جامعة الملك عبدالله
للعلوم والتقنية
King Abdullah University of
Science and Technology

الإلهام طريق الاكتشاف
Through Inspiration, Discovery

Validating the chemical analysis of nanocarbons with certified reference materials

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KAUST

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Nanocarbons

nanotextured

Carbon fibers
Pyrolytic carbons
Glass-like carbons
High-density isotropic carbons
Intercalation compounds
Diamond-like carbons

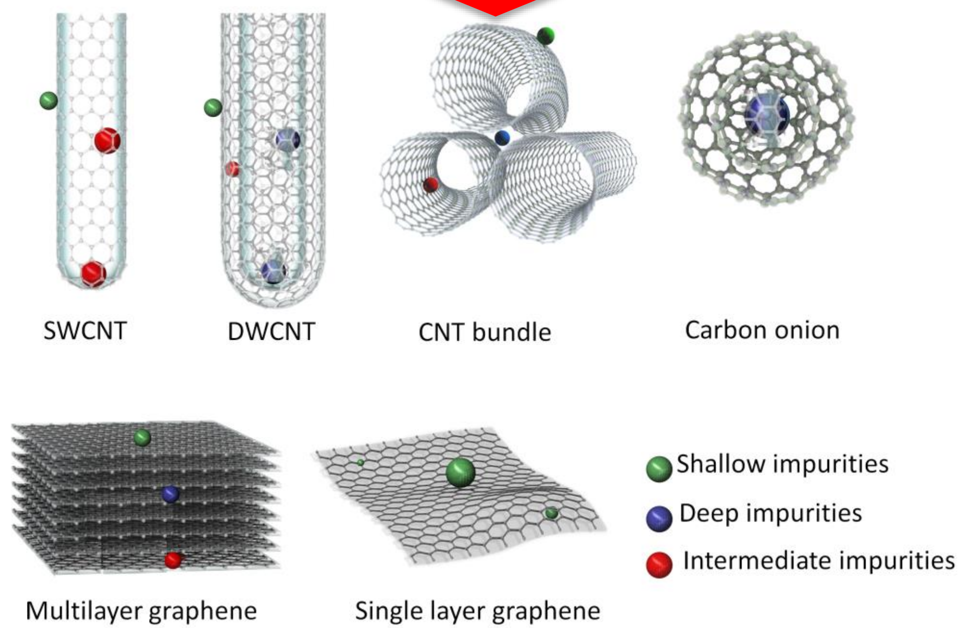
nanosized

Carbon clusters
Fullerenes
Carbon nanotubes
Graphene

Production methods:

- Physical (mechanical exfoliation)
- Chemical (CVD, laser ablation, arc-discharge, chemical exfoliation)

Catalysts, acids, etc.



S. P. Patole et al., Talanta 148 (2016), 94

Metrology

How to ensure that the **Nanocarbons** (graphene, nanotubes, etc.) you produce (in Lab or Industry) **are what you say they are**?

How to sustain that statement in your production line?

- Lack of fast, reliable **Metrology** tools for Nanocarbons is a decades old issue for both **Industry** and **Academia**
- Deficient batch-scale **Quality Control** is a major roadblock for wider usage of Nanocarbons

Metrology


Nanocarbons Industry
Customer satisfaction
Standards for quality control
Market
Health & Environment protection
Low cost, fast Metrology tools
Certification

Metrology

How can we routinely measure the concentration of elements in batches of Nanocarbons?

A **low-cost**, **fast** and **reliable** technique that is universally **accessible** is urgently needed!

Inductively Coupled Plasma (ICP)

So, what’ stopping us from routinely using **ICP-MS** or **ICP-OES**?

Two key challenges:

