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ERC Teleseminar

The Importance of an Extensive Elemental Analysis of Carbon Nanotube Soot

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Chemistry

Carbon Nanotubes (CNTs)

SWCNT

Commonly used in biomedical applications such as cancer therapies and cellular imaging

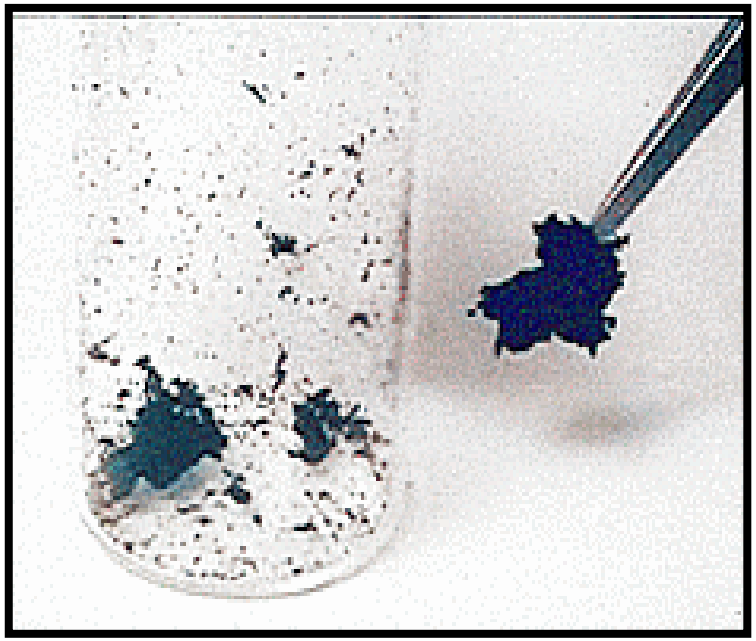
MWCNT

Used in composite materials, energy storage, sensors, and miscellaneous consumer products

Commercially Available SWCNT Soot

- Unrefined and purified SWCNT soot are analytically challenging samples known to contain a heterogeneous mixture of:
  - SWCNT Structures
  - Metal Catalysts
  - Non-Tubular Carbons
    - Fullerenes
    - Graphitic Nanoparticles
    - Amorphous Carbon
  - Residual Solvents
  - Catalyst Support Material

