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# Development of efficient digestion procedures for quantitative determination of cobalt and molybdenum catalyst residues in carbon nanotubes

Linda Ayouni-Derouiche <sup>a</sup>, Marie Méjean <sup>a</sup>, Pauline Gay <sup>a</sup>, Marie-Laure Milliand <sup>a</sup>, Pierre Lantéri <sup>a</sup>, Laury Gauthier <sup>b</sup>, Emmanuel Flahaut <sup>c,d,\*</sup>

<sup>a</sup> University of Lyon, Institute of Analytical Chemistry, Lyon, France

<sup>b</sup> Université de Toulouse, INP, UPS, EcoLab (Laboratoire d'Ecologie Fonctionnelle et Environnement), ENSAT, Avenue de l'Agrobiopole, 31326 Castanet Tolosan, France

<sup>c</sup> CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France

<sup>d</sup> Université de Toulouse, UPS, INP, Institut Carnot Cirimat, 118, route de Narbonne, F-31062 Toulouse Cedex 9, France

## A B S T R A C T

Whatever the method used for the synthesis of carbon nanotubes (CNTs), they always contain residual catalysts in variable amount. Many methods have been proposed in the literature to purify CNTs, but their efficiency strongly depends on the experimental conditions. Although the presence of residual catalysts in small amount is generally not a problem for many applications, this can become a critical issue when a high purity is required, typically for magnetic properties or for biomedical applications (because of the intrinsic toxicity of most catalysts). Quantification of the amount of residual catalysts is usually obtained by classical chemical analysis, which requires a preliminary digestion (complete mineralisation) of the CNT samples. In this work, we systematically compared 3 different digestion protocols and optimised one, reaching 100% dissolution within a very limited time (1 h) together with the requirement of only a few milligrams of sample, and safe experimental conditions. This method can be easily transferred for use in research laboratories, making accessible the quantitative analysis of CNT samples, and has been validated following ISO/IEC 17025:2005 for linearity, specificity, intermediate precision, limits of detection and quantification.

## 1. Introduction

Since last decades nanosciences have become a priority research line in many fields. Carbon nanotubes (CNTs) discovery in 1991 [1] has opened investigation areas for many appli-

cations and they quickly have become the most intensively studied because of their unique 1D-structure and related physico-chemical properties [2]. For example, CNTs are a hundred times stronger than steels [3] and can withstand electrical current densities three orders of magnitude higher

\* Corresponding author at: CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France.

E-mail address: [flahaut@chimie.ups-tlse.fr](mailto:flahaut@chimie.ups-tlse.fr) (E. Flahaut).

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than copper [4]. Carbon nanotubes can also be functionalized for biomedical applications (imaging, cancer treatment, implants, etc.) [5]. There are three common methods used for the synthesis of CNTs: laser ablation, electric arc discharge and chemical vapour deposition [6]. Catalysts are needed to enhance the synthesis (yield, selectivity): metals and especially transition metals such as Fe, Ni, Y, Co or Mo [7] are generally used for this purpose.

Purification can be considered as the critical step so as to remove all undesirable components involved in synthesis and that are responsible for quality degradation of CNTs properties. This includes unwanted carbon by-products such as amorphous carbon, but also residual catalytic particles. Techniques such as flocculation [3], microfiltration [8], chromatography [9,10], centrifugation [11], thermal treatments [12], microwave assisted purifications [13,14] and dry [15] or wet oxidation ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ , etc.) [16] are often used and even combined to improve the purity. Efficiency of these techniques is essential not only to reach the theoretical properties of CNTs but also because of the potential implication of these impurities in terms of toxicity of CNTs samples. However, the analytical side has only been poorly developed, especially for quantitative analysis. Characterisation of CNTs samples is generally performed by qualitative or semi-quantitative techniques as Raman spectroscopy [9,14], thermo gravimetric analysis (TGA) [9,14], transmission electron microscopy (TEM) [14], scanning electron microscopy (SEM) [12], X-ray photoelectron scattering (XPS) [17], X-ray fluorescence(XRF) [18]. However, accurate quantification is needed to determine the amount of residual catalysts. Neutron activation analysis (NAA) can be chosen for its direct analysis capability and sensitivity [19,20]. However the need of a nuclear reactor makes the technique inconsistent for laboratory scale routine analysis.

