Tutor/s

Dra. Ana Maria De Juan Capdevila
Departament d'Enginyeria Química i Química Analítica, Universitat de Barcelona (UB)

Dr. rer. nat. habil. Michael Maiwald
Bundesanstalt für Materialforschung und -prüfung (BAM)

M.Sc. Lukas Wander, Dr. rer. nat. Andrea Paul
Bundesanstalt für Materialforschung und -prüfung (BAM)

Treball Final de Grau

Evaluation of two compact near-infrared spectrometers for the detection of microplastics in soil samples.

Evaluació de dos espectròmetres compactes d'infraroig proper per la detecció de microplàstics en mostres de sòl.

Arnau Luco Colilles

June 2019

Each time the discovery of new facts, the overthrow or extension of accepted theories, reminded us that science is never finished.

Charles Fabry

To my family, who encouraged me to keep advancing on my project when I needed most. Also to my friends, who always were interested in my work and my progress and had supported me during all this time. To Dra. Anna de Juan, who has provided all the assistance during these months.

And most especially, to all BAM group (both microplastics section and 1.4 Process Analytical Technology), that were present from the very beginning of my thesis until the last time, guiding me and advising me in order to make the best of myself in my research. With special mention to Fritz Fink (helping me in my laboratory duty), to Martin Bornemann, Klas Meyer and Simon Kern (more than just colleagues), and my supervisors, who had been helping with everything I needed, inside and outside the field of work, during my stay in Germany: Dr. Michael Maiwald, Dr. Andrea Paul and Lukas Wander. Thanks for so much!

REPORT

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1. SUMMARY

In the last years, the Process Analytical Technology (PAT) research field has become of great importance due to its connection with the industrial world. This industry related research, along with the evolutionary progress that technology has seen lately, has allowed that key analytical techniques in an industrial environment have undergone a radical development. One of these techniques has been the near-infrared spectroscopy (NIRS). This technique, currently common in "online" industrial analysis, has seen a remarkable revolution, especially since the introduction of the microelectromechanical systems technology (MEMS) in the spectroscopy field. Nowadays it is possible to find compact spectrometers no bigger than a wristwatch in the market. Although there is an unavoidable question: can these compact spectrometers actually compete against the traditional spectrometers?

In this project different calibration parameters of two compact NIR spectrometers ("Spectral Engines Oy NIR-One Sensor NM2.0", with 1550 to 1950 nm range; and "NeoSpectra Si-ware", with 1300 to 2550 nm range) were evaluated, and the obtained results were compared with a reference spectrometer ("Bruker Optik GmbH Matrix-F", with 15000 to 4000 cm^{-1} range). In order to obtain the different calibration parameters, a sequence of quality performance tests were conducted. The results obtained after the different experiments carried out with both compact spectrometers prove that their performance is more than acceptable for routine analysis.

Afterward, model samples of different microplastics in soil at different known concentration were analyzed with all three spectrometers. Chemometric models capable to identify and classify microplastics in soil were established. For this analysis five of the most used plastics worldwide were used: polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). After the Principal component analysis (PCA), it can be seen that only the NIR-One NM2.0 is capable to differentiate all types of microplastics in soil at concentrations of 1–2 %, while the NeoSpectra Si-ware is unable to identify the PET sample.

Keywords: near-infrared (NIR), compact spectrometers, microplastics identification, chemometrics.

2. RESUM

En els últims anys, la recerca en el camp de la Tecnologia Analítica de Processos (PAT) ha esdevingut molt important a causa de la seva connexió amb el món industrial. Aquesta recerca lligada a la indústria, junt amb el salt evolutiu que ha viscut la tecnologia en aquests darrers anys, ha permès que tècniques analítiques claus en el món industrial hagin sofert una evolució radical. Una d'aquestes tècniques ha estat l'espectroscòpia per infraroig proper (NIRS). Aquesta tècnica, actualment quotidiana en anàlisi industrial "online", ha patit una revolució notable, sobretot des de la introducció de la tecnologia de sistemes microelectromecànics (MEMS) al camp de l'espectroscòpia. Avui dia es poden trobar al mercat espectròmetres compactes no més grans que un rellotge de polsera. Tot i això la pregunta és inevitable: poden competir actualment aquests espectròmetres compactes amb els espectròmetres de tota la vida?

En aquest treball s'han avaluat els diferents paràmetres de calibració de dos espectròmetres compactes d'infraroig proper ("Spectral Engines Oy NIR-One Sensor NM2.0", amb rang de 1550 a 1950 nm; i "NeoSpectra Si-ware", amb rang de 1300 a 2550 nm) i els resultats obtinguts han sigut comparats amb un espectròmetre de referència ("Bruker Optik GmbH Matrix-F", amb rang de 15000 a 4000 cm^{-1}). Per a obtenir els diferents paràmetres de calibració s'ha procedit a fer un seguit de tests de rendiment de qualitat. Els resultats obtinguts dels diferents experiments realitzats amb ambdós espectròmetres compactes demostren que el seu rendiment és més que acceptable per a anàlisi rutinària.