1. Lack of **Certified Reference Materials** for Nanocarbons

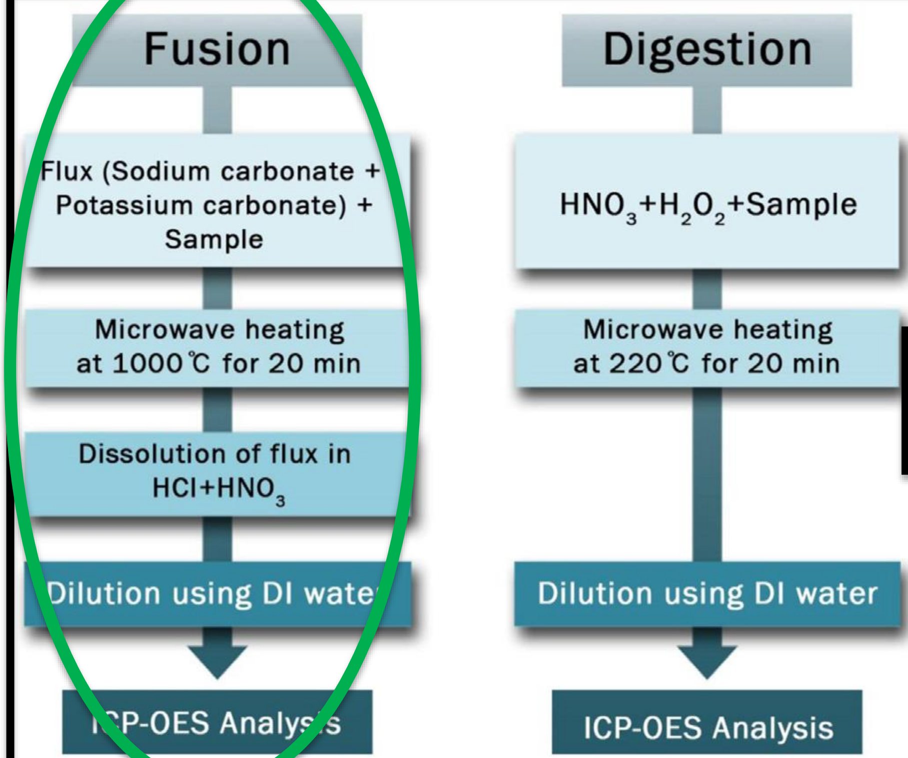
   (ICP methods rely heavily on standards for results validation)

2. Lack of a universal **Sample Preparation** method for Nanocarbons

   (recipes have to be tailored for each material, sometimes production batch)

ICP Sample Preparation

Our approach (**Fusion method**):
Disintegrate the carbon lattice by **high temperature molten salt** exposure



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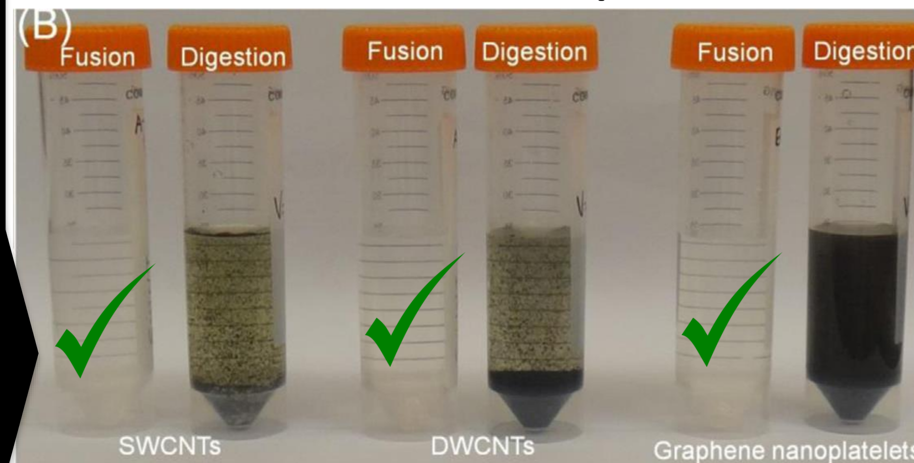
Commercial samples



The Fusion approach results in **complete disintegration** of the Nanocarbons (clear solutions, no deposit)

Similar results obtained for commercial **Graphite** and **MWCNTs**

ICP-OES Analysis

Fusion is an efficient method to prepare the analytes but…

Table 2
ICP-OES data showing mean concentrations (in µg g^{-1}) and %RSTD of impurity elements in SWCNT, DWCNT and graphene nanoplatelet solutions prepared using microwave-assisted fusion and microwave-assisted acid digestion methods. Each mean concentration was calculated from four aliquots.