Inductively coupled plasma atomic emission spectrometry (ICP AES) or mass spectrometry (ICP MS) are the relevant techniques for elemental quantitative analysis. Nevertheless, suitable solutions are needed for ICP analysis and samples thus have to be first digested. CNTs like all carbon matrices (coal, graphite) are extremely refractory samples and so it is very difficult to dissolve them. Generally for carbon samples dry ashing is recommended to fully oxidise the carbon structure and then ashes are dissolved in suitable acids like nitric acid for instance. However this is a time consuming technique because of a long heating program for at least several hours [21]. This procedure is generally used for analysis of large samples but in the case of CNTs synthesis at laboratory scale, very low quantities – typically only a few milligrams – are generally available. Wet acid digestion is widely used for elemental analysis. For many samples, open systems commercially available are sufficient to give a complete digestion. With these systems, a maximum temperature of about 180 °C can be reached, which is not enough to attack more refractory compounds such as some oxides, polymers or of course carbon matrices. Attempts by Strong et al. [9] to dissolve CNTs in aqua regia gave an uncompleted digestion with black residues. Closed pressurised systems and microwaves are often used because thanks to the combination of the pressure and of microwave action, digestion is more efficient for a larger variety of compounds, including carbon samples.

Reported results by Yang et al. [22] after microwave digestion are promising but a filtration step is mentioned, suggesting only partial digestion. Mortari et al. [23] realised a very interesting study using microwave technology first in conventional microwave system and then with microwave induced combustion. The first one was performed with aqua regia solutions but lead also to uncompleted digestion. Microwave induced combustion (MIC) presents the advantage to combine positive effects of pressurised wet digestion and combustion, which is a suitable method to oxidise carbon based materials. Indeed, by this method clear solutions were obtained for a commercial multiwall CNTs sample. As the material was commercial, quantity available was enough to use 20–400 mg and it was possible to press the powder in order to avoid electrostatic problems often encountered while weighing CNTs. For CNTs prepared or processed (e.g. functionalised) at laboratory scale, a sample quantity of about one or two milligrams is usual. Besides, MIC technology is an upgrade of a conventional microwave system, which is not possible for all kinds of systems.

Regarding microwave-assisted digestion of CNTs, this technique was recently used by different groups for the purification of CNTs samples [24,25], but without any analytical aim as the goal was only to dissolve some impurities, but not to fully dissolve the samples for further elemental analysis.

It is also worth mentioning that some important analytical developments have been proposed recently for the quantitative analysis of CNTs in complex matrices and especially “environmental samples” such as biological tissue, soils or sediments. These methods are essentially based on TGA analysis and require complementary analysis of the CNTs samples by other techniques such as Raman spectroscopy [26] or mass spectroscopy [27]. These approaches are very interesting (although rather difficult to apply to “real” environmental samples) but do not give any information about the composition of the CNTs themselves.

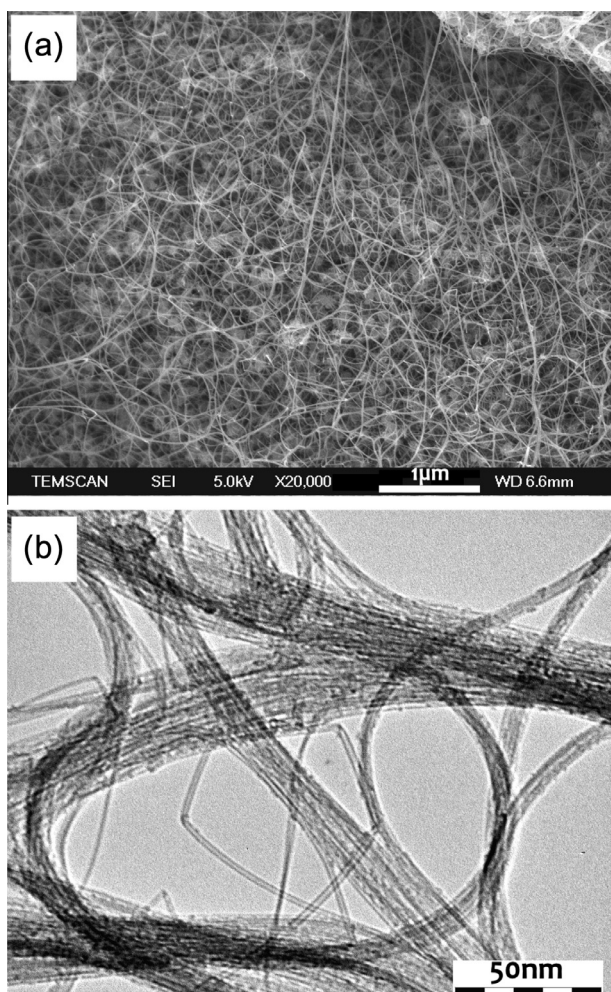
In this paper we compare three wet digestion methods (involving open or closed systems) specifically developed for the analysis of small CNTs samples (typically of the order of 1 mg) by ICP AES for the quantification of Co and Mo residual catalysts in double wall carbon nanotubes synthesised at laboratory scale [28]; we finally propose an optimised process (experimental design approach) suitable for the quantitative analysis of laboratory scale CNTs samples which should be very useful for further research developments in this field. The use of DWNTs is also justified by their ideal position between single and multi-walled CNTs in terms of chemical resistance. Indeed, the chemical resistance of CNTs to oxidising conditions is a compromise between the number of walls and the global amount of structural defects, the latter generally increasing with the former. The DWNTs used in this work have a rather low Raman  $I_D/I_G$  ratio (ca. 0.15) and can thus be considered of rather good structural quality. The outer wall can be considered as a shield with limited structural defects, thus efficiently protecting the inner one. Moreover, DWNTs used in this work contain a low amount of residual metals (ca. 4 wt.% in total) and are thus well suited for the development of an accurate analysis technique. The main challenges of this work were to develop an analytical method which would be efficient using only one milligram of CNTs.

