Determination of total phenolic compounds in compost by infrared spectroscopy

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M.M. Cascant [a], M. Sisouane [b], S. Tahiri [b], M. EL Krati [b], M.L. Cervera [a], S. Garrigues [a,*], M. de la Guardia [a]

[a] Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner Street, Research Building, 46100 Burjassot, Valencia, Spain
[b] Laboratory of Water and Environment, Department of Chemistry, Chouaïb Doukkali University, Faculty of Sciences El Jadida, Morocco

ABSTRACT

Middle and near infrared (MIR and NIR) were applied to determine the total phenolic compounds (TPC) content in compost samples based on models built by using partial least squares (PLS) regression. The multiplicative scatter correction, standard normal variate and first derivative were employed as spectra pretreatment, and the number of latent variable were optimized by leave-one-out cross-validation. The performance of PLS-ATR-MIR and PLS-DR-NIR models was evaluated according to root mean square error of cross validation and prediction (RMSECV and RMSEP), the coefficient of determination for prediction (R^2_{pred}) and residual predictive deviation (RPD) being obtained for this latter values of 5.83 and 8.26 for MIR and NIR, respectively.

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1. Introduction

Phenolic compounds are widely distributed in the nature. They are mostly derived from various agricultural and industrial activities, including waste discharge from wood preservatives, coking, textiles, plastics, dyes, paper, herbicides industries and the partial degradation of phenoxy contaminants in remediation processes [1]. Palm et al. (2001) considered the concentration of phenolic compounds as a good parameter to manage the organic matter amendment in agriculture [2]. Composting is a bioremediation technique that offers the advantage of degrading the organic wastes and provides suitable fertilizers for soils. Through mineralization and humification, the organic wastes can be transformed in a humic acid rich substance that can offer plant nutrients. The compost process reduces the volume of the final product and decreased gradually the concentration of phenolic compounds [3]. The contaminants in the waste are degraded during composting, and the final product could be used as a soil amendment [4]. Several researches in literature reported the level of phenolic compounds as a conventional parameter of compost quality, and also as an indication about the stability of the product which is related to low levels whereas the high concentration of phenols evidences their instability [3].

The concentration of total phenolic compounds (TPC) in vegetables and in biowastes is frequently determined by using classical chemical methods like titration including a previous extraction step. These using methods are accurate but they need a big amount of reagents, skilled labor and time for analysis. Therefore, a rapid and simple alternative is required.

Infrared spectroscopy in both, near (NIR) and middle (MIR) regions offers non-destructive, fast and relatively cheap possibilities for qualitative and quantitative analysis of different compounds in food and environmental samples, being thus employed for the determination of phenolic compounds in different vegetal materials [5–8]. Attenuated total reflectance (ATR) MIR spectrum provides information about the frequencies of fundamental molecular vibrations and generally exhibits sharp absorption bands and distinct spectral [5]. On the other hand NIR included the part of the electromagnetic spectrum comprised between 14,000 and 4000 cm^{-1}, related with overtones and combination of the fundamental vibrations of C–H, O–H and N–H bonds in organic molecules [7]. So, both infrared methodologies could be complementary to evaluate the presence of molecular compounds in samples of different nature.

However, in our knowledge, there is no reported research work to determine the TPC in compost by NIR or MIR and thus, the main objective of this study has been the development of a fast, non destructive and simple method for the direct determination of TPC in compost samples based on the built of partial least square (PLS) models from samples analyzed by the Folin-Ciocalteu reference method.

2. Experimental

2.1. Chemical reagents

Pure methanol HPLC grade (99.99% purity) from Scharlau (Barcelona, Spain) was used for the extraction of phenolic compounds; gallic acid (3.4.5-trihydroxybenzonic acid) was used as reference compound to build the calibration by using Folin-Ciocalteu phenol reagent from Scharlau (Barcelona, Spain) and sodium carbonate from Guinama (Valencia, Spain) was employed for pH adjustment before measurement.

2.2. Instruments

Fourier transform-NIR spectra of all samples were obtained in the diffuse reflectance (DR) mode using a Multipurpose Analyzer (MPA) from Bruker (Bremen, Germany), equipped with an integrating sphere, a quartz beam splitter, and PbS detector.

MIR spectra were obtained by using Fourier transform middle infrared, model Tensor 27 from Bruker equipped with a DLaTGS detector. Sample spectra were measured by ATR mode using a DuraSampleIR accessory for solids from Smiths Detection Inc. (Warrington, UK) with three-reflection diamond/ZnSe DuraDisk plate.

An Hewlett Packard 8452A diode array spectrophotometer (Palo Alto, USA) was employed to perform the determination of TPC content by the Folin-Ciocalteu colorimetric method.

