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NEW APPROACHES FOR ANALYSIS METHODS OF THE INPUTS USED IN ECOLOGICAL AGRICULTURE

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Abstract

Ecological agriculture is nowadays considered a potential solution to obtain healthier and nutritious food products but also to minimize the environmental impact by using as inputs, natural resources without resorting synthetic chemicals. The inputs (organic and mineral fertilizers, soil amendments, plants protection products, etc.) accepted for ecological agriculture are regulated by Commission Regulation (EC) No 889/2008 and by Regulation (EC) No 2003/2003 of the European Parliament and of the Council. The quality of inputs is very important and therefore it is mandatory to subject them to chemical analysis, from two perspectives: to characterize their nutritional value for crops and also to evaluate the level of contaminants. Having in view the above mentioned aspects, this paper presents a systematic review of the methods used for nutrient (macro-, oligo-/microelements) and contaminants (heavy metals, pesticides) quantification.

Key words: contaminant, ecological agriculture, input, nutrient, pesticide.

INTRODUCTION

An important amount of the food produced worldwide is obtained from intensive agricultural farms, but even if the costs are lower, the impact may result by contribution to environmental pollution.

Recently, it has been observed that ecological agriculture has gained importance and this is due to consumer demand for healthy food products and to the necessity of environment protection by promoting sustainable farming practices (Saracin and Vasile, 2015). The restriction to use chemicals and pesticides contribute to minimizing pollution effects.

Ecological agriculture rely on organic and some mineral fertilizers, biofertilizers (Vlahova, 2014; Vlahova and Popov, 2014), soil amendments, use of natural pest controls that has to comply strict standards, the accepted products being regulated by Commission Regulation (EC) No 889/2008 and by Regulation (EC) No 2003/2003 of the European Parliament and of the Council.

Derived from plant or animal products by different techniques (decomposing, fermentation etc.), inputs destined for ecological agriculture present a great importance due to their beneficial

effects on soil structure, biological activity and represent an important lever to preserve soil quality and to provide healthy food products.

The inputs used for ecological agriculture must be subjected to chemical analysis to characterize their nutritional value for crops, to evaluate the level of contaminants and also to avoid the tendency of fraud in organic food sector that has been evidenced with increase of demand for ecological products.

Having in view the above mentioned aspects, this paper presents a systematic review of the methods used for nutrient (macro, oligo/microelements) and contaminants (heavy metals, pesticides) quantification.

Accordingly, literature studies indicate as suitable analytical methods for nutrient and heavy metals contents, the following: **atomic absorption spectrometry** (AAS), **inductively coupled plasma mass spectrometry** (ICP-MS), **inductively coupled plasma optical emission spectrometry** (ICP-OES).

Concerning pesticide residue analysis, recommended methods are **gas chromatography-mass spectrometry** (GC-MS), **high performance liquid chromatography** (HPLC).

METHODS USED FOR INPUT ANALYSIS

1. Atomic absorption spectrometry (AAS) is a very sensitive technique able to detect 70-80 elements in concentrations lower than 1 ppm from different samples (biological fluids, water, soil, drinks, food, pharmaceutical samples etc.) (Janusa and Beck, 2002).

This technique is based on measurable signal (proportional to the concentration) produced by free gaseous atoms of analyte which have absorbed electromagnetic radiation at a specific wavelength (Fernandez et al., 2018).

The components of AAS spectrometer are: (i) a source of radiation (commonly a hollow cathode lamp), (ii) atomizer (flame or furnace), (iii) monochromator and (iv) detection system (Fernandez et al., 2018).

In order to be subjected to analysis, the sample it has to be atomized, this requirement being solved by using flames or graphite furnace. Air-acetylene flame is sufficient hot for atomization of the majority of macro, micro/oligoelements found in inputs used for ecological agriculture. There are some exceptions, including Mo, for which it is recommended to use nitrous oxide-acetylene flame (Fernandez et al., 2018).

AAS present some chemical interference as (i) formation of less volatile compounds; (ii) formation of more volatile compounds; (iii) the analyte could be transformed into refractory species. All these inconvenient are surpassed using hotter flames, optimizing flame conditions, adding chelating agents etc. (Hill and Fisher, 2017).

AAS technique presents many advantages: low costs, easy to use, high precision and sensibility. As disadvantages it worth to be mentioned that can be analyzed solutions (excepting when graphite furnace is used as atomizer) and some problems with refractory elements.

Determination of metals from inputs for organic agriculture using AAS technique is preceded by sample digestion, the adopted methods being adapted to the nature of the input.

A sum of methods collected after literature review is presented in Table 1.