## 2. Experimental section

### 2.1. Material and reagents

Double-walled carbon nanotubes (DWNTs) (Fig. 1) were synthesized at the CIRIMAT/LCMIE laboratory using a Catalytic Chemical Vapour Deposition (CCVD) technique and a CoMo-MgO catalyst as described earlier [24]. The mean intensity ratio between the D and G bands ( $\lambda = 488$  nm) was ca. 15% (not shown). Nitric acid 68%, sulphuric acid 95%, hydrochloric acid 37%, hydrofluoric acid 40%, were purchased from Prolabo Normapur AnalaR. Hydrogen Peroxide 30% was purchased from Sigma Aldrich. Stock standard solutions at 1000 mg/L for each metal were obtained from SPEX CertiPrep. Dilutions were done as required before analysis. Deionised water (18 MOhm) was obtained from demineralised resins (Veolia).

A Mettler Toledo MX5 micro balance with an accuracy of 1  $\mu$ g was used for weighing samples. Electrostatic effects were avoided with a U ionizer from Mettler Toledo.



**Fig. 1 – SEM (a) and (b) TEM images of the DWNTs sample used in this work. The SEM image corresponds to the raw CCVD sample (before removal of catalytic material and support), and the TEM image was taken after removal of the catalytic material and support by HCl washing.**

**Table 1 – ICP AES settings. The number of replicates was 3. The read time depends on the element, and on the wavelength used: Mo at 281.6 and 284.8 nm: 5 s per replicate; at 202.3 and 204.6 nm: 15 s per replicate. For Co at 238.9 nm: 5 s per replicate; at 228.6 and 230.8: 15 s per replicate.**

Power (W)	1150
RF generator (MHz)	27.12
Ar plasma flow rate (L min <sup>-1</sup> )	12
Ar auxiliary flow rate (L min <sup>-1</sup> )	1.0
Ar nebulizer flow rate (L min <sup>-1</sup> )	0.60
Spray chamber	Standard cyclonic
Nebulizer	Standard concentric
Mo wavelength (nm)	228.6–230.8–238.9
Co wavelength (nm)	202.3–204.6–281.6–284.8

The open digestion system used in this work was manufactured by Institute of Analytical Sciences prototype team. Sonication was performed in an ultrasonic bath (Bransonic 1510, VWR). The electric Bunsen was purchased from VWR.

For the closed digestion system, an Ethos Touch Control microwave (Milestone) was used. The HPR 1000/10S rotor was equipped with 10 position sample carousel of 100 mL PTFE vessels. PTFE vessels are chemically resistant and are closed with caps that prevent any contamination or losses. A reference PTFE vessel was used to control the temperature reaction during the run. Because of the low quantity of CNTs used, 100 mL PTFE vessels were not suitable. Therefore PTFE insets were used to improve the throughput as three insets per vessel could be placed. A second microwave was used: the Ultra Wave (Milestone). A sample holder with fifteen positions tubes was placed in a PTFE vessel where 120 mL of water, 5 mL of hydrogen peroxide and 1 mL of nitric acid were placed. The whole cavity was filled with nitrogen and submitted to a 40 bar initial pressure.

