

CARBON NANOTUBE ANALYSIS USING THE TSI® LIBS DESKTOP ANALYZER

APPLICATION NOTE LIBS-019

Carbon Nanotubes (CNTs) are used in an ever increasing number of applications, from engineering applications (lighter, stronger, more flexible materials) to medical applications in cancer research. Laser-Induced Breakdown Spectroscopy (LIBS) is very well suited to help with the analysis of metallic residues in the CNTs, stemming from catalysts, substrates and impurities.

Samples

Two different samples of CNTs were analyzed. The physical and chemical characteristics are shown in Table 1 below:

Table 1: Physical and Chemical Characteristics of CNT Samples

	Purity	Ash content	OD (nm)	Length (µm)	C (%)	Ni (%)	Co (%)	Fe (%)
SWCNT	>60%	<1.5%	1-2	5-30	96.3		2.91	
MWCNT	>90%	<1.5%	50-80	10-20	97.3	1.88		0.56

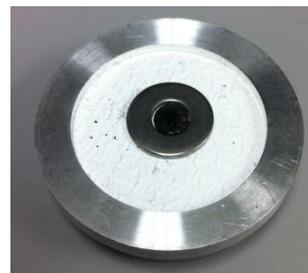
In order to get a wider range of compositions, a number of mixtures of the two CNT samples from Table 1 were prepared. Table 2 below shows the relative amounts (by mass, in %) of the two samples in the mixtures:

Table 2: Mixing ratios for CNT samples

	MWCNT	Mix 5	Mix 2	Mix 3	Mix 1	Mix 4	Mix 6	SWCNT
% SWCNT	0	7	29	53	64	96	99.2	100
% MWCNT	100	93	71	47	36	4	0.8	0

Sample Preparation

Mixtures were prepared by weighing amounts of the two samples in Table 1 and mixing them in a plastic bag. For all samples, the powder (mixture or pure) was pressed into a pellet of 7 mm diameter and 2 to 3 mm thick in a fume hood. Each pellet had a mass of ~40 mg. Pellets were placed in a holder to keep the pellet in place during analysis – and facilitate transport and storage.



Sample Analysis

Samples were analyzed in a TSI LIBS Desktop Analyzer. The TSI LIBS Desktop Analyzer used a 50 mJ 1064 nm Nd:YAG laser and a 4 channel broadband spectrometer. Instrument settings were as follows:

- Laser output: 60%
- Spot size: 100 μm
- Sample shots: 5 (shots per spot)
- Layout: 4 \times 8 grid (32 spots total)
- Spacing: 0.5 mm \times 0.5 mm
- Acquisition delay: 1 μs

Data Analysis

The spectra of the 32 spots per pellet were averaged to increase the signal to noise ratio. The averaged spectrum of Mix 3 is shown below.