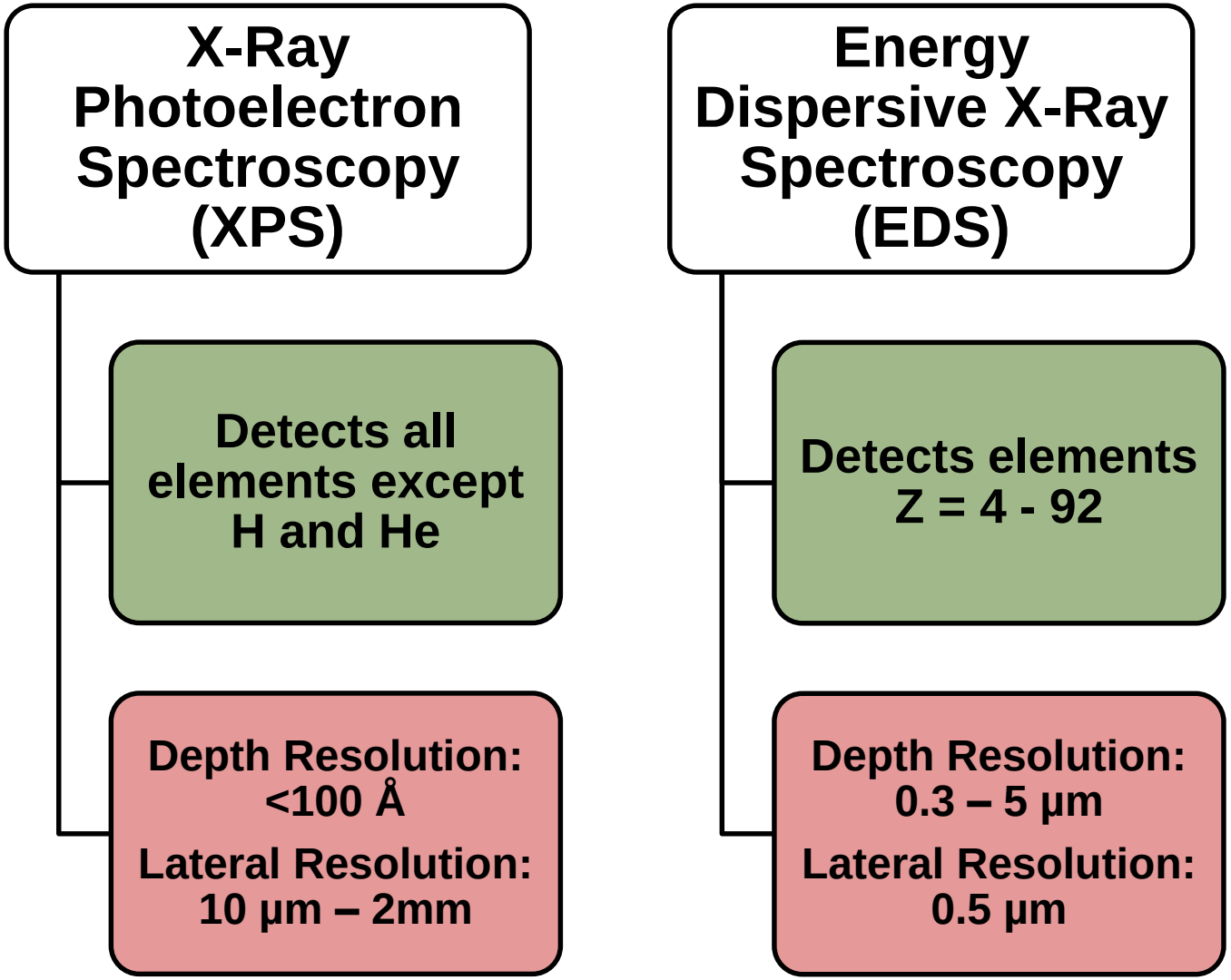
As-received soot



Common Analytical Techniques

- **NIR Spectroscopy**
  - Relative SWCNT purity factor
- **UV-Vis-NIR Spectroscopy**
  - Determine abundance of SWCNT chiralities
- **Raman Spectroscopy**
  - Relative SWCNT quality factor
- **Thermogravimetic Analysis**
  - Estimation of metallic and carbonaceous components

