

# TRUMAC CN, A TOOL TO EVALUATE THE QUALITY OF FERTILIZERS HUMIC COATING

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## Introduction

The term "humic substance" is a generic name given to a large number of amorphous and colloidal organic polymers formed during the decomposition of the organic matters. The humic substances can be divided into three principal fractions based on their solubility in the acids and/or the bases. The soluble fraction in the acids and the bases is called acid fulvic. It has the weakest molecular weight. That which is soluble in the bases but precipitates in the acids is the humic acid, and that which is insoluble in the acids and the bases is humin.

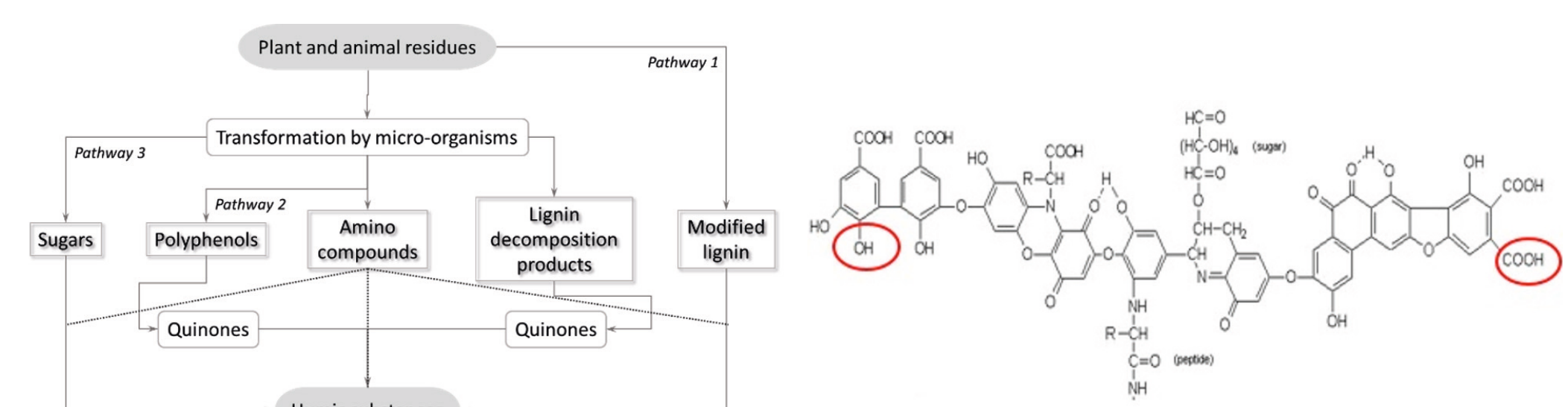


Figure 1: Pathways for humic substances formation (after Stevenson, 1994)

Figure 2: Humic substance

Humic substances are of interest in agronomy through their stimulating effect on plant growth. However, the different possible formation pathways imply heterogeneity in their composition, making their characterization difficult.

Currently, humic substances are mainly extracted from leonardite, but they represent a significant way of recovering organic waste, thus reducing the inputs necessary for agriculture, while being part of a sustainable waste recycling policy.

The protocols for characterization of humic substances can be divided into two groups: destructive protocols and non-destructive protocols. The destructive protocols are based on hydrolyses of the organic material and successive extractions under different pH conditions. The analysis will therefore consist in identifying and assaying structural units (or monomers) serving as a basis for the macromolecules constituting humic substances, identifying the functional groups of these structural units and carrying out an elemental assay (C, H, N and O). The methods implemented in these different assays are chemistry or separation and conventional identification methods (gas chromatography, [ultra] high pressure liquid chromatography, mass spectrometry, etc.). However, they do not provide information on the actual arrangement of structural units in macro-molecules. The non-destructive protocols are based on physical methods which do not necessarily require the extraction of the compounds to give a characterization (UV spectroscopy [ultraviolet], IR spectroscopy [infra-red], NMR spectroscopy [nuclear magnetic resonance]). However, they often require calibration for quantitative use, which requires strict monitoring of a destructive protocol.