Elements	SWCNTs				DWCNTs				Graphene nanoplatelets			
	Fusion		Digestion		Fusion		Digestion		Fusion		Digestion	
	(µg g^{-1})	(%RSTD)	(µg g^{-1})	(%RSTD)	(µg g^{-1})	(%RSTD)	(µg g^{-1})	(%RSTD)	(µg g^{-1})	(%RSTD)	(µg g^{-1})	(%RSTD)
Al	38	3.8	430	5	2	2.9	550	6	50	3.1	450	1.7
B	57	7.4	160	3.5	70	5.4	93	4.5	50	1.7	120	3.5
Co	25,110	12	48,250	1	31,300	11	610	10	6700	6	ND	NA
Fe	2360	13	5020	0.5	3100	11	2700	5	880	7	1940	1
Mo	9650	13	11,620	0.5	9830	11	2940	5	120	12.4	110	18.4
Ni	ND	NA	15	10.5	ND	NA	14	13.2	120	11	210	0.7
S	200	23	240	6	50	24	360	8	6880	6	6250	2.1

ND: not detectable; NA: not applicable.

S. P. Patole et al., Talanta 148 (2016), 94

…comparing the results from the classical Digestion and the Fusion approaches reveals **gross disparities in elemental concentrations**.

What can we do about this?

Certified Reference Materials

There are **three available CRMs** in the market for Nanocarbons
All are based on **SWCNTs** (none for graphene yet)

National Institute for Standards and Technology, U.S. (**NIST**)
- **SRM2483**, **RM8281**

National Research Council Canada (**NRC**)
- **SWCNT-1**

But… apart from the teams that have developed this product there are no reports yet on its use from the Community.

Certified Reference Materials

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2483

Single-Wall Carbon Nanotubes (Raw Soot)

Table 1. Certified Mass Fractions Values for SRM 2483 (Dry-Mass Basis)[a]

	Mass Fraction	Units
Ba[b,c]	119.0 ± 3.4	mg/kg
Ce[b,c]	192.7 ± 7.3	mg/kg
Cl[b,d]	0.2125 ± 0.0089	%
Co[b,d]	0.963 ± 0.017	%
Dy[b,c]	8.36 ± 0.17	mg/kg
Eu[b,c]	2.27 ± 0.13	mg/kg
Gd[c,d]	10.57 ± 0.95	mg/kg
La[b,c]	104.0 ± 4.0	mg/kg
Mo[b,d]	3.406 ± 0.029	%
Sm[b,c,d]	13.09 ± 0.90	mg/kg