Common Elemental Analysis Techniques



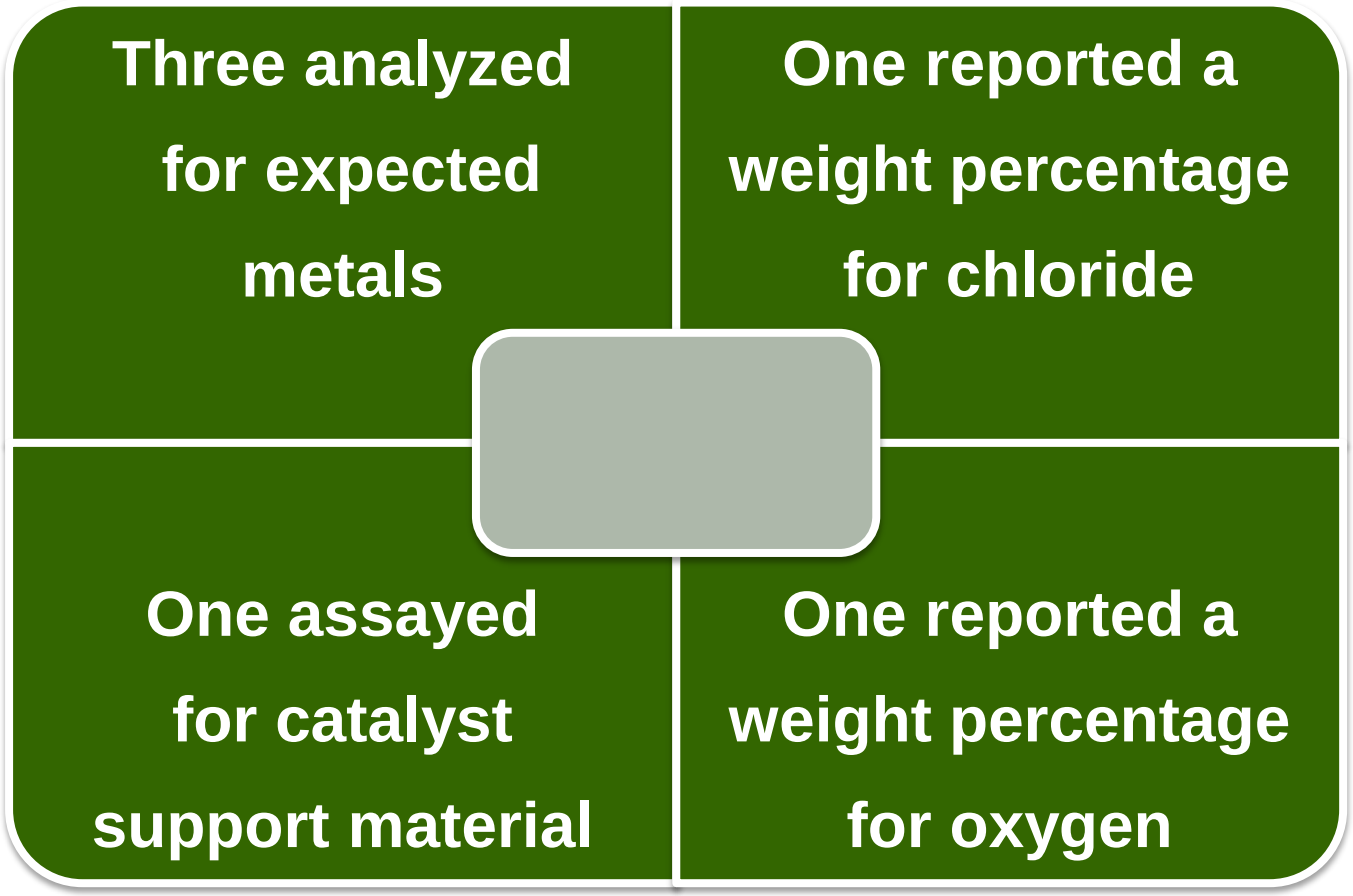
Bulk Methods for Elemental Analysis

- **CHNS/O Analysis**
  - Rapid, relatively inexpensive, readily accessible
- **ICP-MS Analysis**
  - Rapid, relatively inexpensive, readily accessible
  - Nine decade analytical working range
  - Detection limits at or below part per trillion (ppt)
  - Cannot analyze CHNS/O or most radioactive elements

Current Literature

Korneva (2008)	Plata et al.(2008)	Zeisler et al.(2011)	Cherkasov et al.(2013)
3 elements	55 elements	30 elements	7 elements
1 MWCNT Product	11 SWCNT products	1 SWCNT product	1 MWCNT product
CHN	CHN ICP-MS	NAA ICP-MS	CHNS/O TGA-MS

Current Literature



Why Elemental Analysis?

- Imperative for:
  - Ensuring product quality
  - Batch to batch reproducibility
  - Generating accurate environmental health and safety (EH&S) risk assessments

Goal of this work:

Develop a routine laboratory procedure for an extensive elemental analysis for as-received SWCNT soot using readily-available bulk methods of analysis

CoMoCAT™ SWCNT Soot CVD Synthesis and Purification

- **Bimetallic catalyst**
  - $Co(NO)_3$ and $(NH_4)_6Mo_7O_{24}$
- **Catalyst support**
  - SiO_2
- **Heat to 700 - 1000 °C at 1 - 10 atm**
- **Introduce carbon source (CO)**
- **Purification**
  - Amorphous carbons removal by air oxidation at ≤300°C
  - Metal oxides dissolved with **HCl**
  - SiO_2 dissolved with **HF**

SouthWest Nanotechnologies Inc., Norman, OK

R & D Magazine, Oct 2011 Issue, "Carbon Nanotubes Chart Their Own Course"

Bulk Elemental Analysis of SWCNT Soot

- Instrumental techniques:
  - % Carbon, % Hydrogen, % Nitrogen, % Oxygen ,and % Sulfur (CHNS/O)
  - Oxygen Flask Combustion / Anion Chromatography (OFC / AC)
  - Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
  - Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS)

None of the Top -10 CNT manufacturers use these techniques in their certificate of analyses.

77 element analysis – essentially 99% of elements that are not radioactive or noble gases.