Posteriorment, s'han analitzat amb els tres espectròmetres mencionats mostres de diferents microplàstics en sòl a diferents concentracions conegudes per tal de generar un model quimiomètric capaç d'identificar i classificar microplàstics en sòl. Per aquesta anàlisi s'han utilitzat cinc dels plàstics més usats al món actualment: polietilè (PE), polietilè tereftalat (PET), polipropilè (PP), poliestirè (PS), i clorur de polivinil (PVC). Després de l'anàlisi de components principals (PCA) es pot veure com només l'espectròmetre NIR-One NM2.0 és capaç de diferenciar els diferents tipus de microplàstics en sòl a concentracions superiors a l'1–2 %, mentre que el NeoSpectra Si-ware és incapaç d'identificar la mostra de PET.

Paraules clau: infraroig proper, espectròmetres compactes, identificació de microplàstics, quimiometria.

3. THEORETICAL BACKGROUND

3.1. NIR SPECTROSCOPY

NIR spectroscopy has been used as an analytical tool since the beginning of the second half of the 20th century thanks to the technical revolution providing computer-operated compact spectrometers with fiber optics and the development of advanced chemometric tools, like Partial Least Squares Regression (PLSR).

The NIRS technique uses the near-infrared region of the electromagnetic spectrum (between visible and mid-infrared regions, 750/800 nm to 2500 nm), where the overtones and combination bands of vibrational bands are detected. This way, for being overtones, in the NIR region the observed transitions have low absorption coefficients as a result of the quantum mechanical forbidden transition to higher vibrational states.

For the NIR spectrometry analysis can be measured two different magnitudes: transmittance or reflectance. The resulting spectra are strongly related due to the fact that reflectance indicates the portion of light the sample reflects compared to the amount of incident light, while transmittance is related to the light portion the sample can absorb over the incoming light. Whereas reflectance is a surface phenomenon transmittance is a bulk phenomenon.

Nowadays NIRS is widely used for compound quantification with a great presence of CH-, NH- and OH- groups; as in the agricultural–, food– and the oil industry [1], and is gaining ground in the PAT field. The application of the MEMS technology (Micro-Electro-Mechanical Systems) in spectroscopy allows the size of the spectroscopic sensors be reduced to a microchip and so, reducing the size of the spectrometer and lowering their prices, it could become even more important.

3.1.1. Instrumentation

For the NIRS analysis, the sample must be illuminated with a specific wavelength light (between 700 and 2500 nm). To obtain that a tungsten lamp can be used as a light source, like the one used in UV-visible analysis.

The cells used when measuring absorbance as a magnitude are made with quartz of low hydrogen content or fused silica because they had no absorbance bands in the near-infrared range.

The detectors are usually InGaAs, InSb and PbS photoconductors,.

3.1.2. Interferometers

Although there are spectrometers that use dispersive elements, since 1950s NIR spectrometry is commonly performed using a measurement technique called Fourier-transform (FT-NIR) [2]. This implies that the final absorbance/reflectance spectrum is the product of the Fourier-transform analysis of an interferogram.

To obtain this interferogram it is necessary to have an interferometer in the infrared spectrometer. An interferometer is an optical element that, using the superposition of a light beam that has been split in two and have travelled a slightly different distance, allows creating an interference pattern depending on whether the interference after the superposition is a constructive or a destructive one.

There are several types of interferometers according to the method of splitting they use.

3.1.2.1. Michelson interferometer

The Michelson interferometer is the most common interferometer used in these techniques. This interferometer (developed by Albert Abraham Michelson in the late of 19th century) has a beam splitter as a dividing element, and the difference of path between the light beams is determined by the shift of a mobile mirror respect a fixed one.

3.1.2.2. Fabry-Perot interferometer

The Fabry-Perot interferometer or etalon (developed by Charles Fabry and Alfred Perot in 1899) uses a plate with two highly reflecting surfaces with some transmittivity that allow the light beam to be divided and form interferences depending on the distance between both reflecting surfaces and the times the light beam is reflected between them.

Because this interferometer has no mobile elements, it is usually more robust than the sensors containing a Michelson interferometer [3].

3.2. MICROPLASTICS

Nowadays the plastic contamination of the environment is one of the hot topics worldwide that the humankind is facing [4–6]. And with this plastic issue another problem, unknown to most of the population, has come out: microplastics (MP).

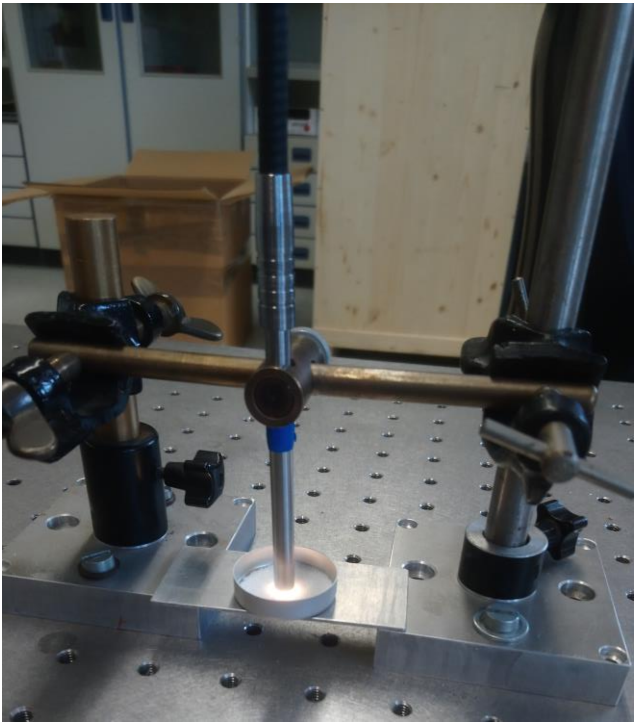


Figure 1: PS pellet being analysed by NIRS.