2. Inductively coupled plasma mass spectrometry (ICP-MS) is an elemental analysis technique able to determine low concentrations (ppb) and ultra-low-concentrations (ppt) of most elements

form periodic system. Sample solution is introduced with a peristaltic pump into the equipment, nebulized in spray chamber and converted into aerosols which typically constitute 2-5% from sample. The aerosols are injected into argon plasma (6000-8000K temperature) and suffer several transformations: desolvation, vaporization, atomization, ionization. Resulted ions are sorted in the basis of their mass.

ICP-MS techniques analyze samples in solution, this providing good control over homogeneity, ease calibration and good precision. This technique uses low volume of solution, has possibility to detect isotope composition of elements, present a large linear range and is capable of multi-element analysis. Disadvantages of the ICP-MS are spectral interferences caused by polyatomic ions or ions with the same mass as the analyte (Beauchemin, 2017). The solid sample is recommended to be destructured with acid solutions and microwave digested (Table 2).

3. Inductively coupled plasma optical emission spectrometry (ICP-OES) also named *inductively coupled plasma atomic emission spectroscopy* (ICP-AES) is a technique that allows determination simultaneously up to 70 elements in a single sample analysis. Detection limits for these elements are in the ppb range. This technique is recommended for refractory elements (silicon, aluminum etc.) but is not suitable for halogens and inert gases (Boss and Fredeen, 2004).

The analyzed samples, usually liquids, are converted into aerosols which are injected into the plasma where temperature reaches 7000K. Here, the aerosols are desolvated, vaporized, atomized, excited and/or ionized. The excited atoms and ions emit their characteristic radiation measured by a spectrometer (Boss and Fredeen, 2004).

For solid samples, direct analysis it is possible by means of vaporization are available (laser ablation or electrothermal vaporization) (Carey and Caruso, 1992). Otherwise, solid sample must be turned into solution, usually by acid digestion (Table 3). A special attention must be paid to siliceous samples when for digestion protocol is used hydrofluoric acid which requires a special sample introduction system (alumina injector) into ICP-OES (Arslan and Tyson, 2008).

Table 1. An overview of input analysis by AAS technique

Input	Sample preparation	Quantified elements	References
compost	microwave digestion with aqua regia (35% HCl and 65% HNO ₃)	<i>Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Zn</i>	Bozym and Siemiatowski, 2018
compost	digestion with HNO ₃ and HClO ₄	Ca, Cu, Mg, Zn	Albuquerque Nunes et al., 2015
compost, vermicompost, manure	sample is dried at 105°C, treated with an acidic mixture HNO ₃ :H ₂ SO ₄ :HClO ₄ , 10:1:4 and heated at 200°C	<i>Cd, Cu, Pb, Ni, Zn</i>	National Center of Organic Farming, 1985
fertilizers containing organic matter	a sample of 5 g is heated at 450°C till calcination is done; the residue is treated with aqua regia, HNO ₃ :HCl, 1:3 (v/v).	<i>Cd, Cu, K, Ni, Pb, Zn</i>	FAMIC, 2016
fish waste compost	digestion with H ₂ SO ₄ and H ₂ O ₂ 30%	Ca, Mg	Lopez-Mosquera et al., 2011
fish waste compost	microwave digestion with HNO ₃ 1.4 g/cm ³	<i>Cd, Cu, Cr, Ni, Pb, Zn</i>	Radziemska et al., 2018
foliar fertilizers	sample is treated with concentrated H ₂ SO ₄ and concentrated HNO ₃ (1:6, v/v) and it is heated on sand bath until a white fume appear	Cu, Fe	Răuță and Dorneanu, 1984
foliar fertilizers	sample is treated with concentrated HNO ₃ until solution is clear and it is heated on sand bath	Mn, Mo	Răuță and Dorneanu, 1984
manure	a) calcination at 550°C for 4 hours; resulted residue is treated with HCl; b) sample (0.1-0.5 g for solid samples, 10-15 mL for liquid samples) is treated with 10 mL concentrated HNO ₃ and microwave digested; c) sample (0.1-0.5 g for solid samples, 10-15 mL for liquid samples) is treated with a mixture of HNO ₃ -H ₂ O ₂ -HCl.	Ca, Cu, Fe, K, Mg, Mn, Zn	Peters, 2003
mineral fertilizers	sample is treated with diluted HCl (HCl d = 1.18g/ml and distilled water, 1:1, v/v) and heated	Ca, Co, Cu, Fe, Mg, Mn, Zn	Regulation (EC) 2003/2003
mineral fertilizers	sample is treated with a mixture of HCl and HNO ₃ and then is boiled for 30 minutes	Ca, Mg	Răuță and Dorneanu, 1984
organic fertilizers	sample is calcinated at 500°C for 2 hours; the residue is treated with HCl and boiled for 30 minutes	Ca, Mg	Răuță and Dorneanu, 1984
pig manure	digestion with HCl 37%, HNO ₃ 69% and H ₂ O ₂ 30%	<i>Cd, Cu, Pb, Zn</i>	Lupascu et al., 2009
vermicompost from cow dung and biogas plant slurry	digestion with concentrated HNO ₃ and concentrated HClO ₄ (1:1, v/v)	<i>Cr, Cu, Fe, Zn</i>	Yadav et al., 2013

Contaminant elements are marked with italic.