Metals quantification was performed by ICP AES, ICAP 6300 model (Thermo Fisher Scientific, Germany). Operational parameters are described in Table 1.

### 2.2. Digestion methods

#### 2.2.1. Open system

One milligram of CNTs was weighed in a platinum crucible and placed in a quartz tube specially designed for our open system which is called a matra. A 2 mL mixture of 1:1 HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> was added. The matra was heated at 250 °C for 12 h. Sonication during a few minutes was then necessary to unstuck black residual deposit. The matra was then introduced for a few seconds in an electric bunsen pre-heated at 600 °C to enhance dissolution of residual particle and was finally heated again at 250 °C for 12 h.

#### 2.2.2. Closed system Ethos Touch Control

One milligram of sample was weighed in a platinum crucible and transferred into a PTFE inset first discharged of static electricity. Preliminary assays were realised with various temperature programs and with various acid and oxidising agent mixtures (HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HF, H<sub>2</sub>O<sub>2</sub>) in variable amounts according to an experimental design. The three parameters of this experimental design were:



- Heating temperature with 2 levels: 230 and 250 °C. A program with a progressive heating during 15 min and a plateau during 30 min was selected.
- CNTs mass to reagent mixture volume ratio with 2 levels: 0.25 (final volume: 4 mL) and 0.5 (final volume: 2 mL).
- Reactive mixture with 6 levels: HNO<sub>3</sub>/HCl (1:1), HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1:1), HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (0.8:0.2), HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl/HF (0.625:0.125:0.125:0.125), HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl (0.72:0.14:0.14), HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (0.8:0.1:0.1).

This led to a completely randomized design of 24 experiments.

### 2.2.3. Closed system ultra wave

One milligram of sample was weighed in a platinum crucible and transferred into a borosilicated glass tube from which electrostatic electricity was removed prior to use. A 2 mL mixture of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1:1) was added. Two parameters were investigated:

- Heating temperature with 3 levels: 200, 230 and 250 °C.
- Plateau time: 15, 30 and 45 min.

For all the digestion procedures, digests were diluted with deionised water in 25 mL flask and finally analysed by ICP AES.

## 2.3. Validation method

Validation method followed ISO/IEC 17025:2005 [29] for linearity, specificity, intermediate precision, limits of detection and quantification. Linearity was studied following the maximal deviation acceptable (MDA) approach. Standard calibrations of 0–0.25–0.5–1–2 mg/L levels for Mo and 0–0.5–1–2–5 mg/L levels for Co were realised for eight different days. Deviations between theoretical concentrations and calculated ones using linear regression model were obtained and compared with MDA which we decided to put at 5%. This corresponds to the maximal relative measure uncertainty asserted to routine analysis.

Specificity enables to proof that analytical response is only due to the substance of interest, with no interference matrix effect. Following NF 17025, spiked solutions were analysed with 5 spikes levels distributed on standard calibration. Cobalt and Molybdenum spikes were done on a carbon nanotube sample free from these elements provided by Anton Paar. A regression line was obtained with the correlation between theoretical spiked concentrations and calculated ones. Slope confidence interval and y-intercept confidence interval obtained from this regression line were calculated. Method is specific when 1 is included in slope confidence interval (ICa) and 0 is included in y-intercept confidence interval (ICb).

Intermediate precision was evaluated by the closeness between a reference value and results obtained in intermediate precision conditions defined here as 5 days. Three levels as reference values were chosen on the linearity field and obtained by spiking a blank matrix, CNTs free from Molybdenum and Cobalt. Three replicates for each level were analysed

on 5 days. The following statistical parameters were then calculated:

$$Z_b: \text{three replicated average}$$

$$Z_{bb}: Z_b \text{ average}$$

$$S^2: \text{three replicates variance}$$

$$S_{Zb}^2: Z_b \text{ variance}$$

$$S_{\text{repet}}^2: \text{variances average}$$

$$S_B^2 = S_{Zb}^2 - (S_{\text{repet}}^2/r) \text{ with } r = 3$$

$$S_{IP} = \sqrt{(S_B^2 + S_{\text{repet}}^2)}$$

To validate intermediate precision, Eqs. (1) and (2) must be checked:

$$Z_{bb} - 2S_{IP} > \text{REF} - \text{MDA} \times \text{REF} \quad (1)$$

$$Z_{bb} - 2S_{IP} > \text{REF} + \text{MDA} \times \text{REF} \quad (2)$$

MDA is still define at 5%. Limits of detection and quantification (LD and LQ) were evaluated with calibration curve equation.

$$\text{LD} = 3S_b/a \quad (3)$$

$$\text{LQ} = 10S_b/a \quad (4)$$

S<sub>b</sub>: standard deviation of y-intercept; a: slope.