## Goal of the study

To avoid long and tedious analytical techniques, we used the Trumac CN to assess the humic substance content of coated fertilizers and to assess the quality of the coating.

Having available a series of eight "humic substances" substrates (Sub-01 to Sub-08) and three mineral fertilizers in the form of granules (SUPP-01 to SUPP-03), we prepared four coated fertilizers (Eng-01 to Eng 4) on which various analyses were carried out to check the carbon contents on the coated fertilizers, both in quantity and quality of coating.

To make the coated fertilizers, two aqueous solutions mixing several of the humic substances were prepared and sprayed on the mineral fertilizers, simultaneously with a supply of additional humic substances, used as glue, in a mixer. All these steps were done in quantitative ways, thus making it possible to measure the carbon and nitrogen content at each step (on raw materials and products) and to check the quality of the preparation work.

ENG-02 and ENG-03 fertilizers are prepared from the same carrier fertilizer (SUPP-03).

## Analyses carried out

The determination of the C and N content was carried out on the raw materials, on the solutions and on the coated fertilizers (as is, grinded and granulated form, by granule). We have sought to maintain test doses in the order of 500 mg. Humic substances and aqueous solutions were analysed in duplicate and coated fertilizers were analysed in triplicate.

## Results

### Raw material analysis

Table 1 shows the percentages of carbon and nitrogen measured on the raw materials: humic substances (SUB) – coating solutions (SOL) – mineral fertilizers (SUPP). The nitrogen contents are generally very low for humic substances (from 0.01% to 3.19%), the coating solutions having nitrogen contents of less than 1%. For carbon, the contents of humic substances are much more variable (from 0.68% to more than 35%). Both solutions contain around 15% carbon.

Samples	Mean Nitrogen (%)	Standard deviation	RSD %	Mean Carbon (%)	Standard deviation	RSD %
SUB-01	0,01	0,002	15,01	8,72	0,208	2,38
SUB-02	0,03	0,011	41,49	0,68	0,009	1,31
SUB-03	0,02	0,009	49,65	7,61	0,050	0,65
SUB-04	0,22	0,000(4)	0,20	3,67	0,004	0,11
SUB-06	3,19	0,005	0,14	11,46	0,421	3,67
SUB-07	0,69	0,003	0,47	36,34	0,028	0,08
SOL-01	0,92	0,001	0,07	16,42	0,066	0,40
SOL-02	0,28	0,003	0,99	14,93	0,090	0,60
SUPP-01	24,39	0,592	2,43	3,12	0,109	3,49
SUPP-02	17,70	0,006	0,04	0,78	0,010	1,24
SUPP-03	45,96	0,153	0,33	20,74	0,066	0,32

Table 1: Determination of the C (%) and N (%) content on raw materials: humic substances (SUB) – coating solutions (SOL) – mineral fertilizers support (SUPP)

Based on the coated fertilizer preparation sheets, it was possible to calculate a theoretical carbon and nitrogen content, and to compare these contents with the contents measured directly on the fertilizer granules (Table 2). Except for the ENG-04 fertilizer which has a very low carbon content (around 2%), the average contents obtained during the analysis of the coated fertilizer granules are similar (from 101.5% to 104.6%) values obtained by calculation. The variation coefficients are less than 4%, except for carbon of the ENG-04 fertilizer (5.18%).

	ENG-01 SUPP-01	ENG-02 SUPP-03	ENG-03 SUPP-03	ENG-04 SUPP-02
Mean <sub>calc</sub>	21,69	3,81	40,89	19,48
SD <sub>calc</sub>	0,59	0,15	0,15	0,11
RSD %	2,73	3,93	0,37	0,54
Mean <sub>analy</sub>	22,69	3,90	41,51	19,87
SD <sub>analy</sub>	0,09	0,13	0,44	0,14
RSD %	0,41	3,28	1,05	0,69
Mean <sub>analy</sub> versus Mean <sub>calc</sub> (%)	104,6	102,3	101,6	102,1

Table 2: Determination of the C (%) and N (%) content on coated fertilizers

For the four coated fertilizers, the analyses carried out show that the granule preparation process meets the expected levels. The lower carbon contents, however, show more variations (ENG-04).