Microplastics are plastic polymer particles of small size (below 5 mm) [7], mostly not visible to the human eye, that are abundant in water, soil and air at unknown quantities. MP can be easily incorporated or ingested by animals and humans, and with yet unknown effects on long term for those organisms.

According to their origin they can be sorted in two different groups:

- Primary microplastics: those that had been produced as such, basically used in beauty care products (creams, makeup, ...)

- Secondary microplastics: are the result of decomposition and degradation of bigger plastics and comprise the major number of plastic debris. This decomposition can be due to mechanical erosion or photodegradation (with sun exposition). These processes causes visible pieces of plastic be fragmented and evolve into microplastics, small enough to make unable to locate them without using special equipment.

Actually, most of the techniques used for analysing microplastics are based on micro-spectroscopic techniques such as Raman or FTIR. Recently, succesful approaches using TED-GC-MS were established [8]. The problem with those methods is the expensive equipment needed. Instead, the use of NIRS could be an important step to lower the costs of MP analysis due to the lower price of the instrumentation required.

4. OBJECTIVES

The four main objectives and subgoals of this work are the following:

a) Characterize and quantify the different calibration parameters of both two compact near-infrared spectrometers
    - Stabilization of signal depending on time/temperature
    - Signal to noise ratio
    - Linearity
    - Precision of the instruments
    - Trueness of the instruments

b) Compare the calibration parameters of both compact spectrometers with the values of a reference NIR spectrometer

c) Check the feasibility of both compact spectrometers in the microplastic analysis

d) Being able to carry out an identification and classification model of microplastics in soil with both two compact spectrometers
    - Establish a qualitative model (identification by classification)

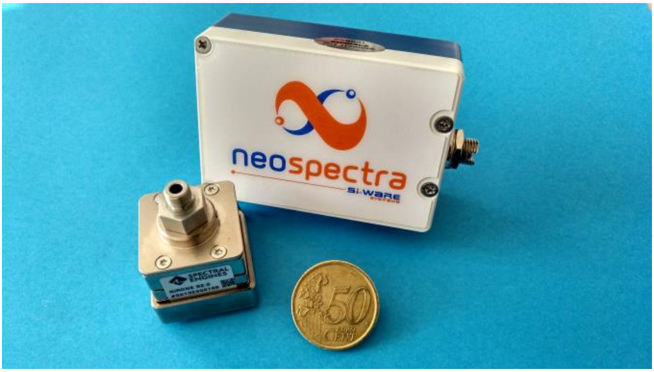


Figure 2: Spectral Engines Oy NIR-One Sensor NM2.0 and NeoSpectra Si-ware.

5. EXPERIMENTAL SECTION

The experimental work was divided into two big blocks in order to facilitate the data collection. It was split in the compact spectrometers evaluation section and the creation of an identification model of MP in soil. The spectrometers used in both sections were the Spectral Engines Oy NIR-One Sensor NM2.0 (NIR-One NM2.0), which uses a Fabry-Perot interferometer, and the NeoSpectra Si-ware, with a Michelson interferometer. As reference spectrometer it was used the Bruker Optik GmbH Matrix-F (Matrix-F), which also has a Michelson interferometer.

5.1. EVALUATION OF COMPACT NIR SPECTROMETERS

The evaluation of the calibration parameters of both compact spectrometers was made with the following characteristics:

- NIR-One NM2.0: three different configurations (internal light source with 10 % intensity and 100 % intensity and external light source) were used. The software parameters used (except in instrument stability) for spectrum were averaging 13 full scans and 676 points average in each wavelenght, 5 nm resolution and absorbance as measured magnitude.

- NeoSpectra Si-ware: the only possible configuration (external light source) was used. The software parameters used in each spectrum were 40 seconds scan time (except in time development), 8 nm resolution and the magnitude measured was the reflectance.

5.1.1. Instrument stability

In order to know the time needed for the spectrometers to give a stable and constant signal the following experiment was performed.

Firstly, the external light source was switched on for 30 minutes in order to obtain a constant light beam (recommended for the provider = 20 minutes, not applicable for NIR-One NM2.0 internal light source configuration). Then, the spectrometer was connected to the system. Five measurements of a PS pellet were recorded each 5 minutes during 1 hour. In the NIR-One NM2.0 spectrometer the temperature was also recorded. It was repeated three times for configuration.

The software parameters in the NIR-One NM2.0 were 100 points avg., 10 scan avg., 5 nm resolution. In NeoSpectra Si-ware case, the scan time used was 2 seconds.