Limit of quantification must then be validated by the MDA approach in the intermediate precision conditions with a MDA fixed at 60%. Spikes at equivalent concentration to the LQ were added on the blank matrix.

## 3. Results and discussion

The first system tested was the open system designed in the laboratory and which can reach higher temperature than commercial systems. By this way clear digest solutions were obtained but more than 24 h were required. As no double-walled carbon nanotubes (DWNTS) reference material exist, results of open system were taken as a reference since no residue was present in digest solutions. Nine replicates were prepared and results are listed in Table 2.

Dispersion of cobalt results has to be noticed. However in certain coal reference material confidence interval is equivalent, this is the case for SRM 1632 c where value of Ni is 9.32 ± 0.51.

**Table 2 – Open digestion system results.**

	Co (%)	Mo (%)
	2.93	1.16
	3.03	1.20
	3.28	1.32
	3.01	1.19
	2.91	1.16
	2.82	1.13
	2.91	1.19
	3.13	1.27
	2.73	1.12
Average	2.97	1.19
Standard deviation	0.16	0.06

This method is too time consuming and this is why closed systems known for their efficiency were tested. A conventional high pressure microwave-assisted procedure was evaluated on the Ethos Touch Control. The 24 experiments of the randomized experimental design are detailed in Table 3.

A maximum of recovery was obtained in experiment 18 for Mo and in experiment 20 for Co with respectively 99.16% and 99.33%. With these experimental conditions it can be considered that an equal efficiency digestion as open system – taken as reference – was obtained but in only 1 h (45 min of microwave cycle and 15 min for cooling) instead of 24 h.

In both cases, the mixture  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  (N/S/O) was used. The mixture  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  is well known as piranha reagent, which has to be manipulated with high precautions. Hydrogen peroxide was added drop wise under fume hood. The reaction with sulphuric acid is exothermic and if precautions are not taken, projections can occur. Maximum recoveries were obtained at different temperatures for Co and Mo. It has been decided to perform further experiments with the highest one, which theoretically must corresponds to the best digestion efficiency.

As we aim to develop a method that can be safely used in laboratories for routine quantitative analysis, we decided to

**Table 3 – Experimental design. 6 reactive mixtures:  $\text{HNO}_3/\text{HCl}$  (N/C) (1/1),  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (N/S) (1/1),  $\text{HNO}_3/\text{H}_2\text{O}_2$  (N/O) (0.8/0.2),  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HCl}/\text{HF}$  (N/S/C/F) (0.125/0.125/0.125/0.625),  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HCl}$  (N/S/C) (0.1425/0.1425/0.7175),  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  (N/S/O) (0.8/0.1/0.1). 2 CNTs mass to reagent mixture volume ratios: 0.5 and 0.25. 2 temperatures: 250 and 230 °C.**

Experiment	Conditions	Cobalt		Molybdenum	
		Reference Co (%)	2.97% Recovery (%)	Reference Mo (%)	1.19% Recovery (%)
1	N/S 0.5 230	2.68	90.24	1.07	89.92
2	N/S 0.25 230	2.62	88.22	1.06	89.08
3	N/C 0.5 230	2.62	88.22	1.04	87.39
4	N/C 0.25 230	2.56	86.20	1.04	87.39
5	N/O 0.5 230	2.59	87.21	1.01	84.87
6	N/O 0.25 230	2.65	89.23	1.05	88.24
7	N/S 0.5 250	2.67	89.90	1.09	91.60
8	N/S 0.25 250	2.72	91.58	1.07	89.92
9	N/C 0.5 250	2.64	88.89	1.04	87.39
10	N/C 0.25 250	2.67	89.90	1.05	88.24
11	N/O 0.5 250	2.6	87.54	1.03	86.55
12	N/O 0.25 250	2.75	92.59	1.1	92.44
13	N/S/C/F 0.5 230	2.42	81.48	0.97	81.51
14	N/S/C/F 0.25 230	2.58	86.87	1.05	88.24
15	N/S/C/F 0.5 250	2.47	83.16	0.98	82.35
16	N/S/C/F 0.25 250	2.68	90.24	1.07	89.92
17	N/S/O 0.25 230	2.91	97.98	1.14	95.80
18	N/S/O 0.50 230	2.93	98.65	<b>1.18</b>	<b>99.16</b>
19	N/S/O 0.25 250	2.89	97.31	1.1	92.44
20	N/S/O 0.50 250	<b>2.95</b>	<b>99.33</b>	1.16	97.48
21	N/S/C 0.25 230	2.71	91.25	1.1	92.44
22	N/S/C 0.50 230	2.62	88.22	1.03	86.55
23	N/S/C 0.25 250	2.73	91.92	1.1	92.44
24	N/S/C 0.50 250	2.6	87.54	1.03	86.55