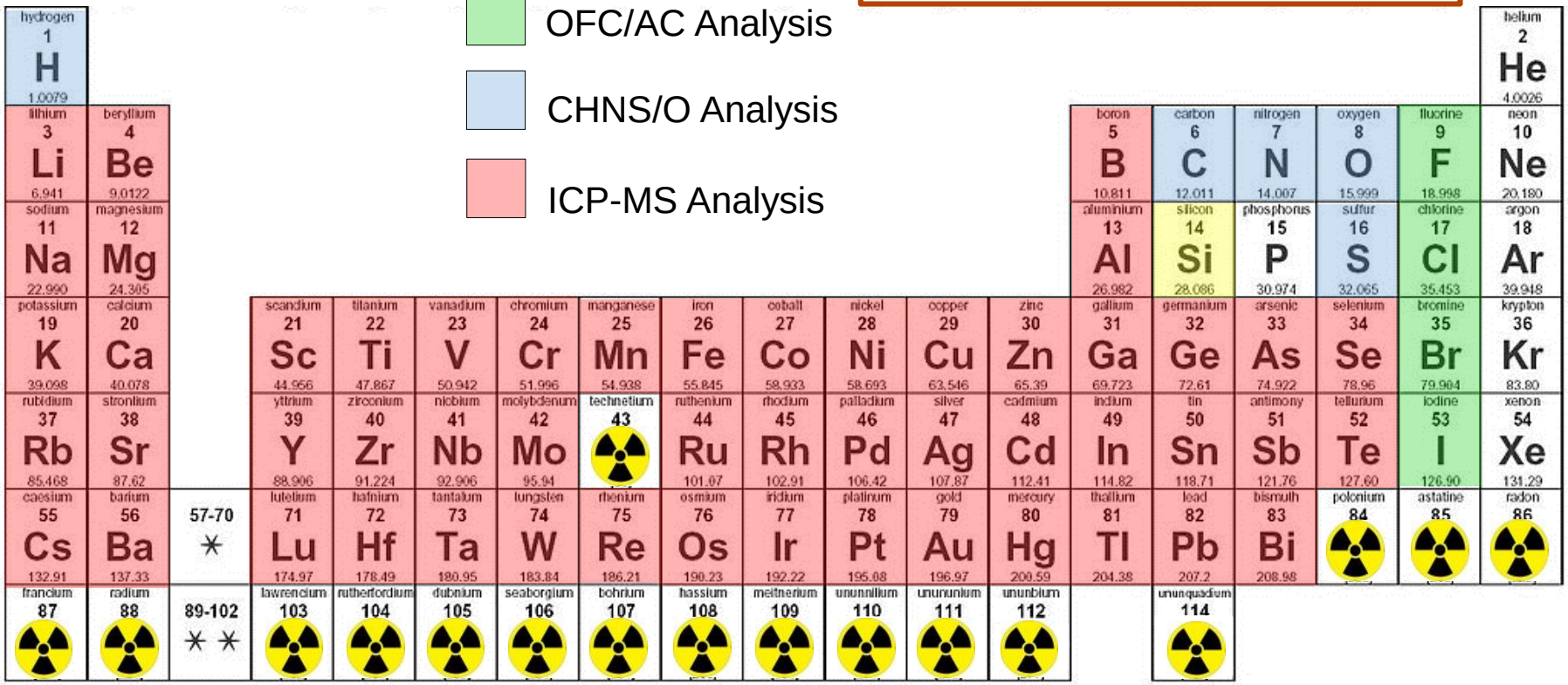
GF-AAS Analysis

OFC/AC Analysis

CHNS/O Analysis

ICP-MS Analysis

77-Element Analysis!



Bulk Elemental Analysis: Samples

- Two products of CoMoCAT® SWCNT soot:
  - Product I (2009)
    - Lot No. SG76-0013 (1.0-g)
    - Enriched with (7,6) SWCNTS
  - Product II (2005)
    - Lot No. UT4-A001 (1.0-g)
    - Not enriched
- Results will be evaluated with respect to each product's certificate of analysis
- An assessment will be presented to estimate whether trace elemental impurities in airborne soot pose an EH&S concern