NATIONAL RESEARCH COUNCIL CANADA

NRC·CNRC

Certificate of Analysis

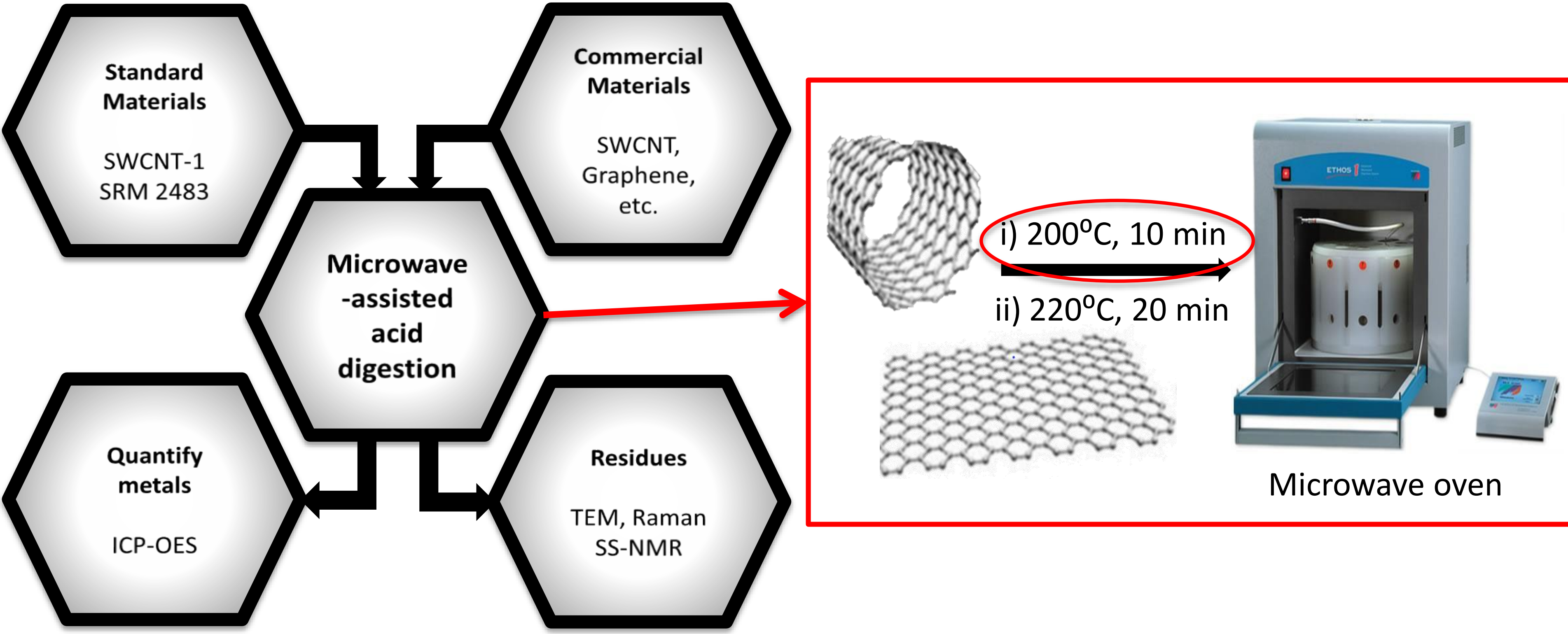
SWCNT-1

Single-Wall Carbon Nanotube Certified Reference Material

Table 1: Certified Mass Fraction Values

Element	Mass fraction	Units
Co (a,b)	15.9 ± 1.0	g/kg
Ni (b,c)	14.4 ± 0.8	g/kg
Mo (b,c)	7.3 ± 1.1	g/kg
Fe (b,c)	2.2 ± 0.2	g/kg
Pb (c)	6.8 ± 0.9	mg/kg
Hg (c)	< 10 a	mg/kg

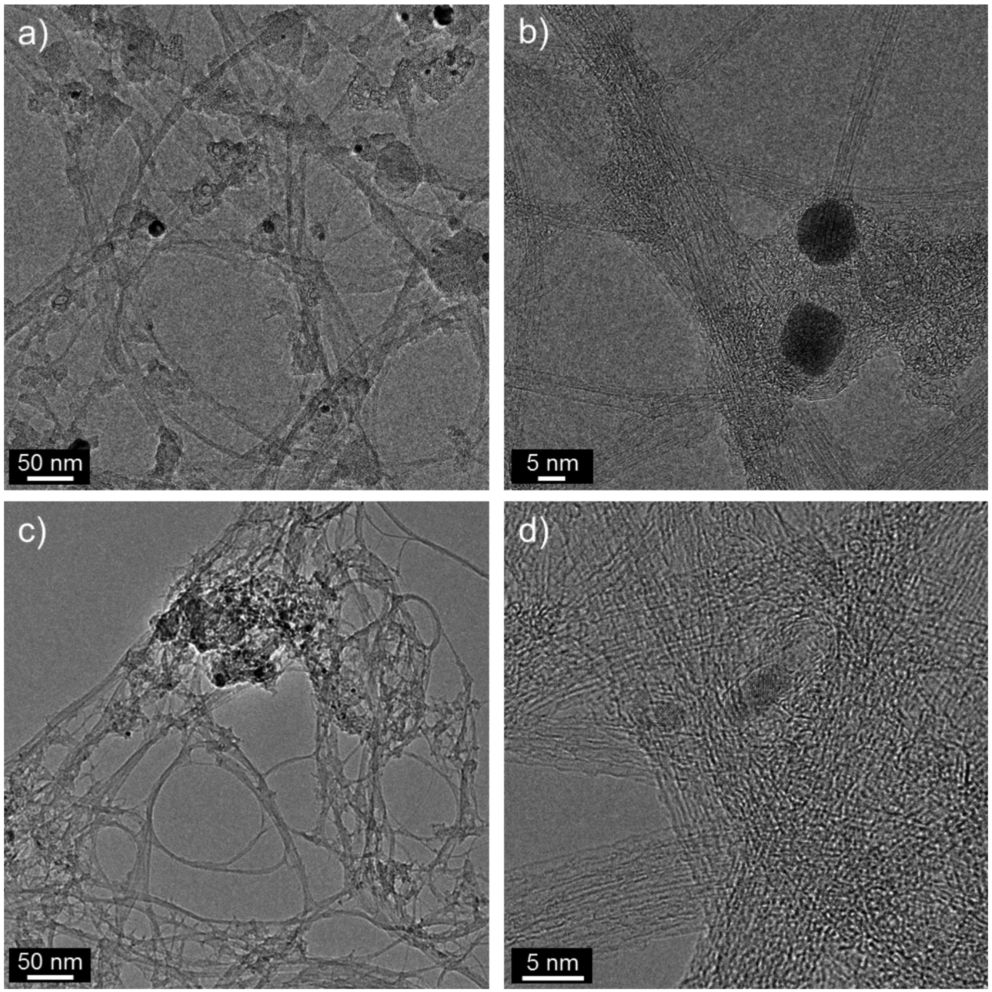
Sample Preparation (Wet Digestion)

