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AN OVERVIEW OF METHODS USED FOR QUANTIFICATION OF HEAVY METAL CONTENTS IN VEGETAL SAMPLES

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Introduction

Heavy metals environmental presence is mainly a result of human activities associated with agriculture (use of fertilizers and pesticides), industrial purposes and in some situations is a consequence of natural causes as volcanic activity, soil erosion, geological weathering. Phosphate fertilizer application is a significant contributor of trace element presence, being a common impurity, especially for arsenic, cadmium and lead accumulation in cropland soils and therefore in plants.
Lately, atmospheric deposition of metals has been considered as an important source of metals (arsenic, cadmium, lead) enter the soils and there are many studies related with this subject.
The heavy metals of particular concern are lead, cadmium, chromium, mercury, arsenic due to their harmful effects on human health because of their tendency to accumulate in tissues and to be stored in organs (liver, kidney).
In Regulation (EC) No 1881/2006 the EU Commission has set maximum levels (MLs) for lead, cadmium, mercury and tin in different foodstuffs (meats, fish, crustaceans, mollusks, cephalopods, cereal, legumes, pulses, fruit and fruit juices, fats, wines, milk, canned food and beverages).
Continuous monitoring of heavy metals content in vegetal products is a priority for food control and a risk assessment strategy for human health. Having in view importance of its surveillance, the aim of this paper is to identify, on the basis of literature data, the most suitable procedures and techniques used for accurate determination of heavy metals in vegetal samples.

Heavy metals accumulation in vegetal products

The accumulation of heavy metals in plants is discussed in literature from two perspectives: (**i**) elevated levels of heavy metals produce a wide variety of physiological changes in plants (inhibit the ability of the plant to synthesize chlorophyll, high oxidative stress, suppression of plant growth) that affect crop yield and quality and (**ii**) related to negative effects on consumers' health (chronic diseases, disturbances at central nervous system level, renal dysfunctions).

The uptake of metals from soil depends on different factors such as their soluble content in soil, soil physico-chemical properties. The accumulation of metals varies greatly both between cultivars and varieties. Also, uptake, transfer and accumulation of heavy metals vary with growth stage.
Generally, plants accumulate larger quantities of metals in leaves than in fruits or seeds and the highest contents of arsenic, lead, and cadmium were reported for leafy vegetables.

Methods for heavy metals quantification in vegetal products
Usually for heavy metals assessment from vegetal samples, there are two steps to be followed by analyst: *sample digestion* **(a)** and *quantification* **(b)** using a suitable analytical technique chosen according to metal characteristics and its concentration in the analyzed sample.
a) For *digestion* are used different methods as calcination, microwave digestion in acidic medium, digestion with acids under heating, digestion with mixtures of concentrated acids.
The selection of appropriate digestion method ensures the correct determination of metals and it has been proven that certain digestion procedure impact the determination of metals. Accordingly, selection of digestion method is a critical step for obtaining accurate results.
Microwave assisted digestion in closed vessel is used frequently because assures rapid dissolution of sample matrix, needs small volumes of oxidizing reagents and prevent losses by volatilization of certain components.
b) *Quantitative determination* of metals is achieved mainly using atomic absorption spectrometry (AAS), hydride generation atomic absorption spectroscopy (HGAAS) for hydride forming metals, cold vapor atomic absorption spectroscopy (CVAAS) (mainly for mercury analysis from different samples), inductively coupled plasma - optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS).
Beside above mentioned techniques, literature mention X-ray fluorescence (XRF) and neutron activation analysis (NAA) which are able to analyze simultaneously many elements without destroying the sample by digestion. Also, anodic stripping voltammetry (ASV) was reported as a valuable method for assessment of heavy metals in plant samples.
In the extenso paper are presented all analytical methods mentioned in abstract detailing digestion procedures, the type of analyzed vegetal samples and heavy metals quantified by each method.

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