**Table 4 – Results with experiment 20 conditions for 3 different diluted  $\text{H}_2\text{O}_2$  solutions.**

$\text{H}_2\text{O}_2$ purity (%)	Cobalt Reference 2.97%				Molybdenum Reference 1.19%			
	Co (%)	Average (%)	Standard deviation (%)	Recovery (%)	Mo (%)	Average (%)	Standard deviation (%)	Recovery (%)
5	2.98	2.97	0.02	99.89	1.12	1.12	0.01	94.12
	2.97							
	2.95							
10	2.99	2.98	0.02	100.34	1.17	1.16	0.01	97.76
	2.96							
	2.99							
15	2.99	3.00	0.08	100.90	1.21	1.19	0.03	100.00
	3.08							
	2.92							

**Table 5 – Repeatability assays for H<sub>2</sub>O<sub>2</sub> at 10% in the experiment 20 conditions.**

H <sub>2</sub> O <sub>2</sub> purity	% Co	% Mo
10%	3.02	1.20
	3.01	1.17
	3.00	1.19
	3.00	1.20
	3.04	1.25
	3.03	1.18
	3.01	1.18
	3.04	1.19
	3.03	1.20
	3.03	1.19
	3.05	1.19
	3.06	1.26
3.03	1.20	
Standard deviation	0.02	0.03
Average recovery (%)	101.89	100.84

perform further experiments with more diluted hydrogen peroxide at 5, 10% and 15% instead of 30%. Results are presented in Table 4.

Reactions using these conditions were much less exothermic, even if for H<sub>2</sub>O<sub>2</sub> at 15% a beginning of effervescence was still observed. For H<sub>2</sub>O<sub>2</sub> at 10 and 15% recoveries were relatively similar to those obtained with H<sub>2</sub>O<sub>2</sub> at 30%. In Table 5 twelve replicates with the more diluted solution H<sub>2</sub>O<sub>2</sub> at 10% were prepared in order to evaluate standard deviation.

Standard deviations were very low compared to those obtained using the open system (Table 2) and recoveries were close to 100%. This method performed on Ethos microwave system lead to a total CNTs digestion (one milligram sampling) in 1 h. Safety was optimised using diluted H<sub>2</sub>O<sub>2</sub> at 10% instead of 30%. The developed method can be transferred to routine analysis taking into account precautions for analysts and a specific procedure for piranha waste collection. In order to evaluate if the use of piranha solution could be completely avoided and if a better efficiency could be obtained, a last protocol using the Ultra Wave setup was investigated.

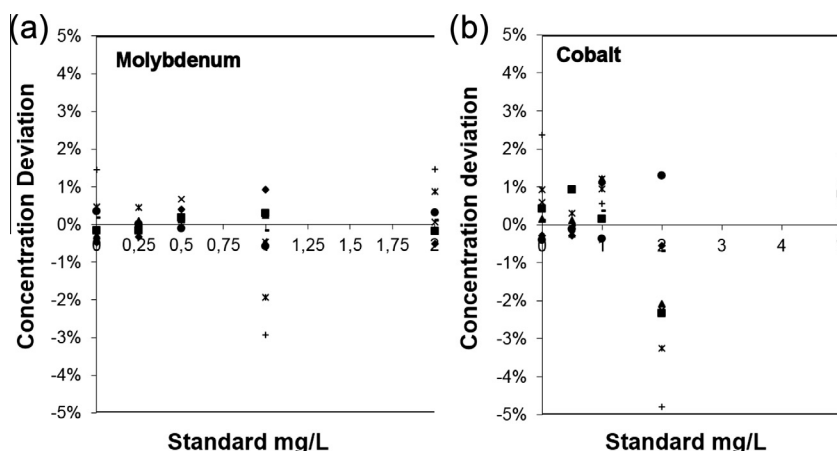
A two step heating followed by the plateau is usually recommended with the UltraWave digestion system. Firstly two assays with only nitric acid and with nitric acid/sulphuric acid mixture were performed with the following temperature program: 10 min to reach 150 °C, 15 min to reach 230 °C and a plateau of 30 min. For nitric acid assay, residues were present in important quantity whereas for the mixture the solution was almost clear. This last composition was thus retained for further experiments.