### Influence of grinding

Table 3 compares the measured carbon and nitrogen contents of coated fertilizers, in the form of granules, as used and in the form of ground material. These results illustrate the benefit of grinding, particularly on samples with a low carbon content.

	Nitrogen (%)		Carbon (%)	
	Granulated	Grinded	Granulated	Grinded
Mean	15,87	15,80	1,70	1,85
SD	0,03	0,02	0,14	0,01
RSD %	0,19	0,10	8,08	0,65

Table 3: Determination of the C (%) and N (%) content on coated granulated and ground fertilizers (ENG-04 SUPP-02)

### Coating quality

To assess the quality of the coating, for each fertilizer, 96 granules were randomly placed in a microplate. Among these 96 granules, 10 were taken at random and analysed individually (N % and C %).

	ENG-01 SUPP-01	ENG-02 SUPP-03	ENG-03 SUPP-03	ENG-04 SUPP-02
Mean (g)	0,0816	0,0438	0,0596	0,0524
Minimum (g)	0,0492	0,0339	0,0287	0,0300
Maximum (g)	0,1303	0,0629	0,1080	0,0907
Range (g)	0,0811	0,0290	0,0793	0,0607
Standard deviation	0,02771	0,00787	0,02459	0,02195
RSD (%)	34,0	18,0	42,7	41,9

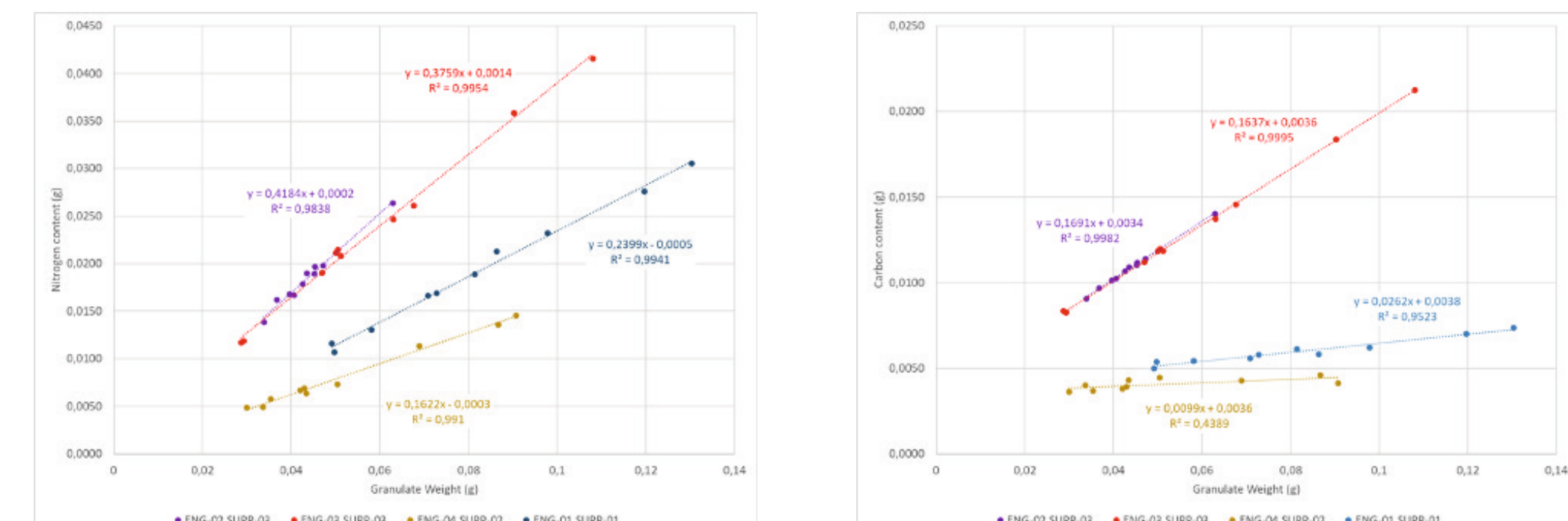
### 3. Coated fertilizers obtained : pellet size distribution