Bulk Elemental Analysis: Experimental Details

- CHNS/O Analysis
- OFC / Anion Chromatography
- ICP-MS
- GF-AAS

CHNS Analysis: Pregl-Dumas Technique

- Perkin Elmer 2400 Series II CHNS/O Analyzer
- 5.0 mg of CNT soot sample is encapsulated in Sn or Al vials and introduced into the combustion chamber
- Samples are combusted completely in the presence of excess oxygen and combustion reagents at 1100 °C, then NO_x gases are reduced to N_2
- Product gases (CO_2, H_2O, SO_2, and N_2) are captured in the mixing chamber and homogenized before being separated using gas chromatography
- As the gases elute, they are measured by a thermal conductivity detector
- Results are reported as mass percent

Oxygen Analysis: Unterzuacher Method

- Perkin Elmer 2400 Series II CHNS/O Analyzer
- 5.0 mg of CNT soot sample is pyrolyzed in a He/H_2 (95%:5%) atmosphere at 1100 °C
- Products of the reaction containing oxygen are converted to CO over the platinized carbon reagent
- CO and other gasses pass through a scrubber to remove interferents
- CO is controlled, separated, and detected using gravimetric determination
- Results are reported as mass percent

OFC/AC: Schöniger flask technique

- 10 mg of CNT soot sample is electrically ignited (or ashed) in an oxygen-filled flask
- During this process the elements are converted to their ionic forms
- The resulting solution is diluted, filtered, and analyzed using anion chromatography with conductivity detection
- Results are reported as mass percent

ICP-MS

- Thermo X-II Series ICP-mass spectrometer and a Varian 820MS ICP-mass spectrometer
- 5.0 mg of CNT soot sample is placed into a pre-cleaned 50-mL plastic test tube
- 100 µL of both 37% HCL and 69% HNO_3 is added to the test tube (acid digestion)
- The sample is agitated in an ultrasonic bath for 10-30 min before being diluted with 2% HNO_3 blank and allowed to settle overnight
- Ions are separated using a quadrupole mass analyzer
- Results are reported in parts per million (ppm)

GF-AAS

- Varian AA280Z GF-AA spectrometer with Zeeman background correction
- 5.0 mg of CNT soot sample is placed into a pre-cleaned 15-mL plastic test tube
- 100 µL of both 37% HCL and 69% HNO_3 is added to the test tube (acid digestion)
- Sample is agitated in an ultrasonic bath for 20 min before 9.8 mL of 2% HNO_3 blank solution is added
- Mixture is centrifuged for 30 minutes before detection using the atomic line of Si
- Results are reported in parts per million (ppm)

Bulk Elemental Analysis: Basic Approach

1. Sum the weight percentages of elements detected using CHNS/O and OFC/AC analyses

2. Use GF-AAS and ICP-MS to determine the identity and composition of the remaining weight percentage

Bulk Elemental Analysis: Basic Approach

1. Sum the weight percentages of elements detected using CHNS/O and OFC/AC analyses

Approach is only valid if all carbon nanomaterials present in the soot are combusted by the end of the analyzers' heating cycle

Raman spectroscopic analyses were performed on soot products heated to 1000°C

CHNS/O Results

Element	Product I Mean ± SD (%)	Product II Mean ± SD (%)
C	83.48 ± 0.63	78.25 ± 1.01
H	0.70 ± 0.07	0.55 ± 0.01
N	0.38 ± 0.02	0.35 ± 0.03
S	0.00 ± 0.00	0.00
O	8.96 ± 0.71	10.11 ± 2.15

OFC/AC Results

Element	Product I Mean ± SD (%)	Product II (%)
Br	0.00 ± 0.00	0.00
Cl	0.07 ± 0.10	0.07
F	1.02 ± 0.02	0.25
I	0.00 ± 0.00	NA

CHNS/O + OFC/AC

Product I (Mass %)	Elements	Product II (Mass %)
83.48	**C**	78.25
0.70	**H**	0.55
0.38	**N**	0.35
8.96	**O**	10.11
1.02	**F**	0.25
0.07	**Cl**	0.07
94.60	**Total %**	**89.57**

Remaining Percentages

Product I:

100% - 94.60% = 5.40% Remaining

Product II:

100% - 89.57% = 10.43% Remaining

To determine the identity and amount of elements in the remaining percentages, GF-AAS and ICP-MS analyses were performed

GF-AAS Results

Element	Product I (ppm)	Product II (ppm)
Si	133.96	9.52

ICP-MS Results: Product I

(Only metals reporting ≥ 0.001% of sample are listed)

