeded 15% for some elements, namely, Al, Ca, Fe, and La. The extent of this range is not too unusual: pilot studies and key comparisons organized by the Consultative Committee for Amount of Substance (CCQM) reveal differences among

Table 4. Elements Determined by INAA and PGAA in SWCNT-1

element, unit	laboratory ^a	method	N_j^b	n_i^c	range of X_j	difference of X_j , % ^d
Na, mg kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA	5	24	160.1–171.2	6.5
Mg, mg kg ⁻¹	3	r-INAA	1	3		
Al, mg kg ⁻¹	1, 3, 4	r-INAA, k_0 -INAA	4	17	429–565	24.0
K, mg kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA	5	18	3177–3295	3.6
Ca, mg kg ⁻¹	3, 4	r-INAA, k_0 -INAA	2	7	2415–2873	15.9
Ti, mg kg ⁻¹	3, 4	r-INAA	2	7	181–205	12.0
V, mg kg ⁻¹	1, 3, 4	r-INAA, k_0 -INAA	4	17	4.19–4.70	10.9
Cr, mg kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA	5	17	284–314	9.3
Mn, mg kg ⁻¹	1, 3, 4	r-INAA, k_0 -INAA	4	17	135.6–136.7	1.1
Fe, g kg ⁻¹	1, 3, 4	r-INAA, k_0 -INAA	4	17	2.24–2.82	20.7
Co, g kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA, PGAA	9	38	15.15–16.81	9.9
Ni, g kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA, PGAA	7	30	13.68–15.37	11.0
Br, mg kg ⁻¹	4	r-INAA, k_0 -INAA	2	7	1.30–1.71	24.0
Mo, g kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA, PGAA	9	39	6.96–7.95	12.4
La, mg kg ⁻¹	1, 3, 4	r-INAA, k_0 -INAA	4	14	0.79–1.16	32.0
W, mg kg ⁻¹	4	r-INAA, k_0 -INAA	2	8	1.66–1.79	7.4
Au, mg kg ⁻¹	1, 2, 3, 4	r-INAA, k_0 -INAA	5	18	0.131–0.151	13.1
H, g kg ⁻¹	3	PGAA	1	3		
B, mg kg ⁻¹	3	PGAA	1	3		

^a1, ANSTO; 2, CENA; 3, NIST; 4, NPL. ^bNumber of laboratory means, X_j , including those obtained by the self-validation principle. ^cNumber of individual results, x_i , including those obtained by the self-validation principle. ^d $(X_j(\max) - X_j(\min))/X_j(\max)$.

laboratory means determined mostly by national metrology laboratories range from 5% to 15%.¹⁶ For CRM SWCNT-1, several reasons for the variation of inter- and intralaboratory results may be considered: (i) minor differences of nuclear data, namely, radionuclide half-lives, used in relative and k_0 standardization; (ii) interbottle and within-bottle heterogeneity; (iii) variation due to absorbed water content (all results are reported on “as-received basis”); (iv) uncorrected spectral (fission) interferences. The differences of half-lives used in relative standardization²¹ compared to those contained, e.g., in the k_0 software package Kayzero for Windows²² are minimal (zero or up to $\pm 0.05\%$) for most radionuclides employed in this work, except for ²⁴Na (-0.25%), ⁴²K ($+0.32\%$), and ¹⁸⁷W (-1.17%). Obviously, the resultant variances observed cannot be explained by the above differences of half-lives. Homogeneity testing using SS-GFAAS have revealed that SWCNT-1 CRM is homogeneous for certified metal contents at the level of 1 mg.^{13,15}

However, a minor heterogeneity of other analytes may be due to different sources of the elements in the synthesis and purification of the material. By analogy to NIST SRM 2483, a sampling error of about 3% using 25–40 mg test masses may be expected for some elements.³² No larger differences can be expected due to the possible absorbed moisture. La data could be positively biased if an elevated level of U is present and the formation of fission radionuclides ¹⁴⁰Ba–¹⁴⁰La is not taken into account (half-life of the parent radionuclide is 12.75 days). Only one laboratory (L4) reported a value of U below the detection limit of 1.4 mg kg⁻¹, which cannot be made responsible for the La differences detected. Thus, the above-discussed reasons cannot explain the inter- or intralaboratory differences observed (Table 4), and all the results obtained were used for deriving consensus values and their uncertainties. An example of Mo mass fractions (laboratory means \pm standard deviations) determined in the individual laboratories, including those obtained by the self-validation principle, is schematically depicted in Figure 1. For deriving consensus values of element mass fractions from results obtained in this study, the NIST