5.1.2. Noise (S/N ratio)

In order to measure the S/N ratio, two different experiments were performed:

- Maximum signal: the signal given by a reference Spectralon with 99% reflectivity (according to provider) was registered 5 times. In NIR-One NM2.0 the software parameters (point and scan avg.) were optimized to search those giving the highest S/N ratio value (676 and 13 respectively).
- PS signal: a PS pellet spectrum was recorded 5 times. In this experiment was also checked the effect the resolution has with the noise, doing the experiment four times with the NIR-One NM2.0 (2, 5, 10, 20 nm resolution) and the available resolutions with the NeoSpectra Si-ware (8, 16 nm).

5.1.3. Linearity

In order to measure the linearity with the best possible reproducibility, different pills of PE powder free of additives with KBr pills at mass fractions between 0 and 25 % were prepared, and the signal obtained with them was compared with the one obtained with the reference spectrometer (Matrix-F). The measurements were realized in a way that the distance between the optical probe and the sample, as well as the incidence angle, was always the same (all the equipment was fixed on an optical table in order to avoid possible movements and changes).

5.1.4. Precision

In order to measure both wavelength and absorbance/reflectance precision of the compact spectrometers, a short term and intermediate precision study were made, measuring 5 replicates of a PS free of additive pill each 5 minutes during 30 minutes on 3 different days.

5.1.5. Trueness

Finally, in order to measure the wavelength trueness, 5 replicates of PE powder free of additives were registered, and the bands were compared with the theoretical ones [9].

For measuring the absorbance/reflectance trueness, the spectra of Kr and Hg/Ne emission lamps were registered, and the values were compared with the theoretical intensities [10].

5.2. MICROPLASTICS IDENTIFICATION MODEL

5.2.1. Materials

In order to calibrate chemometric model for microplastics identification 5 different types of cryo-milled plastics were used: polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). Those were the ones chosen to work with because they represent almost the 70 % of the global produced plastics (data from 2017) [11]. Moreover, artificially aged polypropylene (PPa) by action of elevated oxygen partial pressure and UV radiation [12] was used. Both, the microplastics and the standard soil (LUFA2.3 type) used were the same kind that was used in Paul et al. (2019) [13]. All materials were sieved and had a particle size below 125 µm.

5.2.2 Sample preparation

Six different concentration mixtures were prepared with each polymer in soil (0.5, 1, 2, 3, 4, 5 % w/w), with a total weight of 1 gram per sample, making an amount of 36 different mixtures of one single polymer with soil. For more detailed information, consult **Table 1**. All samples were kept under atmospherical conditions. Each sample was mixed in order to obtain a homogeneous mixture.

Polymer type	w(0,5 %)/wt-%	w(1 %)/wt-%	w(2 %)/wt-%	w(3 %)/wt-%	w(4 %)/wt-%	w(5 %)/wt-%
PE	0.442 (a)	1,080	2,001 (a)	2,881	4,006	5,003 (a)
PET	0,498 (a)	0,995	1,908	2,957	3,956	4,467
PP	0,569 (a)	1,062	2,015	2,982	4,023	4,783
PPa	0,549 (a)	1,139 (a)	1,946 (a)	2,971	3,997	4,680
PS	0,484 (a)	1,002	2,329	3,011	4,039	5,038
PVC	0,503 (a)	1,103 (a)	2,007	3,007 (a)	3,939 (a)	5,047

(a) These mixtures were used in Paul et al. article (2019) [13].
All mixtures were weighed under the same conditions with the same analytical balance.
The analytical balance used had a precision of 0,01 mg.

Table 1: Real mass fraction in wt-% of microplastics in soil for the different mixtures.

5.2.3. Spectral parameters

The measurement parameters used for each spectrometer were the following ones:

- NIR-One NM2.0: the configuration used was only with the external light source. The software parameters were the same used for the spectrometer evaluation (averaging 676 points for each wavelenght and 13 full scans for spectrum). The magnitude recorded was the absorbance. 5 replicates for each sample were made, removing and placing the optical probe after each measurement in order to avoid possible representation problems.

- NeoSpectra Si-ware: it was used the only possible configuration (external light source). The software parameters used were 40 seconds scan time at 8 nm resolution. The magnitude registered was reflectance. It was recorded 5 replicates per sample, removing and inserting the optical probe again into the sample after each replicate (also for a more representative obtention of data).

- Matrix-F: it was used the reflectance optical probe (REFLECTOR-NIR-12S-300/090724/1), gaining the data in absorbance units and making 5 replicates for each sample (withdrawing and placing again the probe between measures). The spectral resolution was adjusted at 8 cm^{-1} and 64 scans were averaged for each spectrum.

In addition to the microplastics mixtures, 5 replicates of pure LUFA2.3 soil were also measured with each spectrometer.