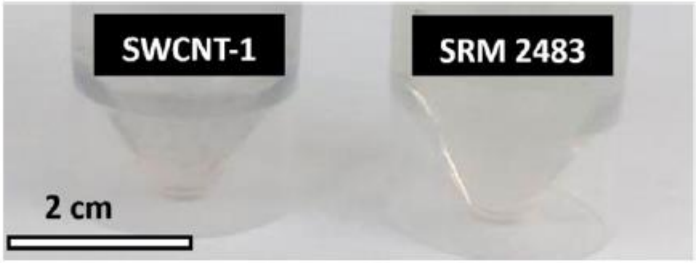


F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Certified Reference Materials

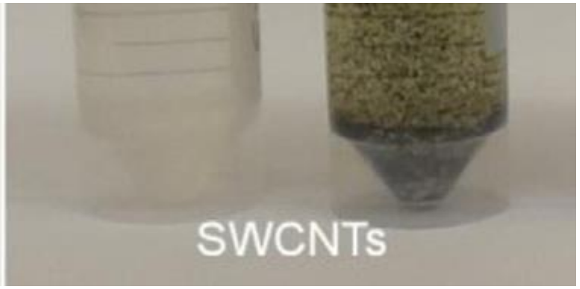
SWCNT-1 **CRM2483**





Postdigestion samples of SWCNT-1 and SRM2483.

Previously…

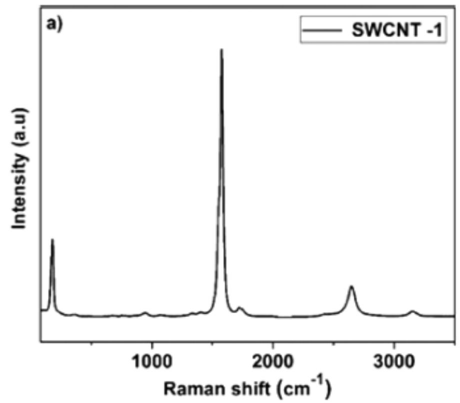


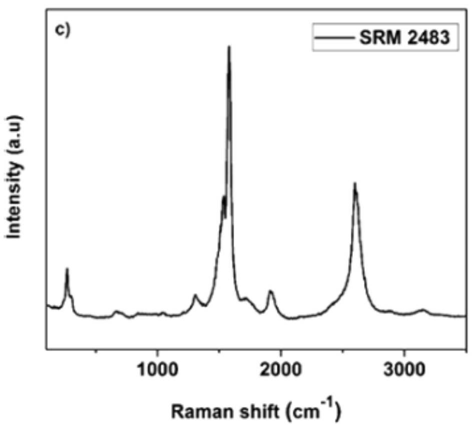
Successful wet digestion of SWCNT CRMs!
Really?

F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Certified Reference Materials

Raman spectroscopy (532 nm)

