CURRENT DEVELOPMENT STUDIES OF SINGLE-WALLED CARBON NANOTUBE REFERENCE MATERIAL AT NATIONAL INSTITUE OF STANDARDS AND TECHNOLOGYG (NIST)

R. Oflaz Spatz, R. Zeisler, R. L. Paul,

National Institute of Standards and Technology, 100 Bureau Dr. MS 8395, Gaithersburg, MD 20899-8395

ABSTRACT

Carbon nanotubes are promising candidates for numerous applications because of very unique nanostructures and possess remarkable mechanical and electronic properties. Also carbon nanotubes (CNT) are one of the first major nanoscale manufactured products to enter the market. Therefore, reliable and reproducible quantitative measurement and characterization of carbon nanotube samples are important for progress in understanding of these materials and the development of new applications incorporating these materials. An additional value is the development of an information base for CNT toxicology. For this reason there is an urgent need for standards for carbon nanotube (CNT) manufacturers, as well as for scientific and health-related investigations done with CNTs. In response to this need, we are in the process of developing a single-walled carbon nanotube reference material (SWNT). We were involved in the characterization of a candidate SWNT reference material for elemental content using instrumental neutron activation analysis (INAA) and cold neutron prompt gamma activation analysis (CNPGAA).

The characterization of residual catalyst and impurity metals in CNT materials ranging from raw soot to highly defined purified material represents a broad analytical task: the metals may be present as major constituents or at trace and ultra-trace levels, they may be loosely adducted to the matrix, or firmly incorporated, or chemically bound. Instrumental neutron activation analysis (INAA) and cold neutron prompt gamma activation analysis (CNPGAA) allows the determination independent from these physical and chemical properties and provides reliable results over the full range of potential elemental content in the investigated sample. Both neutrons and gamma rays are highly penetrating in the sample materials thus providing an outstanding non-destructive analytical capability for determining the composition of the entire sample volume. In addition, the neutrons react with the nucleus of the atoms independent of the oxidation state, the chemical form, and the physical surrounding of the desired element. NAA requires no or minimal sample preparation for the irradiation and measurements, thus virtually excluding chemical blanks and losses or gains of the element of interest before the irradiation.

ANALYSIS

Powdered CNT samples are prepared by pelletizing, weighing, and packaging in irradiation containers for NAA using neutron capture prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (INAA) procedures. Aliquots are poured into a stainless steel die to form pellets under about 1 ton load. The pellets are weighed, each pellet representing about 100 mg of CNT material for PGAA and 25 mg for INAA, and heat-sealed in bags made from fluorinated ethylene propylene (FEP, Teflon) film (hydrogen free) for PGAA and in bags made from 6.3 μm thick polypropylene film for INAA.

Quantitative analysis is undertaken by the comparator method with known standard samples irradiated and measured under the same conditions as the unknown subsamples. Standard samples in form of element solutions pipetted on filter papers or pure elements or compounds (as mixtures with graphite as required) are prepared in a similar way for the irradiations.

Quality assurance (check) samples of suitable certified reference materials (e.g., SRM 1632c Coal, SRM 2702 Marine Sediment, SRM 349a Waspaloy, SRM 348a High Temperature Alloy) are included in the assays, irradiating and measuring these samples the same way as the unknown samples. Empty Teflon bags, polypropylene bags, and titanium foil flux monitors are prepared to assure NAA process control. Titanium foil flux monitors are irradiated at regular intervals to monitor any changes in the neutron fluence rate. Empty Teflon as well as polypropylene bags are irradiated and measured like the samples to serve as a background measurement.

RESULTS

A number of single wall, multi wall, and soot like CNT materials were analyzed in preparation for the development and characterization of a NIST certified Standard Reference Material, SRM 2481 Carbon Nanotube Soot. Table 1 presents initial results on some of these materials including the candidate SRM 2481. The results illustrate the variety of catalyst and contaminant elements and their content. NAA procedures are well-suited for the characterization of the CNT materials because of the extensive dynamic range of NAA, which makes it possible to determine element mass fractions from the percent range down to trace levels through selection of irradiation and counting conditions. It appears that NAA provides reproducible determinations of catalysts residues at the percent level, whereas contaminant elements, such as rare earth elements that are possibly associated with catalyst and other production substrates, are to be determined at the mg/kg level. PGAA and INAA procedures comple-

ment each other in elemental coverage and provide in most instances independent results for the catalyst elements and some trace contaminants. PGAA provides results for hydrogen, which may be associated with residual moisture in the CNT materials. Investigations of the possible link between hydrogen mass fractions and moisture content are underway to determine an acceptable mass basis of the SRM material. With these capabilities analysts may find in the characterization of CNT materials a new domain for NAA application. Other analytical techniques such as inductively coupled plasma mass spectrometry will need procedures that assure complete sample digestion and must develop proper dilution procedures for the digests to accommodate the broad range of elemental mass fractions.

Table 1. INAA results for some single-wall CNT materials: the initial experimental lot for the development of an SRM, a commercially available material, and the candidate material for SRM 2481. PGAA results are included as indicated. Mass fraction values are expressed in mg/kg unless noted in %, uncertainties are 1s standard deviation.

	SRM development		Commercial SWCNT		SWCNT SRM	
Element	Average	1s	Average	1s	Average	1s
Al	269	75	272	2	730	6
As			<0.6		12.7	0.5
B_{PGAA}	13.7	1.7	2.7	0.3	74.2	1.6
C	71.2%	1.7%	98%	4%	97.8%	0.6%
Ca	377	127	237	30	ND[a]	
Ce	10.4	6.2			212	17
Cl			0.149%	0.007%	0.198%	0.003%
Cl_{PGAA}					0.218%	0.009%
Co	0.97	0.09	0.308%	0.003%	0.943%	0.005%
Co_{PGAA}					1.00%	0.02%
Cr	10.4	3.3	0.115%	0.001%	14	2
Cu	16	1.7	16.2	2.7	184	10
Dy	6.03	0.43			7.5	0.1
Fe	564	41	820	80	<700	
Gd_{PGAA}	8.32	0.06			9.90	0.10
La	2.16	0.59	8.4	0.1	106.3	1.6
Lu	0.15	0.05			ND[a]	
Mn	7.06	0.37	41.2	0.3	4.0	0.1
Mo	<20		0.19%	0.01%	3.32%	0.04%
Mo_{PGAA}					3.66%	0.10%
Na	257	23	22	3	0.116%	0.004%
Ni	22.0%	0.3%	<0.2%		ND[a]	
Ni_{PGAA}	22.2%	0.2%	<0.012 %		<0.012%	
Sc	0.3	0.02			<0.001	
Sm	1.4	1	<0.03		12.1	0.3
Sm_{PGAA}	3.0	0.6			13.9	0.3
Ta	73	12	0.76	0.13	ND[a]	
Tb	0.11	0.02			<0.4	
Ti	24	11			<40	
Th	<0.3		2.54	0.05	18.0	0.6
V	2.28	0.33	3.01	0.07	6.5	0.1
W	100	19	<1		6.7	0.6
Y	7.25%	0.44%			ND[a]	
Y_{PGAA}	7.33%	0.11%				
Yb	27	11			ND[a]	

[a]not determined

NSTI-Nanotech 2009, www.nsti.org, ISBN 978-1-4398-1782-7 Vol. 1, 2009