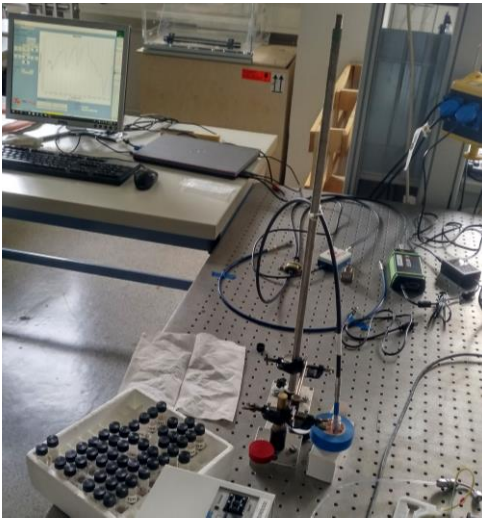


Figure 3: MP in soil mixtures analysis with NIR-One NM2.0 and NeoSpectra Si-ware spectrometers.

6. DISCUSSION OF SPECTROMETERS EVALUATION

6.1. INSTRUMENT STABILITY

With the data obtained from the experiments, a representation of the temperature variation (in 5 minute steps) versus time elapsed was made, and the results between all 3 replicates with each spectrometer configuration were compared. The stabilization was considered complete showing less than 0.1 % of signal change.

In the internal light source configurations of NIR-One NM2.0 the signal stabilized after 30 minutes, while in the external light configuration this stabilization occurred in 10 minutes. With the NeoSpectra Si-ware needed 25 minutes to stabilize the signal.

With the values found both miniaturized spectrometers behave very comparably to classical instruments.

6.2. NOISE (S/N RATIO)

Regarding the S/N ratio, the results obtained in both experiments (averaging replicates) were:

- Maximum signal: for obtaining a value of S/N the average of the obtained signal in 1550–1950 nm spectral range was divided by the standard deviation. The value of the S/N ratio for the NIR-One NM2.0 100 % intensity of the internal light source was 15600, while with 10 % intensity decreased to 2000, while using the external light source the instrument reading reached 13900. For the NeoSpectra Si-ware the value was much lower with 1200. The reference spectrometer gave a 6500 value. So, the NeoSpectra Si-ware performance is not proper. The maximum S/N ratio with NIR-One NM2.0 was reached averaging 13 scans and 676 points.

- PS signal: in that experiment the signal was the difference between the PS peak (1690 nm) and the mean between 1550 and 1560 nm (lower signal region), and was divided by the standard deviation of that region. The values obtained were 5500 for NIR-One NM.20 (“external light configuration”), 500 for NeoSpectra Si-ware and 12300 for the Matrix-F. This results confirm what stated in the previous test. It could also be seen how the S/N ratio increases while decreasing the spectrometer resolution. This effect is well known and reoprted in Unser et al. 1987 [14].

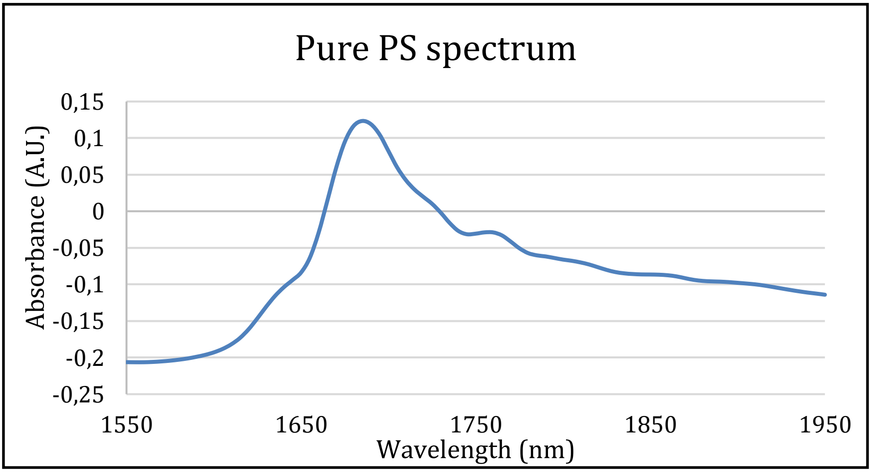


Figure 4: Pure PS NIR spectrum between 1550 nm and 1950 nm recorded with NIR-One NM2.0 spectrometer.

6.3. LINEARITY

In order to know if the spectrometers followed a linear pattern compared to the reference spectrometer, a representation of the absorbance values of three peaks of PE in 1550–1950 nm range (1730, 1765, 1820 nm) taken with the compact spectrometers against the values obtained with the reference spectrometer was made. It can be seen that the loss of linearity appeared at PE amounts over 20 %. Therefore, between 0.5 and 5 % (range were the microplastics in soil study was made) the compact spectrometers worked successfully.

The Pearson correlation coefficient between the NIR-One NM2.0 and the Matrix-F and the NeoSpectra Si-ware and the Matrix-F at 1730, 1765, and 1820 nm peaks were of 0.94 for both NIR-One NM2.0 and NeoSpectra Si-ware, indicating a good correlation between signals.

6.4. PRECISION

For the precision study, an average of the standard deviation of 1690 and 1760 nm PS peaks of respective replicates (short or intermediate term) was done to obtain the values.

On one hand, there was no variation in the peak position neither short nor intermediate term, indicating a high WL precision. On the other hand, the absorbance precision was not that accurate. In the short term the precision was good enough (values in the order of 0.1 %, except the NIR-One NM2.0 external light source configuration, with 0.01 % precision), but in terms of intermediate precision these values increased to 5.5 %.

