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Ionic liquids as a key medium for efficient extraction of copper complexes from chia seeds (*Salvia hispanica* L.)

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ABSTRACT

Due to insufficient information, the aim of study was to concern on the optimization of extraction procedure of selected metal complexes with flavonoids from chia seeds. Evaluation of the amount of elements in compound, not only their total concentration content, is highly important due to the fact, that only a part from total content of metal is absorbed by human body.

At the beginning the total amount of elements in chia seeds was established as 14.51 ± 0.42 μg g^{-1} for copper, 57.44 ± 1.23 μg g^{-1} for manganese, 81.12 ± 1.89 μg g^{-1} for zinc and 0.35 ± 0.13 μg g^{-1} for cobalt. After the most suitable solvent was established, effects of several parameters on the efficiency of metal extraction were studied. Solvent concentration, solid–solvent ratio, extraction method, extraction time and temperature have been investigated as independent variables. The optimal extraction conditions included vortexing during 20 min in 50 °C, using an ionic liquid (1-butyl-3-methylimidazolium bromide) as an extractant, with solid–solvent ratio of 1:20. The determination of total and extractable amount of metals in chia seeds was carried out by standalone ICP MS. In addition, a complementary analysis of extracted metal complexes was performed using SEC-ICP MS method. It was confirmed that the ionic liquid is able to extract different copper complexes in comparison with commonly used solvents. The study indicated that extraction by using an ionic liquid has been successfully applied for determination of metals and metal complexes in chia seeds.

1. Introduction

Salvia hispanica L., commonly known as chia, is an oilseed plant that was once used by the Aztecs not only as a foodstuff, but also as an offering to the gods. Chia is a natural source of omega-3 (α-linolenic acid), fiber (content $>30\%$) and proteins of high biological value. It is a natural source of antioxidants that protect against certain adverse conditions [1], in addition to other important nutritional components such as vitamins and minerals [2,3].

Chia can be assigned to “functional food”, apart from the provision of essential nutrition it also has positive effects on human health. It helps, among others, prevent cardiovascular diseases, inflammatory, nervous system disorders and diabetes [4]. In order to fully understand their health benefits it is important to determine chemical and physical properties of chia seeds. Therefore, design and improve appropriate equipment to process and prepare samples is a key to obtain a good representation of true values from the specimen [2].

Ruiz Medina and co. [5] have reported that the metals concentration in chia seeds is much higher than in any other investigated food with supposed health benefits (pomegranate, açaí berries, goji berries and mangosteen). For example much higher concentration of calcium and manganese was observed in chia seeds than in goji berries. The quantity of Cu, Fe, K, Mg, P and Zn are similar in goji berries and chia seeds, with differences lower than 4-fold (2-fold in most cases).

In addition, chia seeds are rich in natural antioxidants such as tocopherols, phytosterols, carotenoids [6] and phenolic compounds, including chlorogenic acid, caffeic acid, myricetin, quercetin and kaempherol [2,7]. These compounds protects consumers against many diseases and they also have positive effects on human health. The complexation of metals to flavonoids results in more effective pharmacological activities and better availability of minerals as well as reduces their overloading in body [8].

The scientific literature mostly presents the determination of biological active organic compounds and has focused on food with positive health effects, like açaí, goji berries or chia seeds [9,10]. High percentage of those works involve the determination of phenols and flavonoids, and the evaluation of the antioxidant activity [11,12]. Only few publications have described the content of metals in some of these fruits [5,13]. Unfortunately, still little is

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known about metal complexes with bioligands present in plants and fruits rich in biologically active compounds so exhaustive research in this area is still necessary.

Many studies have reported extraction of different bioligands from plant material, but literature data concerning optimization of extraction of metal complexes with bioligands from functional foods is very limited. The aim of this study was the optimize extraction procedure of copper complexes with flavonoids from chia seeds using an ionic liquid, IL (1-butyl-3-methylimidazolium bromide) as an extraction medium [14–16]. A lot of studies found in literature are related to extraction using an ionic liquids but they are focused on heavy metals. For example development of the efficient microextraction of lead from environmental samples (water, hair or plant) [17,18]. Copper has been chosen for this study because it is essential micronutrient element to most life forms. However, other metals necessary for human beings, such as manganese, cobalt and zinc were also observed during the process of the optimization of extraction. The determination of total amount of metals was carried out by standalone ICP MS. In order to confirm the presence of different copper complexes the extracted fractions from chia seeds were also analysed by SEC-ICP MS technique. To the best of our knowledge, there is no report about optimization of extraction of metal complexes from chia seeds.