Table 2. An overview of inputs analysis by ICP-MS technique

Input	Sample preparation	Quantified elements	References
animal manure compost	digestion with HNO ₃ and HClO ₄	<i>As, Cd, Cr, Cu, Ni, Pb, Zn</i>	Yang et al., 2017
ash	ash sample is digested with an acidic solution HNO ₃ 65%, HCl 35%, HF 40%	<i>Cd, Cu, Mn, Pb, Zn</i>	Yu et al., 2013
fluid sludge fertilizers	sample is treated with HNO ₃ and H ₂ O ₂ and is microwave irradiated	<i>Cd, Cr, Ni, Pb</i>	FAMIC, 2016
manure based fertilizers	sample is placed in a Teflon digestion vessel, treated with HNO ₃ , H ₂ O ₂ 30% and subjected to microwave-assisted digestion	<i>As, Cd, Cr, Cu, Zn</i>	Qian et al., 2016
manures, fertilizers, limes	samples are digested with HNO ₃ and HCl for 8 hours; then was added HF and microwave digested.	B, <i>Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Zn</i>	McBride and Spiers, 2001
organic fertilizers	digestion with HNO ₃ , HClO ₄ and HF in Teflon vessels, at temperature	<i>Cd, Co, Ni, Mo, Pb</i>	Kawasaki and Arai, 1996
sediments, organo-mineral fertilizers, sludge	sample is treated with HNO ₃ 7 mol/l, H ₂ O ₂ 30% and microwave-assisted digestion	<i>Cd</i>	Machado et al., 2017

Contaminant elements are marked with italic.

Table 3. An overview of inputs analysis by ICP-OES technique

Input	Sample preparation	Quantified elements	References
compost	digestion with aqua regia, HNO ₃ :HCl, 1:3 (v/v).	<i>As, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Zn</i>	Mladenov, 2018
compost	digestion with aqua regia, HNO ₃ :HCl, 1:3 (v/v).	<i>Cd, Cr, K, Ni, P, Pb</i>	Becher et al., 2018
fish waste and seaweed compost	microwave-assisted digestion with nitric acid	<i>Cd, Cu, Cr, Ni, Pb</i>	Lopez-Mosquera et al., 2011
manure	a) calcination at 550°C for 4 hours; resulted residue is treated with HCl; b) sample (0.1-0.5 g for solid samples, 10-15 ml for liquid samples) is treated with 10 ml concentrated HNO ₃ and microwave digested; c) sample (0.1-0.5 g for solid samples, 10-15 ml for liquid samples) is treated with a mixture of HNO ₃ -H ₂ O ₂ -HCl.	P, K, Ca, Mg	Peters, 2003
chicken manure	microwave-assisted digestion with aqua regia, HNO ₃ :HCl, 1:3 (v/v).	<i>Ca, Cr, Cu, Mg, Ni, Pb, Zn</i>	Ravindran et al., 2017
sludge fertilizers	sample is heated in an electric furnace at 450°C till calcination is done; the resulted residue is treated with aqua regia, HNO ₃ : HCl, 1:3 (v/v).	<i>Cd, Cu, Ni, Zn</i>	FAMIC, 2016
wood ashes	digestion with HF and HClO ₄	<i>Ca, Cu, K, Mg, Ni, Zn</i>	Sinaj et al., 2015
ash	digestion with HF, HNO ₃ and H ₂ O ₂	<i>Ca, Fe, K, Mg, P</i>	Wang et al., 2012
phosphate products and organic fertilizers	microwave digestion with nitric acid at 200°C	<i>As, Cd, Co, Cr, Pb, Mo, Ni</i>	Kane and Hall, 2006

Contaminant elements are marked with italic.

4. Gas chromatography mass spectrometry (GC-MS) is a technique able to analyze volatile molecules which are sufficiently thermal stable, to separate complex mixtures and to quantify pesticides at low levels found in various types of samples. Usually, pesticides occur in complex environmental matrixes and before chromatographic analysis it is required a sample pretreatment (Table 4). After this procedure (matrix preparation, extraction, clean-up), sample is volatilized into GC-MS and separated using a capillary column (filled with stationary phase). The compounds are carried by mobile phase (represented by argon, helium or nitrogen) and when leaving the GC column are ionized using electron ionization or chemical ionization. Positively charged ions are accelerated through mass analyzer (quadrupole, ion trap, cyclotron resonance etc) and separated on the basis of their different mass-to-charge (m/z) ratios (Andreu and Pico, 2004; Sneddon et al., 2007).