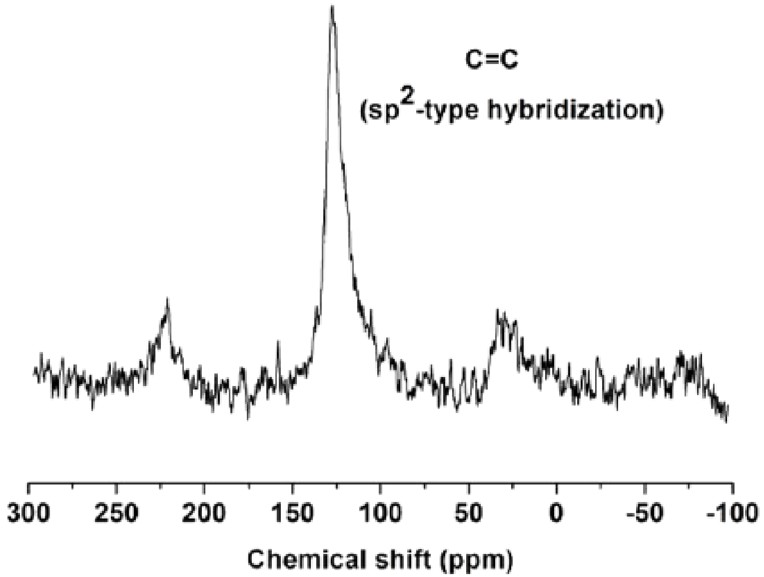




F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Certified Reference Materials

Solid-state NMR (SRM2483)



SS-NMR is a more reliable way to ensure **disintegration of the sp^2-type carbon**

F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Certified Reference Materials

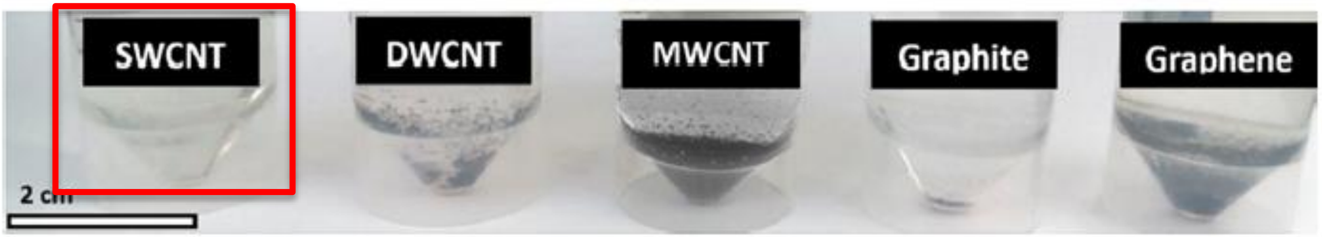
Table 1. ICP-OES Measurements for SWCNT-1 and SRM2483 After the Two-Step Acid Digestion Process

	SWCNT-1 (NRC)			SRM2483 (NIST)		
element	certificate[11] (mg/L)	ICP-OES[a] (mg/L)	recovery (%)	certificate[12] (mg/L)	ICP-OES[a] (mg/L)	recovery (%)
Co	15900 (±100)[b]	13695 (±312)	86	9630 (±17)[c]	7964 (±422)	83
Ni	14400 (±800)[b]	12341 (±455)	86			
Mo	7300 (±100)[b]	7392 (±338)	101	34060 (±29)[c]	29691 (±1215)	87
Fe	2200 (±200)[b]	2138 (±103)	97			
Ce				193 (±7)[c]	170 (±7)	88
Dy				8.4 (±0.2)[c]	8.0 (±0.1)	96
Eu				2.3 (±0.1)[c]	2.1 (±0.2)	91
Gd				11 (±1)[c]	10 (±1)	94
Sm				13 (±1)[c]	6 (±1)	45
Al	494 (±94)	407 (±35)	82	723 (±19)	858 (±62)	119
Ca	2650 (±300)	2150 (±135)	81			
Cr	285 (±26)	205 (±29)	72			
K	3220 (±200)	2170 (±34)	67			
Mg	4180 (±380)	123 (±28)	3	1150 (±11)	988 (±46)	86
Mn	136 (±2)	128 (±3)	94	4.5 (±0.0)	4.2 (±0.4)	93
Ti	193 (±22)	146 (±6)	76			
Na	167 (±7)	176 (±7)	106			
V	4.4 (±0.3)			6.9 (±0.1)	6.1 (±0.3)	88

[a]Mean and standard deviation (±) values obtained with $N = 3$. [b]NRC-certified value. [c]NIST-certified value.