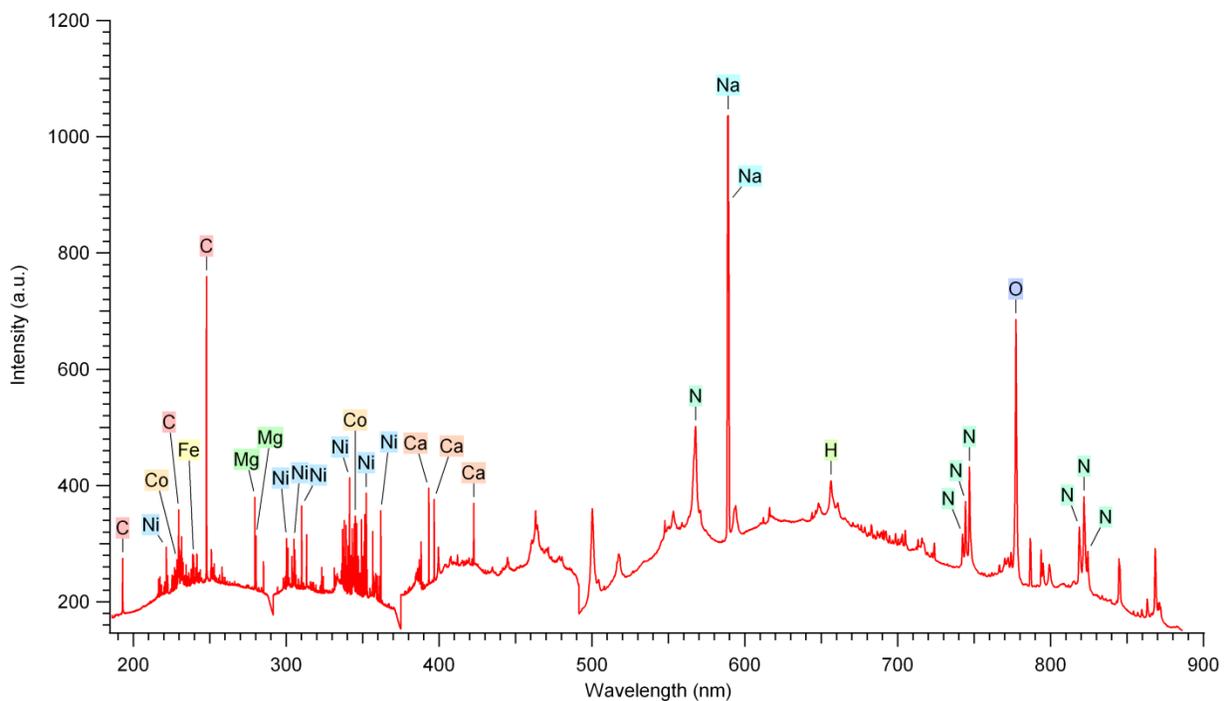


Figure 1: LIBS spectrum (average of 32 shots) of CNT Mix #3

Peaks were chosen for the elements analyzed (C, Co, Ni, Fe) and the peak area was integrated for these peaks for all analyzed mixes. Figure 2 below shows the different regions chosen for the four peaks, again for the spectrum of Mix 3.

As the C concentration does not vary very much between samples (96.3 to 97.3%), the C peak at 247.8 nm is a good internal standard. Therefore, all peak areas were divided by the C 247 peak for creating calibration curves.

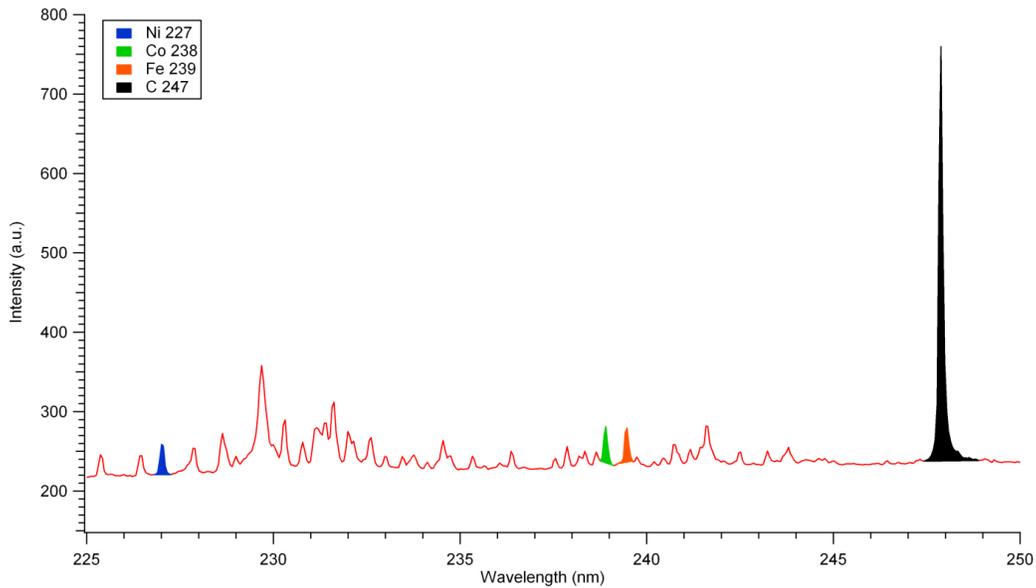


Figure 2: Integrated peak areas for elements of interest, shown for mixture #3.