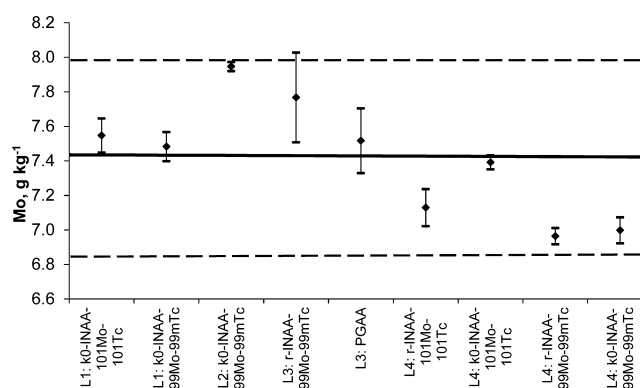


Figure 1. Molybdenum results for SWCNT-1 obtained in individual laboratories by INAA (k_0 and r stand for k_0 and relative standardization, respectively) and PGAA, including those achieved by the self-validation principle in INAA. Error bars show laboratory standard deviations, full line depicts the consensus value, and dashed lines indicate the expanded uncertainty (coverage factor $k = 2$) of the consensus value. For laboratory codes L1–L4 see Table 4.

“Type B On Bias” (BOB) approach³³ was employed, which is an approach to combining results from multiple methods and/or laboratories motivated by the ISO Guide to the Expression of Uncertainty (ISO GUM).³⁴ The combined uncertainties due to within-method uncertainties and between-method uncertainties (bias) calculated using a rectangular distribution were expanded by a coverage factor $k = 2$. Table 5 summarizes consensus values and their expanded uncertainties. Apart from Fe, Co, Ni, and Mo, the consensus values for mass fractions reported in this work were adopted by NRCC as reference values. Table 5 also shows that the reference values agree with the mass fractions certified by NRCC where available within the uncertainty margins. In view of the experimental difficulties with ICPMS, the advantages of INAA as a nondestructive method become apparent, especially for assay of materials difficult to decompose, such as CRM SWCNT-1.

Table 5. Consensus and Certified Mass Fraction Values in SWCNT-1^a

element, unit	consensus value	certified value ^b
Na, mg kg ⁻¹	167 ± 7	
Mg, mg kg ⁻¹	4190 ± 380	
Al, mg kg ⁻¹	494 ± 94	
K, mg kg ⁻¹	3220 ± 210	
Ca, mg kg ⁻¹	2640 ± 310	
Ti, mg kg ⁻¹	193 ± 22	
V, mg kg ⁻¹	4.37 ± 0.31	
Cr, mg kg ⁻¹	285 ± 26	
Mn, mg kg ⁻¹	135.8 ± 1.8	
Fe, g kg ⁻¹	2.55 ± 0.37	2.2 ± 0.2
Co, g kg ⁻¹	15.8 ± 1.0	15.9 ± 1.0
Ni, g kg ⁻¹	14.3 ± 1.0	14.4 ± 0.8
Br, mg kg ⁻¹	1.50 ± 0.37	
Mo, g kg ⁻¹	7.42 ± 0.57	7.3 ± 1.1
La, mg kg ⁻¹	0.96 ± 0.27	
W, mg kg ⁻¹	1.72 ± 0.18	
Au, mg kg ⁻¹	0.139 ± 0.017	
H, g kg ⁻¹	4.23 ± 0.99	
B, mg kg ⁻¹	107.3 ± 3.1	

^aValue ± expanded uncertainty (coverage factor $k = 2$). ^bRef 13.

CONCLUSIONS

The challenging task of elemental characterization of CRM SWCNT-1 was accomplished by a joint effort of NRCC, where sample digestion followed by ICPMS yielded certified mass fractions of Fe, Co, Ni, Mo, Pb, and Hg (below a detection limit), and four laboratories using nondestructive INAA and PGAA methods. The INAA results for Fe, Co, Ni, and Mo were, within uncertainty intervals, in agreement with values determined by the NRCC utilizing sample dissolution and atomic spectrometric detection¹⁴ as well as solid sampling atomic absorption.¹⁵ Mass fractions for an additional set of 13 elements (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Br, La, W, and Au) determined by INAA and two obtained by PGAA (H and B) serve as reference values in CRM SWCNT-1. The advantageous role of INAA and PGAA in the elemental characterization of a material that is difficult to bring into a solution and that is easy to contaminate during preparation of the test portion for subsequent analysis by different analytical techniques has again been demonstrated.¹⁶ It may confidently be expected that the increased number of elements for which mass fractions in CRM SWCNT-1 are known will foster further development of rigorous physicochemical methods for characterization of such materials.

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Author Contributions

R.E.S. and P.G. initiated the research, J.K., R.E.S., and J.W.B. drafted the manuscript, J.K. did the calculation of the consensus values and their uncertainties, all others took part in the analyses and their evaluation.

Notes

The identification of certain commercial equipment, instruments, or materials does not imply recommendation or endorsement by the National Institute of Standards and

Technology. These identifications are made only in order to specify the experimental procedures in adequate detail. The authors declare no competing financial interest.

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