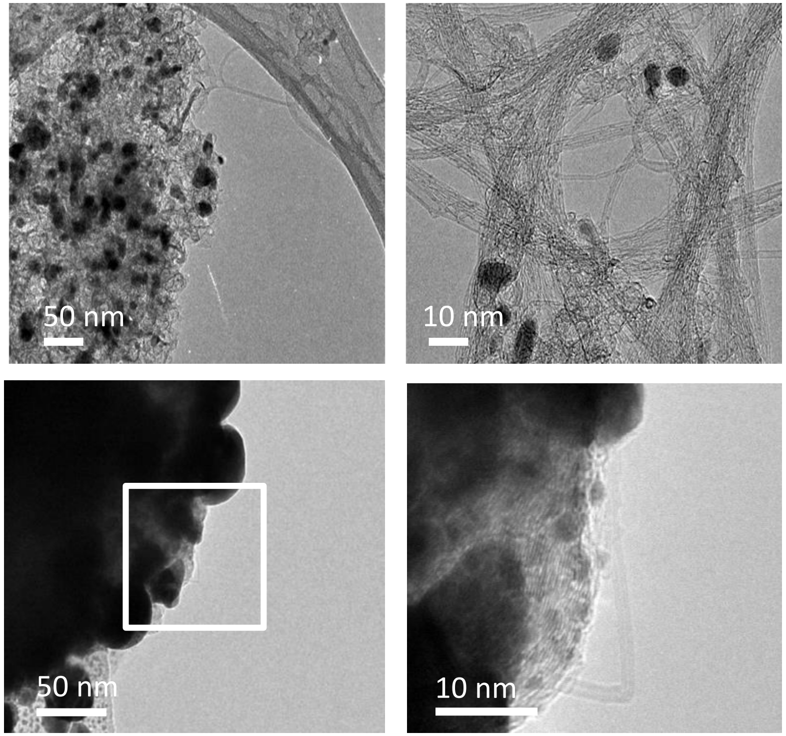
F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

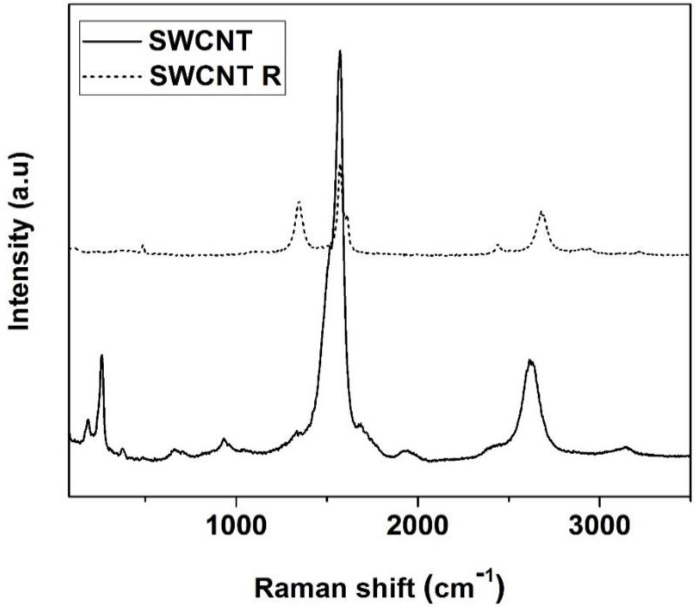
Commercial Samples



Before

After





F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Commercial Samples

element	SWCNT		DWCNT	MWCNT	Graphite	Graphene
	ICP-OES (mg/L)	recovery[a] (mg/L)	ICP-OES[b] (mg/L)	ICP-OES[b] (mg/L)	ICP-OES[b] (mg/L)	ICP-OES[b] (mg/L)
Co	6298	91	302 (±2)	639 (±9)	22 (±1)	19 (±1)
Ni	61	86	53 (±7)	81 (±1)	65 (±11)	273 (±25)
Mo	38900	129	12195 (±50)	194 (±11)	12 (±1)	15 (±1)
Fe	251	92	5089 (±583)	1687 (±17)	5064 (±60)	2060 (±26)
Ce	26	88	1.88 (±0.58)	0.80 (±0.08)		0.69 (±0.30)
Dy	26	88	0.50 (±0.26)		0.26 (±0.06)	0.50 (±0.07)
Eu	26	88	0.13 (±0.04)	0.18 (±0.09)	0.22 (±0.02)	0.18 (±0.04)
Gd	28	90	1.37 (±0.21)	2.39 (±0.06)	1.02 (±0.58)	1.20 (±0.14)
Sm	18	90	19 (±0.2)	23 (±0.3)	24 (±0.2)	23 (±0.8)
Al	661	94	302 (±2)	1080 (±73)	2321 (±31)	51 (±1)
Ca	186	90	62 (±2)	1662 (±35)	883 (±36)	52 (±2)
Cr	723	91	5.78 (±0.11)	26 (±0.2)	5.01 (±0.69)	420 (±2)
K	76	83	50 (±1)	57 (±3)	280 (±60)	63 (±1)
Mg	801	80	124 (±0.4)	1111 (±20)	2373 (±134)	13 (±3)
Mn	21	84	39 (±0.7)	3.21 (±0.11)	65 (±3)	67 (±0.7)
Ti	34	86	0.60 (±0.10)	2.03 (±0.45)	116 (±22)	58 (±0.3)
Na	532	94	110 (±4)	719 (±14)	113 (±30)	54 (±1)
V	14	87	2.30 (±0.25)	2.81 (±0.43)	13 (±1)	4.60 (±0.46)