Figure 3 below shows the linear calibration curves for the three metals analyzed (Ni, Co, Fe). The dotted lines indicate the linear regression curves for the metal calibrations. Error bars indicate 1 standard deviation where several measurements were made.

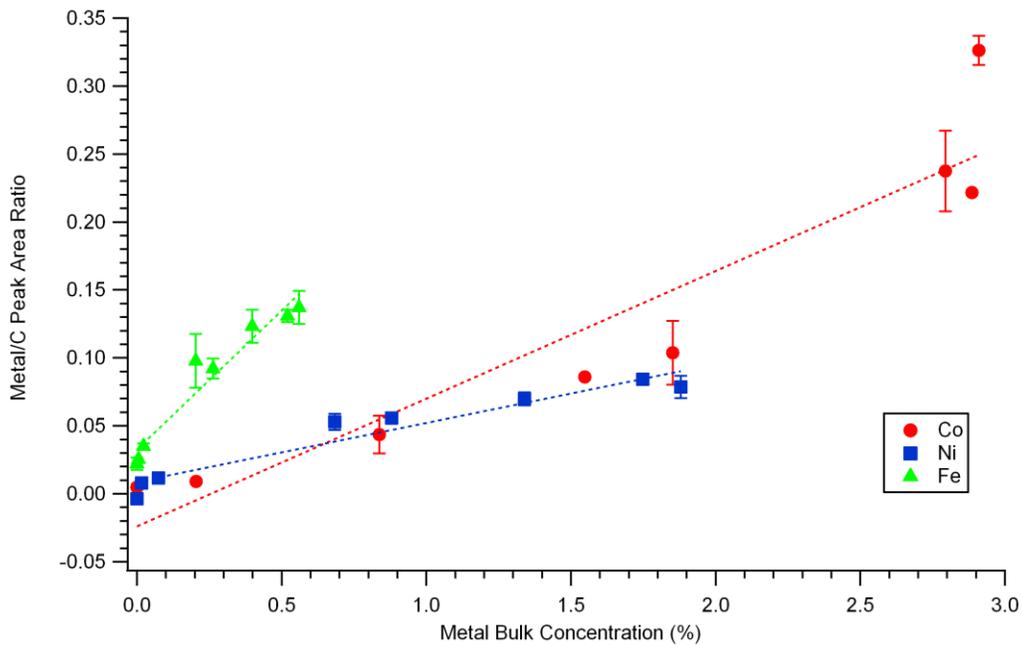


Figure 3: Calibration curves for the 3 metals of interest. Error bars indicate ± 1 standard deviation for samples with several measurements, and dotted lines depict the linear regression curves.

The regression results (slope, intercept, regression coefficient R^2) are listed in Table 3 below.

Table 3: Regression values of merit for metals analyzed

Metal	Co	Ni	Fe
Slope	9.39	4.32	20.47
Intercept	-0.024	0.009	0.033
R²	0.8877	0.9295	0.9378

Concentration Predictions

To test the calibration, the following procedure was used: For each element tested, one datapoint was removed and the calibration curve was calculated with the remaining datapoints (The pure SWCNT and MWCNT were not removed, in order not to have to extrapolate the data). The removed datapoint was then predicted using the new calibration curve.