Element	Mean ± SD (ppm)
Mo	8640.252 ± 5545.348
Co	1079.035 ± 819.983
B	503.941 ± 865.938
Ca	279.142 ± 195.161
Na	109.561 ± 152.385
Al	22.618 ± 21.388
Fe	17.728 ± 16.513
Sn	13.521 ± 4.861
Ni	5.204 ± 3.599

Element	Mean ± SD (ppm)
Mg	3.933 ± 2.212
Cd	3.418 ± 1.249
K	2.874 ± 0.731
W	2.644 ± 2.157
Zn	2.484 ± 1.141
Cr	1.481 ± 1.158
Ce	1.224
Zr	1.158 ± 1.962

Calculations

Sum of average concentrations of all elements (ppm):

$$\sum_{i=1}^{68} A_i = B$$

A_i = average concentration of each individual element analyzed

B = sum of average concentrations

ICP-MS Results: Product I

(Only metals reporting ≥ 0.001% of sample are listed)

Element	Mean ± SD (ppm)
Mo	8640.252 ± 5545.348
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Mg	3.933 ± 2.212
Cd	3.418 ± 1.249
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Ce	1.224
Zr	1.158 ± 1.962
Si	133.960

$$\sum_{i=1}^{68} 8640.252 + 1079.035 + 503.941 \ldots = 10886.902 \text{ ppm}$$

Calculations

Ratio of average concentrations to sum of averages:

$$\frac{A_i}{B} = C$$

A_i = average concentration of each individual element analyzed

B = sum of average concentrations

C = relative concentration of each element

ICP-MS Results: Product I

(Only metals reporting ≥ 0.001% of sample are listed)

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Mo	8640.252 ± 5545.348
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	1.158 ± 1.962
	133.960

$$\sum_{i=1}^{68} 8640.252 + 1079.035 + 503.941 \ldots = 10886.902 \text{ ppm}$$

$$\frac{8640.252\ ppm}{10886.902\ ppm} = 0.794$$

Calculations

Elemental percentage in SWCNT soot *(E%)*:

$$\mathrm{E\%} = \begin{pmatrix} Relative\ concentration \\ of\ each\ element \end{pmatrix} \begin{pmatrix} Remaining \\ Percentage \end{pmatrix}$$

Molybdenum:

$$0.794\ x\ 5.40\% = 4.29\%\ \mathrm{Mo}$$

Summary of 15 Major Elements in CoMoCAT® SWCNT Product I

Element	Product I (%)
C	83.48
O	8.96
Mo	4.29
F	1.02
H	0.70
Co	0.54
N	0.38
B	0.25
Ca	0.14
Cl	0.07
Si	0.07
Na	0.05
Fe	0.01
Sn	0.01
Al	0.01

= 99.98%

Summary of 23 Major Elements in CoMoCAT® SWCNT Product II

Element	Product II (%)
C	78.25
O	10.11
Mo	8.87
F	0.25
H	0.55
Co	1.26
N	0.35
B	0.10
Ca	0.05
Cl	0.07
Si	n.d.
Na	0.02

Element	Product II (%)
Fe	0.03
Sn	n.d.
Al	n.d.
Pb	0.02
Ce	0.02
Ba	0.01
La	0.01
Mg	0.01
Nd	0.01
Ni	0.01
Y	0.01