[a]The recovery for SWCNT was calculated through a spiked sample. [b]Mean and standard deviation (±) values obtained with $N = 3$.

Recoveries for the SWCNT are well within the expected range *(70-130%, method 200.7, EPA-US)*

F. R. Simoes et al., Analytical Chemistry (2016), doi: 10.1021/acs.analchem.6b03407

Conclusions

- Completeness of **wet digestions** need to be analyzed for **residues** (control experiments)
- Solid residues characterization with **SS-NMR** shows significant promising to **assert full disintegration** of the sp^2-type lattice
- ICP-OES analysis provides reliable chemical analysis for wet digested SWCNTs, **validated by relevant CRMs**
- Wet digestion still needs to be customized; here, **molten salts** can be used to prepare **clear analytes of various Nanocarbons** but this methods needs further validation
- **Benchtop, low-cost, routine chemical analysis of Nanocarbons sample batches** is within reach

Through Inspiration, Discovery

Thank you. Questions?

Extra

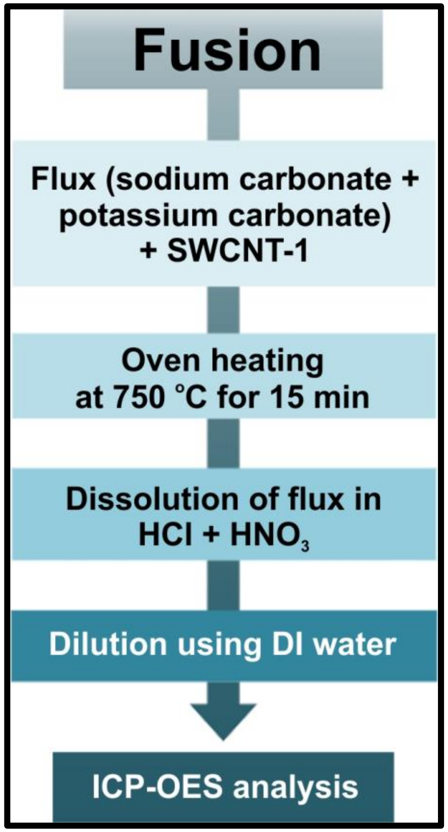
Element	Line wavelength (nm)	Melting Point (°C)
Al	396	660
Ca	316	839
Co	238	1495
Cr	205	1857
Fe	238	1535
Mo	204	2617
Ni	221	1453

Factors affecting recovery of elements:

- Chemical reactions with molten salt
- Contaminations
- Type and ratio of acids
- ICP-OES interferences
- M.P. of elements
- Fusion time

Method Validation

- *Certified Reference Material:* **SWCNT-1** by the National Research Council Canada
- *Instrument calibration:* single-element stock solutions at 1, 10, 100 and 1000 mg/L
- *Validation method:* EPA-US 200.7
- 4 replicates



Element	Certified values (NRC Canada)	ICP-OES (Fusion)	
	(ppm)	(ppm)	recovery (%)
Al	494 ± 94	509	103
Ca	2650 ± 300	2209	83
Co	15900 ± 100	12732	80
Cr	285 ± 26	307	108
Fe	2200 ± 200	2352	107
Mo	7300 ± 100	6651	91
Ni	14400 ± 800	12260	85

- EPA-US 200.7: acceptable recoveries within 80%-120%
- The above results validate our Fusion method as a viable sample preparation approach for ICP-OES