6.5. TRUENESS

Finally, regarding the wavelength trueness, a comparison between the average values obtained with the compact spectrometers of PE 1731 nm and 1765 nm peaks with the theoretical values [9] showed that there was no variation between the peak position. Regarding the absorbance trueness, it was not possible to check that parameter due to the high presence of spectral lines of Kr and Hg/Ne in the studied range (1550–1950 nm) [10].

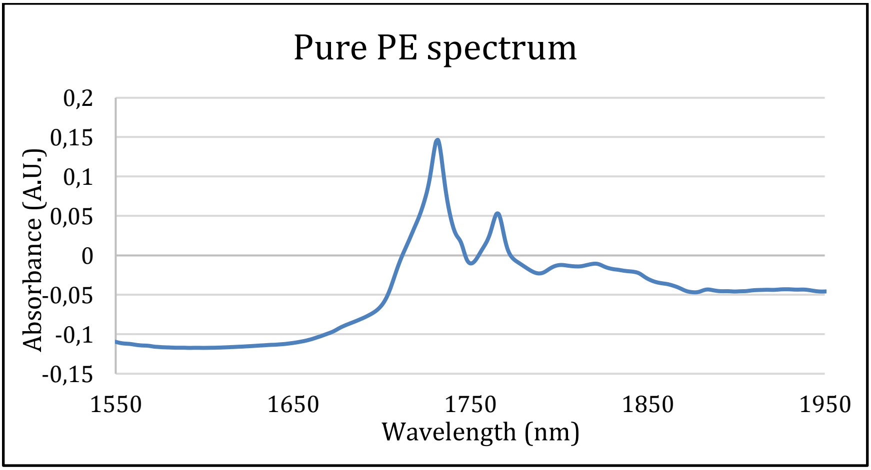


Figure 5: Pure PE NIR spectrum between 1550 nm and 1950 nm recorded with Martix-F spectrometer.

In order to see a comparison of all specifications between the spectrometers (both compact ones and the reference one), consult **Table 2**.

Entrance	Spec.	NeoSpectra Si-ware	NIR-One NM2.0 100%[(a)]	NIR-One NM2.0 10%[(a)]	NIR-One NM2.0[(b)]	Bruker Matrix-F
1	Inst.stab.	25 min.	30 min.	30 min.	10 min.	–(c)
2	S/N (max.)	1200	15600	2000	13900	6500
3	S/N (PS)	500	5300	1000	5500	12300
4	Linearity	0,9351(d) 0,9394(e) 0,9433(f)	–(c)	–(c)	0,9416(d) 0,9394(e) 0,9419(f)	–(c)
5	WL presicion	0 nm (g) 0 nm (h)	0 nm (g) 0 nm (h)	1 nm (g) 1,5 nm (h)	0 nm (g) 0 nm (h)	–(c)
6	Abs. precision	0.1 % (g) 5.5 % (h)	0.1 % (g) 0.5 % (h)	0.1 % (g) 0.2 % (h)	0.01 % (g) 5.5 % (h)	–(c)
7	WL trueness	0 nm	–(c)	–(c)	0 nm	–(c)

(a) Performed with NIR-One NM2.0 with internal light source.
(b) Performed with NIR-On2 NM2.0 with external light source.
(c) The missing values are because they have not been checked.
(d) Pearson correlation coefficient at 1730 nm absorption peak of PE.
(e) Pearson correlation coefficient at 1765 nm absorption peak of PE.
(f) Pearson correlation coefficient at 1820 nm absorption peak of PE.
(g) The value concern to the short term precision study.
(h) The value concern to the intermediate term precision study.

Table 2: Comparison between the spectrometers specifications at their different configurations. This table is a review of all parameters that were tested in the compact NIR spectrometers (NIR-One NM2.0 and NeoSpectra Si-ware) and the reference NIR spectrometer (Matrix-F).

7. DISCUSSION OF MICROPLASTICS MODEL

7.1. DATA PREPARATION

After collection of spectra from the different samples and the pure LUFA2.3 soil, the spectral data were processed by the software “The Unscrambler Xv.10.5.1 (CAMO software, Oslo, Norway)” In general the spectral range 1550 and 1950 nm wavelength was evaluated. The data pretreatment made was a standard normal variate transformation (SNV) followed by a Savitzky Golay 2nd order derivative with 5 spectral smoothing points to perform baseline correction. A total number of thirty-seven samples were measured.

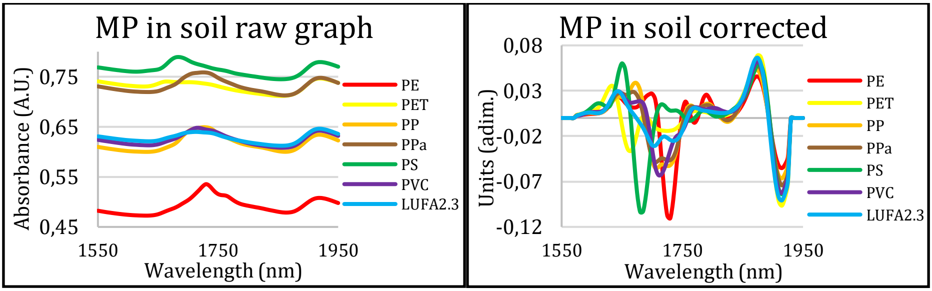


Figure 6: Spectra of all types of samples measured with NIR-One NM2.0 before and after the baseline correction.