2. Experimental

2.1. Chemicals and materials

Ammonium acetate, sodium dodecyl sulfate, tris(hydroxymethyl)aminomethane, methanol, dodecanoic acid, tetrahydrofuran, hydrochloric acid, nitric acid, 1-bromobutane and 1-methylimidazole were purchased from Sigma Aldrich and were of analytical reagent grade. Acetonitrile, ethyl acetate, trichloromethane and hydrogen peroxide were purchased from POCh (Gliwice, Poland). Deionized water (18 MΩ cm) prepared with a Milli-Q system (Millipore Elix 3, Millipore, Saint- Quentin, France) was used throughout. The SEC column was calibrated using size exclusion standard (BIO-RAD, Warsaw, Poland). The calibration curves were prepared using solution of Environmental Spike Mix (1000 mg L^{-1} of Fe, K, Ca, Na, Mg and 100 mg L^{-1} of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, U; matrix 5% HNO_3) purchased from Agilent Technologies.

The chia seeds was obtained from Kenay (Poland, imported from Peru) and stored at 4 °C until analysis.

2.2. Preparation of ionic liquids and SUPRAS

The ionic liquid used in this study was 1-n-buthyl-3-methylimidazolium bromide ([C_4mim]Br), synthesized based on references [19]. For the synthesis a 500 cm^3 flask, equipped with a magnetic stirrer and condenser was used. To a solution of 151.5 g (1.85 mol) of freshly distilled 1-methylimidazole in 100 cm^3 of acetonitrile, and 220 g (2.4 mol) of 1-bromobutane were added. The mixture was stirred at $T=373.15$ K for 96 h and afterward the solution was allowed to cool down when the 1-n-buthyl-3-methylimidazolium bromide crystallized. Crystals were filtered and washed with ethyl acetate. The product was recrystallized from acetonitrile/ethyl acetate mixture (6/1). Crystals were dried in vacuum at $T=353.15$ K for 24 h. The solution of ionic liquid used during extraction was prepared by dilution in MQ water.

The following procedure, based on reference [20] was used to obtain a supramolecular solvent (SUPRAS) with volume ~10 mL. Dodecanoic acid (0.9 g), tetrahydrofuran (15 mL) and hydrochloric solution 0.01 mol L^{-1} (15 mL) were mixed in a 50 mL glass centrifuge tube. The mixture was centrifuged at 3,500 rpm for 15 min. The SUPRAS was formed as a new liquid phase at the top of the solution, with less density than water. It was separated using a syringe and stored in a closed vial until use.

2.3. Instrumentation

Chromatographic separations were performed using Agilent 1100 gradient HPLC pump (Agilent Technologies, Waldbronn, Germany) as the sample delivery system. All connections were made of PEEK tubing (0.17 mm i.d.). Agilent 7500a ICP Mass Spectrometer (Agilent Technologies, Tokyo, Japan) was used as an element-specific detector for quantification of metal content in chia seeds and as on-line HPLC detector. Ni-skimmer was installed in the interface, the position of torch and nebulizer gas flow was adjusted daily with special emphasis to decrease the level of CsO^+ below 0.2% with the aim to minimize the risk of polyatomic interferences caused by oxides. The working conditions were optimized daily using a 10 μg L^{-1} solution of $^7Li^+$, $^{89}Y^+$ and $^{209}Bi^+$ in 2% (v/v) HNO_3.

The screening for the metal complexes was performed by means of size exclusion chromatography coupled to ICP MS. Copper species were eluted from SEC Superdex200 10/300GL (GE Healthcare Life Sciences, Freiburg, Germany) column with 10 mM ammonium acetate buffer (pH 7.4) as a mobile phase. Before the analysis the column was calibrated with a mixture of thyroglobulin (670 kDa), γ-globulin (158 kDa), ovalbumin (44 kDa), myoglobin (17 kDa), vitamin B_{12} (1,35 kDa). Operational parameters are summarized in Table 1.

A Bandelin Sonorex Model 1210 ultrasonic bath (Bandelin, Berlin, Germany), MPW Model 350R centrifuge (MPW Warsaw, Poland), water bath with thermostatically controlled temperature (Mammert, Germany) and sonication probe (Bandelin Sonoplus, Berlin, Germany) were used for extraction procedures. Microwave digestion Speedwave® four Berghof, (Berghof, Chemnitz, Germany) was used for samples' mineralization and extraction procedure.

2.4. Sample preparation

2.4.1. Samples mineralization toward metal determination in chia seeds

The chia seeds were lyophilized and grounded using agate mortar and pestle until a homogenous powder was formed; the powder was stored at 4 °C. In order to determine total amount of elements, samples (0.2 g dry mass) were digested by microwave

Table 1
Operational parameters for HPLC and ICP MS.

Settings	
ICP-MS	Agilent 7500a
RF Power	1350 W
Plasma, auxiliary and nebulizer gas flow	15.0, 1.0 and 1.05 L min^{-1}
Cones	Sampler – Pt, Skimmer – Ni
Monitored isotopes	^{55}Mn,^{59}Co, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{67}Zn, ^{68}Zn,
Dwell time	0.1 ms
HPLC separation	
pump	Agilent 1100
Column	Superdex 200 (10 × 300 mmx10 μm) – GE Healthcare Life sciences
Mobile phase	10 mM ammonium acetate buffer (pH 7.4)
Elution program	isocratic
Flow	0.5 mL min^{-1}
Injection volume	100 μL
Column temperature	24 °C