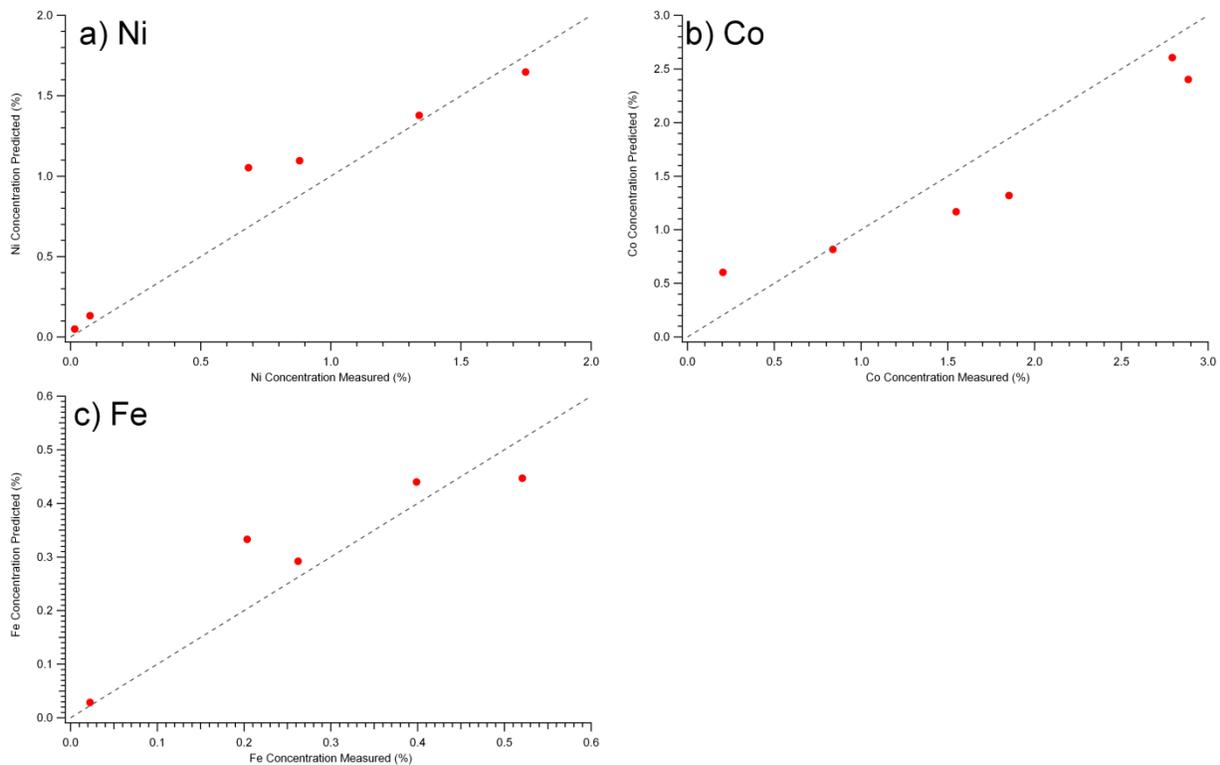


Figure 4: Known versus predicted metal concentration graphs. Known concentrations are plotted on the x-axis, predicted values on the y-axis. Dashed lines indicate 1-1 relationship.

Each graph shows the known metal concentration on the x-axis and the predicted value on the y-axis. The dotted lines indicate the 1-to-1 ratio.

With few exceptions, the predicted values are very close to the measured ones, indicating that this method is very good for metal concentration measurements in Carbon Nanotubes. Results can be improved by including more mixtures, several measurements for each mixture, and improving the homogeneity of the mixtures.

It is important to create a calibration with matrix-matched materials – so CNT impurity analyses should be conducted with CNT standards. Pellets should also be made in a consistent matter, always using the same pressure and dwell time when pressing them, to ensure reproducible sample density.

The LIBS method is an elemental analysis technique, and while it can measure the concentration of carbon (not shown here), it cannot differentiate between pure SWCNT and pure MWCNT. With Raman measurements on the same samples, which could give additional information (SW vs. MW CNT, tube diameter, etc.), it is believed a comprehensive analysis of CNT materials may be possible.

Conclusions

LIBS analysis of several mixes of Carbon Nanotubes with different metal concentrations showed good ability to predict metal impurities and contamination in CNTs. Minimal sample preparation was required to create pellets for analysis.



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