Total = 100.01%

Product II Certificate of Analysis

The University of Texas at Dallas

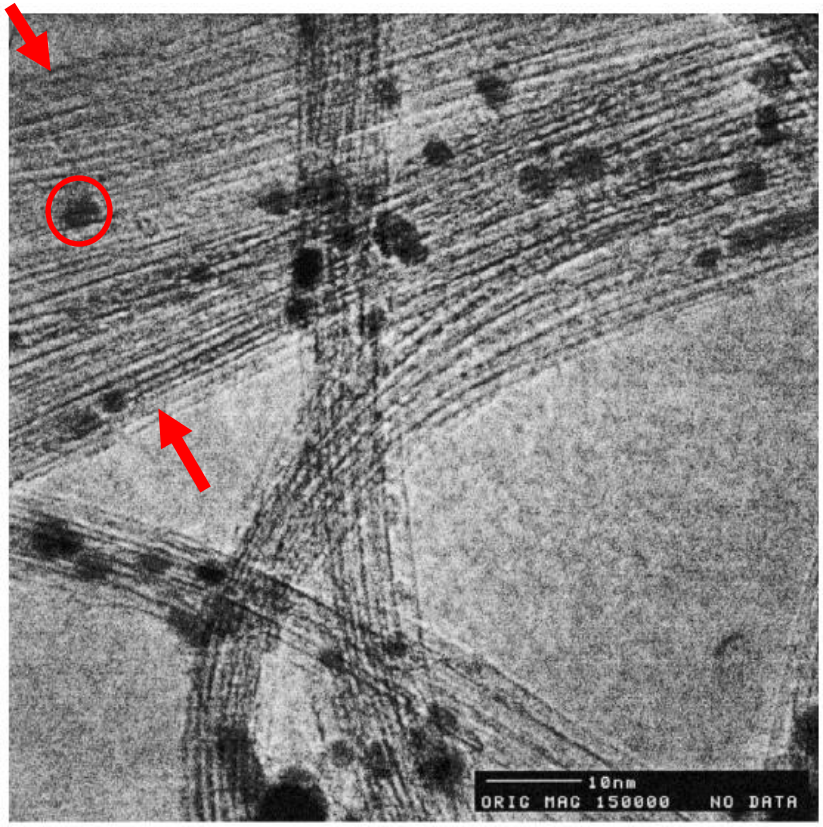
Element	Product II (%)
C	78.25
O	10.11
Mo	8.87
Co	1.26
F	0.25
Si	n.d.

SouthWest NanoTechnologies Inc.

Element	XPS Analysis (%)
C	96
O	3.40
Mo	0.86
Co	0.00
F	0.00
Si	0.00

Ultimately, it is not that XPS analysis is inaccurate, but rather, that it is only representative of areas probed by survey- or high resolution-scan(s).

Product II Certificate of Analysis



TEM of Catalytic metals encased by a carbonaceous shell

SouthWest NanoTechnologies Inc.

Element	XPS Analysis (%)
C	96
O	3.40
Mo	0.86
Co	0.00
F	0.00
Si	0.00

Nikolaev P,, Journal of Nanoscience and Nanotechnology, 2004, 4, 4.

Elemental Analysis Summary

- Carbon – most abundant element
- Product I – 27 elements
- Product II – 36 elements
- Mo and Co – most abundant metals
- Na, Ca, Cl – Ubiquitous presence of salts
- Fe, Pb – somewhat unexpected, presumably from manufacturing environment

So how to do we know if the metals in our products are of EH&S concern, especially during the handling of the dry soot powder?

Concentration + OSHA Permissible Exposure Limit

Substance	OSHA PEL (mg/m^3)
B	15
Ce	15
Si	10
Al	5
Ca	5
Mo	5
Fe	1
Ba	0.5
Co	0.1
Pb	0.05

NIOSH Approach

$$Z \times Y = X$$

Z = airborne levels of SWCNTs during handling

Y = concentration of the element in ng/mg (ppm)

X = calculated exposure level for that element

Maynard, Andrew D. et al Journal of Toxicology and Environmental Health, Part A, 67:7-107, 2004

NIOSH Approach

For Pb:

$$Z \times Y = X$$

$$53\ \mu g/m^3 \times 55.33\ ng/mg = 2.92\ ng\ Pb/m^3$$

2.92 ng Pb/m^3 < 50 µg Pb/m^3 (OSHA PEL)

Level of Pb in Product II should NOT be an EH&S concern during handling

Maynard, Andrew D. et al Journal of Toxicology and Environmental Health, Part A, 67:7-107, 2004

OSHA Permissible Exposure Limits (PELs)

Substance	OSHA PEL (mg/m^3)
B	15
Ce	15
Si	10
Al	5
Ca	5
Mo	5
Fe	1
Ba	0.5
Co	0.1
Pb	0.05

~26,000 ppm

None of the elements detected in these products are of EH&S concern

Summary of Work

- Nanotoxicity assessments without a thorough elemental analysis are useless
  - Avoid falsely attributing potential toxicity to SWCNT soot when source could have been an elemental impurity
- Assessments of product quality without a thorough elemental analysis are useless
  - Batch to batch reproducibility
- Method should find wide applicability
  - Feasible with graphene, graphene-oxide, and pristine and carboxylated MWCNT powders
  - Minimum sample size is 80 mg

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National Institutes of Health
Turning Discovery Into Health

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