5. High performance liquid chromatography (HPLC) is a versatile method used in pharmaceutical, environmental, forensic areas. The sample/analyte in a solvent (mobile phase) is pumped at high pressure through a column filled with stationary phase and carried by a

stream of nitrogen or helium. The time that a specific compound travels through column to the detector is retention time and depends on the pressure, nature of stationary phase, temperature of the column, used solvent/solvents. The detector recognizes the analytes that has passed through the column and sends the information to a computer to generate the chromatogram (Bottcher et al.). The most common is UV detector, but for highly sensitive measurements are also used photodiode array detectors, fluorescence detectors, refractive index detectors, conductivity detectors (<https://www.ssi.shimadzu.com/products/liquid-chromatography/nexera/uhplc-hplc-detectors/index.html>).

Ultra performance liquid chromatography (UPLC) is a superior technique, the main differences between UPLC and HPLC being the size of used particles filled into column (2 μm vs. 3-5 μm) and operating pressures (103.5 MPa vs. 35-40 MPa).

As result, UPLC present an advantage over HPLC in improved separation and detection of analyte, reduced time of analysis, lower solvent consumption, and reduced costs (Taleuzzaman et al., 2015). Some reported methods for pesticide analysis are presented in Table 5.

Table 4. An overview of pesticide analysis by GC-MS technique

Input	Pesticide	Sample preparation	References
compost	dioxins and furans	- extraction with toluene - clean-up using semi-automatic system equipped with three different columns (silica, alumina, carbon)	Conesa et al., 2009
poultry manure	organochlorine pesticides	- modified QuEChERS procedure: extraction followed by a d-SPE clean-up	Aznar et al., 2014
sediments	triazines	- QuEChERS procedure: extraction followed by SPE clean-up	Brondi et al., 2011
sewage sludge	polychlorinated biphenyls and organochlorine pesticides	- extraction with chloroform: resulted extract was dried with sodium sulphate - clean-up using silica gel column; polychlorinated biphenyls were eluted with hexane and organochlorine pesticides with toluene	Erickson and Pellizari, 1979
compost	carbaryl, chlorpyrifos, cypermethrins, diazinon, imazalil, malathion, mefenacet, pirimiphos methyl, thiobencarb	- extraction by pressurized liquid extraction - clean-up by a partition between hexane and acetonitrile followed by d-SPE extraction using a porous carbon made from Moso bamboo (<i>Phyllostachys pubescens</i>)	Kawata et al., 2005
compost	aldrin, endosulfan (α and β), lindane	- extraction by ultrasonication using dichloromethane and acetone - clean-up on silica gel column; elution with dichloromethane and acetone	Muntjeer et al., 2014

QuEChERS - Quick, Easy, Cheap, Effective, Rugged and Safe (Anastassiades et al., 2003); d-SPE - dispersive solid phase extraction, SPE - solid phase extraction

Table 5. An overview of pesticide analysis by HPLC technique

Input	Pesticide	Sample preparation	References
sludge	glyphosate	- extraction using aqueous solution of sodium phosphate and sodium citrate; extract was adjusted to pH 9 and contaminations were removed by washing with hexane; - purification by LLE method; - determination by HPLC with fluorescence detector	Sun et al., 2017
sewage	organochloride pesticides	- extraction: SPME procedure - determination employing HPLC with UV diode array detector	Torres Padron et al., 2006
cattle manure	clopyralid	- extraction: micro LLE - clean-up with SPE cartridge - determination by UPLC-MS/MS, electrospray ionization	Watanabe et al., 2019
compost	isoproturon, bentazone, metalaxyl, linuron	- extraction: SPE procedure - determination by HPLC with diode array detector	De Wilde et al., 2009
peat, compost	isoproturon, bentazone,	- extraction with methanol - determination by HPLC with UV detector	Coppola et al., 2009
poultry manures	bifenthrin, imidacloprid, fipronil	- extraction: SDIE procedure - clean-up by SPE - detection by UPLC	Ong et al., 2017

LLE – liquid liquid extraction; SPME – solid phase microextraction procedure; SPE – solid phase extraction; UPLC-MS/MS - ultraperformance liquid chromatography tandem mass spectrometry; SDIE – solvent direct-immersion extraction

CONCLUSIONS

To take the advantage of growing interest in ecological agriculture, many types of inputs have been promoted, in some cases the quality of them being questionable. As these products have to obey strict standards, their chemical analysis is a very important step to contribute for providing high quality products and to ensure environment protection.

The present paper described the most used methods for inputs analysis to characterize their nutritional value by assessing macro-, oligo-/microelements concentrations and to detect

potential contaminants (heavy metals, pesticides).

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