Three other experiments described in Table 6 were performed in order to optimise the temperature program. Digestion solutions were almost clear in assays B and C contrary to assay A where black residues were still observed in the flask.

For all assays recoveries were very close to 100% which means that the UltraWave system is a very efficient tool to digest carbon nanotubes without using dangerous reagents

**Table 6 – Temperature program optimisation by UltraWave.**

	A	B	C
1st step	10 min/150 °C	10 min/150 °C	10 min/150 °C
2nd step	15 min/200 °C	15 min/230 °C	15 min/250 °C
Plateau	15 min/200 °C	30 min/230 °C	45 min/250 °C
Digestion quality	–	+	+
Co	2.96%	2.91%	2.89%
Co recovery	99.6%	98.0%	97.3%
Mo	1.17%	1.18%	1.15%
Mo recovery	98.3%	99.2%	96.6%



**Fig. 2 – Concentration deviations obtained for eight different days for A molybdenum (0–0.25–0.5–1–2 mg/L) and B cobalt (0–0.5–1–2–5 mg/L).**

**Table 7 – Specificity evaluated by confidence interval of slope ICa and of y-intercept ICb of regression line obtained correlating theoretical and calculated concentrations of spiked solutions.**

	Cobalt	Molybdenum
ICa	1.060 to 0.970	1.038 to 0.977
ICb	0.085 to -0.104	0.022 to -0.035

such as the piranha mixture. In particular, protocol B is the most appropriate for simultaneous analysis of Co and Mo. A rapid, efficient and easily transferable to routine analysis method has so been developed and this method has been validated following NF 17025 [29] for linearity, specificity, intermediate precision, limits of detection and quantification.

As shown in Fig. 2, all deviations were between + and - 5% and so linearity in these level fields was validated. The method is specific (the analytical response is due only to the substance of interest, with no interference) when 1 is included in slope confidence interval (ICa) and 0 is included in y-intercept confidence interval (ICb). As shown in Table 7 developed method is specific for cobalt and molybdenum.

To validate intermediate precision, Eqs. (1) and (2) must be checked (with MDA at 5%).

Fig. 3 shows that intermediate precision was validated for cobalt and molybdenum for the three levels distributed on the linearity field. Limits of detection and quantification (LD and LQ) were evaluated with calibration regression line Eqs. (3) and (4).

Their values are reported in Table 8. Limit of quantification must be also validated by the MDA approach in the intermediate precision conditions with a MDA fixed at 60%. Spikes at equivalent concentration to the LQ were added on the blank matrix. Table 9 shows that calculated values for LQ were validated.

**Table 8 – LD and LQ estimation.**

	Co	Mo
a	1061.83	644.92
S <sub>b</sub>	8.05	1.42
LD (mg/L)	0.02	0.005
LQ (mg/L)	0.08	0.02

**Table 9 – Validation of LQ.**

Cobalt			
Z <sub>bb</sub> + 2S <sub>IP</sub>	0.0896	0.128	REF + MDA × REF
Z <sub>bb</sub> - 2S <sub>IP</sub>	0.0899	0.032	REF - MDA × REF
Molybdenum			
Z <sub>bb</sub> + 2S <sub>IP</sub>	0.0202	0.032	REF + MDA × REF
Z <sub>bb</sub> - 2S <sub>IP</sub>	0.0203	0.008	REF - MDA × REF