7.2. PCA ANALYSIS AND ANALYTICAL MODEL

After the data pretreatment, a PCA was performed with mean centered data using cross validation and the Nonlinear Iterative Partial Least Squares algorithm (NIPALS) [15]. For each spectrometer an individual data analysis was performed.

PCA is an exploratory method of multivariate data analysis that allows to visualize the information of a data table in two graphs (scores and loadings). These graphs show the most relevant information of the samples (scores) and of the variables (loadings).

The obtained results after building the PCA model were that both reference and NIR-One NM2.0 spectrometers were able to build a classification and identification of microplastics in soil model, while the obtained PCA model with the NeoSpectra Si-ware differed from the others:

- NIR-One NM2.0: the 3 first PCs represent 90 % of the information. It was not possible to differentiate PP from PPa. It is possible to identify the PE, PS, and PVC with the first 2 PCs, but it is necessary to use PC-3 in order to identify PET (**Figure 7**).

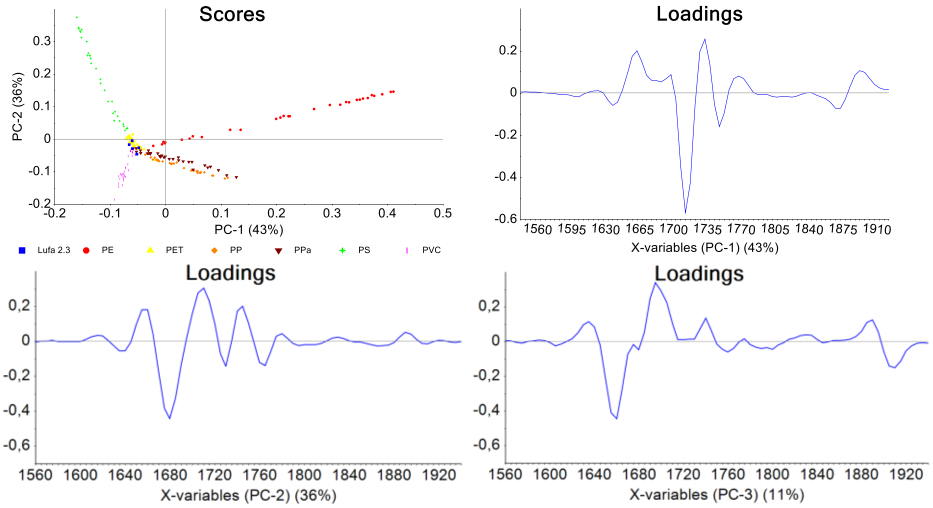
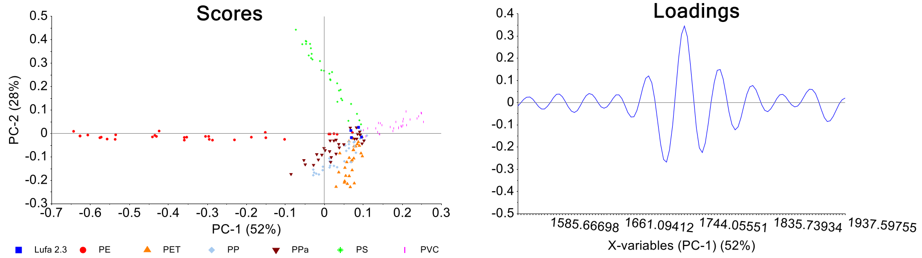


Figure 7: Scores (PC-1 and PC-2) and Loadings (PC-1, PC-2, PC-3) plots of MP in soil mixtures with NIR-One NM2.0.

- NeoSpectra Si-ware: the first three PCs contain 88 % of the spectral information. It is not possible to differentiate the PP from the PPa and the PET. Using the first 2 PCs it is possible to identify PE and PS, and the PVC can be identified using the PC-3 (**Figure 8**).



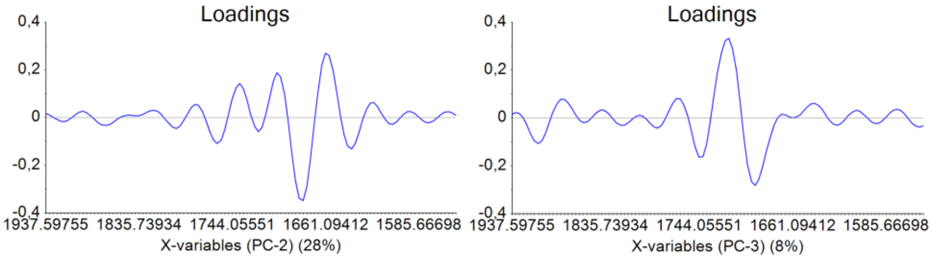


Figure 8: Scores (PC-1 and PC-2) and Loadings (PC-1, PC-2, PC-3) plots of MP in soil with NeoSpectra Si-ware.