Figure 3 summarizes the distribution of the forty granules analysed. Although based on the same medium, ENG-02 and ENG-03 fertilizers have very different distributions. The essential difference between the two fertilizers is the use of two humic substances (SUB-02 and SUB-03) as a coating, in addition to the solution, for ENG-03 while only one (SUB-03) is used for ENG 02.

10 granulates of each fertilizer	ENG-01 SUPP-01		ENG-02 SUPP-03		ENG-03 SUPP-03		ENG-04 SUPP-02	
	% N	% C	% N	% C	% N	% C	% N	% C
Mean	23,22	7,83	42,26	24,92	40,30	23,49	15,64	8,73
Standard deviation	0,817	1,777	1,061	1,238	1,354	3,060	0,751	2,611
RSD (%)	3,52	22,71	2,51	4,97	3,36	13,03	4,80	29,89

Table 4: Determination of the C (%) and N (%) content on individual granulate of coated fertilizers – globalisation of results

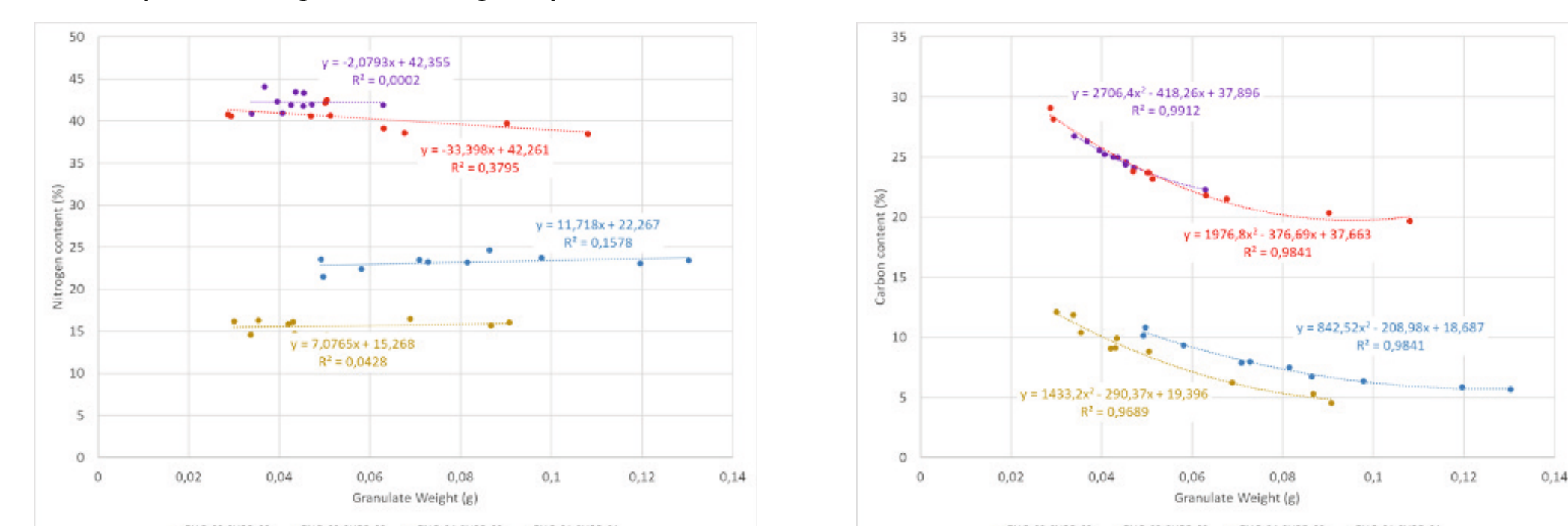
Regarding the origin of the two dosed elements, for the coated fertilizers, almost all of the nitrogen (> 99.9%) is found in the support fertilizer, which leads to a direct relationship between the mass of the granulated and the amount of nitrogen present. For carbon, SUPP-03 contains more than 95% of the carbon, while this percentage drops to around 75% for SUPP-01 and only 35% for SUPP-02.