2.3. Samples

95 Samples of compost, obtained from three different classes sources were evaluated through this study. Samples cover a wide range of TPC from 0.07 to 4.83 mg of gallic acid equivalent per gram of dry weight (mg GAE g^{-1} DW). The aforementioned samples were originated from processes of composting and co-composting mixtures of: (i) sewage sludge, (ii) municipal solid waste and, (iii) various vegetable biowastes; such as sawdust, straw, provence cane, bagasse from sugarcane, palm bark, horse manure, etc. Some of these composts have been studied in deep in our laboratory [9] and other ones are under research. All samples of compost employed were obtained by aerobic fermentation (composting) by using laboratory-scale experiment in laboratory.

The three main classes of compost evaluated in this study include: (i) compost original from mineral mature (Cm=9 samples); (ii) maturity organic compost (Co=68 samples), and (iii) vegetable origin immature compost (Cv=18 samples), all of them representing different stages of the composting process. All samples were analyzed by the reference method and IR spectra recorderd without any chemical sample treatment.

2.4. Reference method for total phenolic compounds determination

The determination of TPC was performed according to the Folin-Ciocalteu colorimetric method following the previously published procedure [10]. The extracts of all samples were obtained by magnetic stirring of 1 g dry powder sample with 10 ml pure methanol for 30 min. Extracts were kept for 24 h at 4 °C and separated by centrifugation using a Digicen 20 centrifuge from Ortoalresa (Madrid, Spain) working at 3000 rpm for 10 min. The supernatants were stored at 4 °C until analysis. A volume of diluted sample extract was added to 0.5 ml of distilled water and 0.125 ml of the Folin-Ciocalteu reagent. The mixture was shaken and allowed to stand for 6 min, before addition of 1.25 ml of 7% Na_2CO_3. The solution was then adjusted with distilled water to a final volume of 3 ml and mixed thoroughly. After incubation in the dark, the absorbance at 760 nm was measured in front of a blank prepared in the same way that samples. Total phenolic content of all samples was expressed as mg GAE g^{-1} DW using a calibration curve established with gallic acid standard solutions. All measurements were performed in triplicate.

2.5. DR-NIR procedure

Samples, dried at 105 °C during 12 h, were placed in clear glass vials of 22 mm external diameter and 48 mm height to obtain NIR spectra by DR. DR-NIR spectra was obtained in Kubelka-Munk units. All NIR spectra were acquired between 14,000 and 4000 cm^{-1} by co-adding 50 scans and using an optical resolution of 4 cm^{-1}. The background spectrum was acquired from the closed integrating sphere using the same instrumental conditions than those employed for sample measurement. Three measurements of each sample were obtained by rotating 120° approximately, the sample vial position between replicates in order to ensure a better representatively of spectra. The mean values of the triplicate spectra of each sample were employed to build PLS calibration models and prediction.

2.6. ATR-MIR procedure

100 mg of sample, dried at 105 °C during 12 h, were deposited on the ATR accessory and pressed. Spectra were recorded in the range between 4000 and 550 cm^{-1}, by accumulating 50 scans per spectrum, at a resolution of 4 cm^{-1}. A spectrum of the clean ATR crystal, obtained immediately before acquiring the spectrum of each sample, was used as background. Mean spectra of triplicate measurement for each sample were used to build the PLS models and for sample prediction.

2.7. Data treatment

The Opus 6.5 software from Bruker was used for data acquisition in both, FT-IR and FT-NIR instruments. Data treatment was carried out using in-house written functions employing Matlab 8.3.0.532 (R 2014a) from MathWorks (Natick, MA, USA). For principal component analysis (PCA) and for partial least square (PLS) calibration and validation model, the PLS Toolbox 6.7.1 from Eigenvector Research Inc. (Wenatchee, WA, USA) was used.

An infrared spectrum consists of many related variables (wavenumbers) which are difficult to be analyzed. The PCA is a well-known technique for reducing the dimensionality of multivariate data while preserving most of the variances and this technique has been used to identify correlations among a set of variables and to transform the original set of variables to a new set of uncorrelated ones called principal components (PCs) [6]. For this purpose the PCA was applied to IR spectra to extract the most informative data set and to identify the different classes of samples.

On the other hand, PLS is a linear model frequently used in chemometrics to establish the relationship between predicted values of a property (axis *y*) and reference values (axis *x*) based on the modelization of signals obtained for a reference population of well identified samples [11]. Before building PLS models, spectra of samples were split in calibration and validation subsets with 76 and 19 objects respectively. To select the most appropriate calibration set the Kennard Stone (K–S) algorithm was used [12]. K–S algorithm starts by spectra preprocessing with the two most distant objects as members of the calibration set. The algorithm takes the objects into the training set based on their Euclidean distance. From already selected objects, calibration set was used to build the models and validation set was employed to evaluate their predictive capability.

To select the best number of latent variable leave-one-out cross validation method was employed being evaluated the root mean