- Matrix-F: the first 3 PCs represent the 94 % of the information. It was not possible to separate the PP from the PPa. With the first 2 PCs it can be identified the PE and the PVC, while the PET and PS can be distinguished with the PC-3 (**Figure 9**).

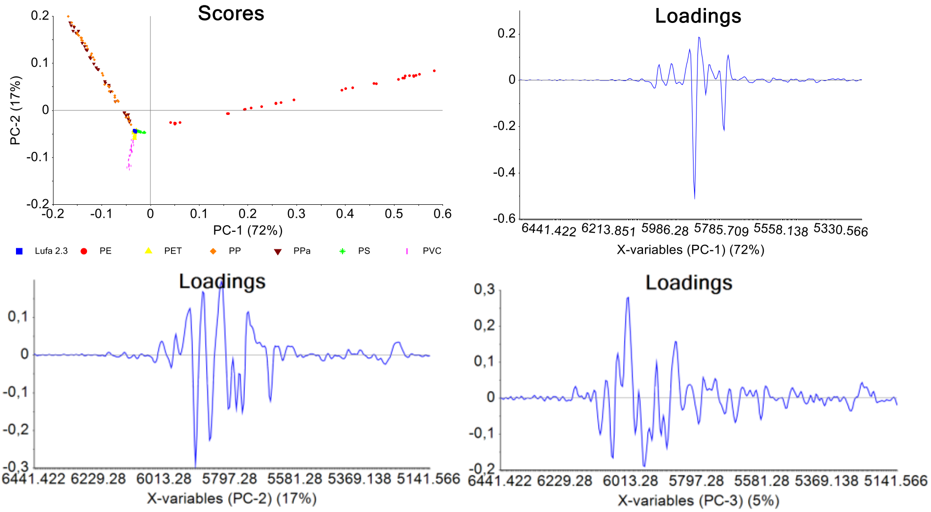


Figure 9: Scores (PC-1 and PC-2) and Loadings (PC-1, PC-2, Pc-3) plots of MP in soil samples with Matrix-F.

Figures 7, 8 and 9 shows the scores and loading plots obtained form data recorded with the 3 spectrometers. Every point in a score plot represents a spectrum of a soil sample with a particular microplastic mixed.

In all three scores plots it can be seen the LUFA2.3 pure soil where all different polymer samples converge. This is what was expected because it could be interpreted as a mixture with a mass fraction of polymer of 0 %.

It can also be seen how the points within a polymer group are distributed in a linear way. This fact is related to the use of different amounts of polymer inside the same microplastic group.

Otherwise, it can be seen how the points distribution in the Matrix-F score plot is much more defined in lines than the NIR-One NM2.0 or the NeoSpectra Si-ware. This could be related to the accuracy of the spectrometers (the linear regression precision increases with it). However, NIR-One NM2.0 shows a much better performance than NeoSpectra Si-ware in terms of precision.

8. CONCLUSIONS

The objectives proposed at the beginning of the project were mostly achieved, and after the analysis done to the two compact spectrometers and the following microplastics in soil sample analysis, it may be concluded that:

a) It was possible to quantify all the calibration parameters in both compact NIR spectrometers except of the absorbance trueness due to the impossibility to compare the spectra obtained from the Kr and Hg/Ne lamps with their theoretical spectral lines. It should be pointed out the fact that for most of the calibration parameters (signal stabilization, S/N and absorbance precision) the NIR-One NM2.0 was superior to the NeoSpectra Si-ware.

b) The different calibration parameters had been successfully compared with the reference NIR spectrometer (Matrix-F). It has been observed that their performance is more than acceptable.

c) Both compact spectrometers can be used for MP analysis due to the presence of typical polymer absorption bands within the wavelength ranges the NIR-One NM2.0 and the NeoSpectra Si-ware are able to detect.

d) Finally, regarding the design of an identification and classification model of microplastics in soil, it can be said that:
    - With the NIR-One NM2.0 a valid identification model for all types of microplastics worked on the project and LUFA2.3 soil has been built.
    - With the NeoSpectra Si-ware the model designed was only able to detect PE, PS and PVC.

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10. ACRONYMS

BAM = Bundesanstalt für Materialforschung und -prüfung (“Federal Institute for Materials Research and Testing”)

FT(IR) = Fourier transform (infrared)

GmbH = Gesellschaft mit beschränkter Haftung (“company with limited liability”)

LUFA = Landwirtschaftliche Untersuchungs- und Forschungsanstalt (“Agricultural Research and Research Institute”)

MP = microplastics

NIPALS = Nonlinear Iterative Partial Least Squares

NIR(S) = near-infrared (spectroscopy)

PAT = Process Analytical Technology

PC = Principal Component

PCA = Principal Component Analysis

PE = polyethylene

PET = polyethylene terephthalate

PP = polypropylene

PPa = aged polypropylene

PS = polystyrene

PVC = polyvinyl chloride

S/N = signal to noise

SNV = standard normal variate

TED-GC-MS = thermal extraction desorption gas chromatography mass spectrometry

UV = ultraviolet

w/w = weight by weight