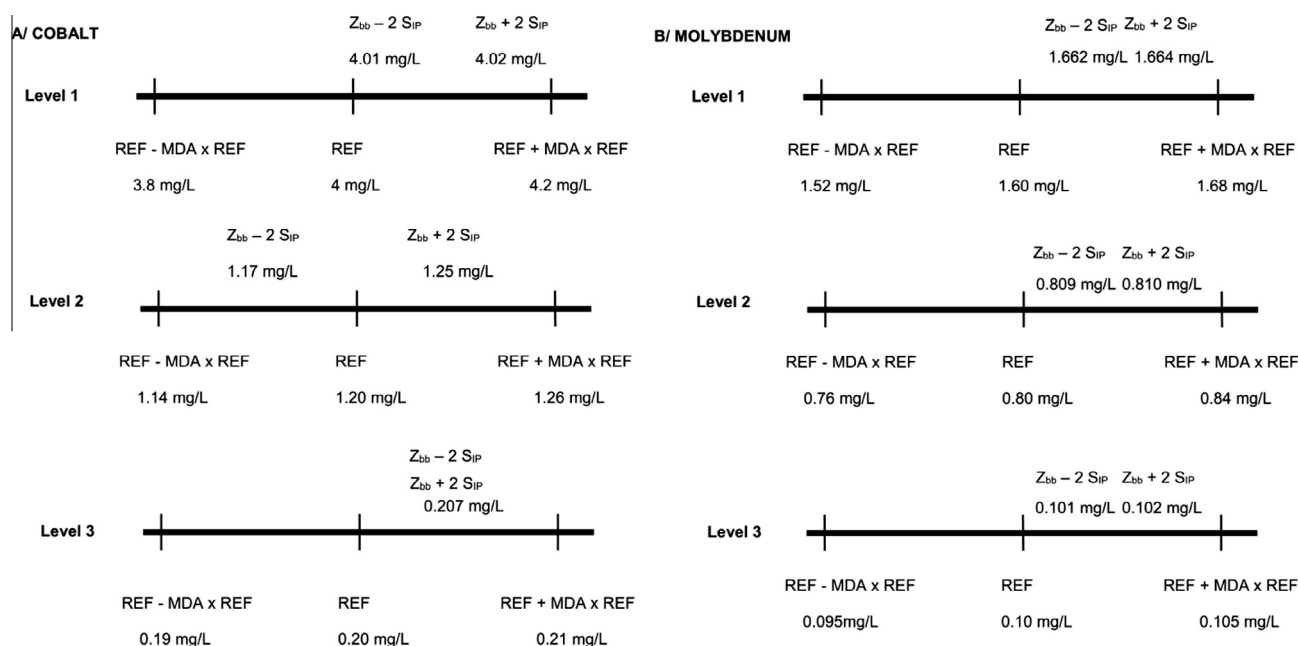
Considering the mass of one milligram, limits of quantification in the sample were respectively 0.2% for Co and 0.05% for Mo, which is acceptable for a first CNTs purity screening.

All parameters were validated for this method, which will thus be easily transferable to routine analysis.

For the sake of comparison, we sent the same CNTs samples to Anton Paar application laboratory to test MIC on a mass of our product lower than 20 mg. Assays were performed on 5 mg and recoveries of 88% for both Co and Mo and black residues were obtained in digest solutions, which is much less than this work.

#### 4. Conclusion

We developed and compared three digestion methods that all lead to clear digest solutions and recoveries close to 100%,



**Fig. 3 – Intermediate precision data for A/cobalt and B/molybdenum.**



meaning that all the analysed metals (Co, Mo in this work) were completely dissolved. However only the last one has been validated to be used as routine analysis because of digestion time limited to one hour (cooling included) and because of relatively safe conditions compared to the other microwave digestions. One of the challenges of this study was to work with only one milligram CNTs samples, which is justified by the very low amounts generally available in academic research laboratories. In the literature, only microwave induced combustion seemed to be competitive with the Ultra-Wave system, but results were obtained on much larger samples [23] (>20 mg), which is unrealistic for routine laboratory quantitative analysis. However, our work shows that microwave induced combustion may not be suitable for low amounts of CNTs samples such as the one used in this work. Finally, we have validated a rapid and complete CNTs digestion method for only one milligram sampling using Ultra Wave closed system and a mixture of nitric and sulphuric acids (one milligram of CNT, was digested with a mixture of 2 mL HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1:1) during less than one hour for a maximum temperature of 230 °C following the temperature program: 15 min for reaching 150 °C, 30 min for reaching 230 °C and a 30 min plateau at 230 °C). Due to their unique position between SWNTs and MWNTs, DWNTs are clearly representative of CNTs “in general” in terms of chemical reactivity. They are more resistant to oxidation than SWNTs and probably as resistant (if not more due to a low amount of structural defects) as most of MWNTs. In the optimised conditions described in this work, all usual catalysts for the synthesis of CNTs should be dissolved (Fe, Ni, Y, etc.). The protocol described here should thus be very general and applicable to any kind of sample of CNTs, although for very large MWNTs (with diameters up to hundreds of nm) some optimisation may be required.

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