### 4. Coated fertilizers – relationship between the amount of element present and the mass of the fertilizer granule

For coated fertilizers using this support (ENG-04), the carbon content, although very low, is much less dependent on the mass of the support granule.

Figure 4 clearly shows that the quantity of nitrogen is directly linked to the coated fertilizer test sample and that the angular coefficient of the regression line practically corresponds to the percentage of nitrogen present.



### 5. Coated fertilizers – relationship between the percentage of element and the mass of the granule analysed

This is because the nitrogen comes exclusively from the support. For carbon, for ENG-02 and ENG-03, for which more than 95% of the carbon comes from the support, the same type of direct relationship between quantity of carbon and mass of the sample is observed, although the angular coefficient of the right no longer corresponds to the percentage of carbon. As the fraction of carbon coming from the support decreases, the amount of carbon is less and less dependent on the mass of the sample, which can be explained by the low amount of coating placed on the fertilizer grains.

For nitrogen, the percentage therefore remains a constant, regardless of the mass of the sample taken (Figure 5). For carbon, this percentage decreases according to a quadratic function of the sample mass, the coefficient R<sup>2</sup> being significantly improved between linear regression and polynomial regression (Table 5).

	C <sub>coated</sub> (%) = a GW <sub>g</sub> + b	C <sub>coated</sub> (%) = a' GW <sub>g</sub> <sup>2</sup> + b' GW <sub>g</sub> + c'
ENG-01 SUPP-01	R <sup>2</sup> = 0,8791	0,9841
ENG-02 SUPP-03	0,9601	0,9912
ENG-03 SUPP-03	0,8145	0,9841
ENG-04 SUPP-02	0,9388	0,9689

Table 5: Evolution of R<sup>2</sup> between linear regression and polynomial regression

Using the masses of the individual fertilizer granules, as well as their C and N contents, the overall percentage of each element was calculated for the ten grains and compared to the percentage obtained on the ground coated fertilizer grains (Table 6).

	ENG-01	ENG-02	ENG-03	ENG-04
Powder	22,69	3,90	41,51	19,87
Globalisation of the 10 individual measurements on fertilizer granules	23,32	7,32	42,26	24,72

Table 6: Comparison of the percentages of N and C, calculated globally for the 10 coated fertilizer granules, with the percentages obtained on the coated fertilizer powder

While the match is excellent for the N contents, the more the C percentage decreases, the more it is overestimated for the individual determinations. Analysis of the raw data, and more particularly the surfaces obtained for carbon, highlighted the importance of very precise blanco calibration. In fact, the areas obtained for the carbon on the individual granules with a low C content are very small (from 350 AU to 2,000 AU) compared to the areas obtained for the carbon contained in the blanco (200 – 300 AU). A very small variation in the C content in the gas analysed will therefore have a strong impact on the percentage since the test sample is very low (of the order of a few tens of milligrams).

Blanco calibration was introduced systematically at the start of the analysis series, which made it possible to increase the difference between the areas measured for blanco and the low carbon samples (based on individual granules). When analysing a test portion of the order of 500mg, the problem does not arise because the quantity of carbon to be measured is high enough so that the corresponding surface is no longer disturbed by variations in the blanco.

	N content (%)			C content (%)			C/N ratio		
	March 28, 2018	October 30, 2018	N <sub>co</sub> /N <sub>air100</sub>	March 28, 2018	October 30, 2018	C <sub>co</sub> /C <sub>air100</sub>	March 28, 2018	October 30, 2018	R <sub>co</sub> /R <sub>air100</sub>
ENG-01	22,69	23,56	103,8	3,90	3,00	76,9	0,172	0,127	74,1
ENG-02	41,51	40,47	97,5	19,87	17,70	89,1	0,479	0,437	91,4
ENG-03	40,78	39,56	97,0	19,60	17,79	90,8	0,481	0,450	93,6
ENG-04	15,80	15,53	97,8	1,70	1,15	67,6	0,108	0,074	69,1
ENG-04 (grinded)	15,87	15,62	98,9	1,85	1,18	63,6	0,117	0,075	64,4

Table 7: Evolution of the C and N content over a period of seven months – Variation of the C/N ratio over the same period

The results obtained on the samples (coated granules) after seven months of storage in the laboratory (in the dark and away from humidity) show that the samples of fertilizers coated with humic substances can change (Table 7): if N content is relatively stable, C content, expressed in %, decreased slightly after this storage, as did the C/N ratio, parameter used in fertilization.

This decrease in carbon content could be explained by the evolution of humic substances used as coating. In fact, assuming that carbon is representative of humic substances, the ENG-02 and ENG-03 samples exhibit C losses of around 10% (for 5% of the C present in the coating). ENG-01 presents C losses of the order of 32.5% (for 65% of the C present in the coating), ENG-04 is intermediate in terms of C present in the coating (25%) and its losses in C are less than those of ENG-04 since they amount to 24%. For ENG-04 (grinded), it should be noted that it is the crushed material that was kept. The losses are greater (36.5%) than those observed for ENG-04 in granular form. The accessibility of the coating materials seems important to explain these losses. It would therefore be useful to study the evolution of humic substances during storage in order to allow manufacturers to provide a product that meets the requirements and farmers to use the right dose of fertilizer.

## Conclusion

This study sought to assess the potential of Trumac CN as a tool for monitoring the quality of the coating of humic substances in coated mineral fertilizers.

The results obtained showed that it was necessary to assess the quality of the coating of mineral fertilizers using humic substances. This assessment was based on the carbon content measured in coated fertilizers and in humic substances used for the coating. Knowing the formulation of the various components of the coated fertilizer, the quality of the preparation of the granules was validated by monitoring the dosage of nitrogen, present mainly in the granules of carrier fertilizer, and carbon. The percentage of carbon expected depending on the humic coating was verified on the final fertilizers. The results obtained show that the coating technique works very well since the C and N contents, measured on the coated fertilizers, correspond practically to 100% to the expected contents.

Analysis of the individual granules demonstrated the importance of the blanco calibration for samples with low C content. When analysing a 500mg test portion, this importance became relative: in fact, the carbon contents obtained on the coated fertilizers in the form of granules or ground corresponded to the contents calculated based on the formulations.

The manufacturer, a supplier of mineral fertilizers coated with humic substances, therefore has a rapid analyser to assess the initial quality of his product and above all, to monitor the development of this product over time. However, it is essential to work with an analyser that allows sufficiently high samples to be taken to analyse fertilizers with a very low C content, thus allowing the detection of small variations, potential signs of deterioration of the product. Indeed, the conservation of coated fertilizers for 7 months has led to the identification of carbon losses linked to the accessibility of humic matter.

Monitoring the individual quality of the coating turns out to be more difficult because the test samples (individual fertilizer granules) are very low. It would be interesting to master the determination of carbon on these granules because the study of the thickness of the coating layer could be a "quality" indicator. The modelling of the thickness calculation, however, requires knowledge of the density of the carrier fertilizer and the material used as coating, as well as the assimilation of coated granules into spheres. With the knowledge of these parameters, a model could be developed.