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Selenium analysis by an integrated microwave digestion-needle trap device with hydride sorption on carbon nanotubes and electrothermal atomic absorption spectrometry determination☆

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ABSTRACT

An integrated microwave assisted digestion (MW-AD) – needle trap device (NTD) for selenium determination in grape pomace samples is presented. The NTD was filled with oxidized multiwall carbon nanotubes (oxMWCNTS) where Se hydrides were preconcentrated. Determination was carried out by flow injection-electrothermal atomic absorption spectrometry (FI-ETAAS). The variables affecting the system were established by a multivariate design (Plackett Burman), indicating that the following variables significantly affect the system: sample amount, HNO_3 digestion solution concentration, $NaBH_4$ volume and elution volume. A Box-Behnken design was implemented to determine the optimized values of these variables. The system improved Se atomization in the graphite furnace, since only trapped hydrides reached the graphite furnace, and the pyrolysis stage was eliminated according to the aqueous matrix of the eluate. Under optimized conditions the system reached a limit of quantification of 0.11 μg kg^{-1}, a detection limit of 0.032 μg kg^{-1}, a relative standard deviation of 4% and a preconcentration factor (PF) of 100, reaching a throughput sample of 5 samples per hour. Sample analysis show Se concentrations between 0.34 ± 0.03 μg kg^{-1} to 0.48 ± 0.03 μg kg^{-1} in grape pomace. This system provides minimal reagents and sample consumption, eliminates discontinuous stages between samples processing reaching a simpler and faster Se analysis.

1. Introduction

Selenium is an essential element of important metabolic pathways, including defense through the immune system, thyroid hormone metabolism, reproductive development and antioxidant defense [1]. In the environment, selenium is present in both soil and water, and can be mobilized through plants or aquatic organisms thus entering the food chain [2]. Vine production offers a byproduct called pomace that includes skins of grape and seeds [3]. An adequate use of agroindustrial residues, such as pomace, could have an impact on agricultural productivity and soil fertility through composting [4]. Therefore, the environmental impact of this practice should be assessed by determining trace elements in pomace with essential and toxic characteristics, like selenium [5].

In order to monitor selenium in pomace samples it is necessary to develop analytical methods with appropriate detection levels. Sample preparation plays a decisive role throughout the analytical procedure, especially for analysis of solid environmental samples, characterized by complex matrices and the presence of trace and ultratraces of analytes [6,7]. The microwave assisted wet digestion (MW-AD) presents great advantages over classical methods, allowing a reduction of the extraction time, less use of reagents and the possibility of on-line coupling to other analytical stages [8–10]. Preconcentration strategies for volatile species generated during hydride generation (HG) processes have been described, resulting in gas-phase trapping techniques [11–13]. HG by sodium tetrahydroborate shows advantages like analyte separation from the matrix, eliminating interferences and increasing sensitivity [14]. Not all species of metals can react with $NaBH_4$ and form hydrides, for total Se determination, only Se (IV) forms the volatile compound, H_2Se. Because of this, the transformation of the different selenium compounds to their Se (IV) species is unavoidable. It is possible to reduce Se (VI) to Se (IV) by the use of hydrochloric acid 6 M, or 1 or 2 M HCl with heating [15].

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Trace analysis where a pretreatment of the sample is required, like MW-AD and HG, can be integrated to preconcentration procedures by a novel approach: needle trap devices (NTD) [16]. The axis of the NTD consists of a sorbent material, packed inside a stainless steel needle. In this methodology the sample passes over the sorbent, where the analytes are trapped and then subjected to thermal or solvent desorption [17]. Its main benefits are that the extraction phase is much larger and has an exhaustive extraction nature, allowing the complete extraction of the analytes present in the sample. It also presents greater robustness and ease of handling during sampling and desorption. Since elution can be achieved with volumes in the microliters order, NTD can be coupled on line to sensible techniques like electrothermal atomic absorption spectrometry (ETAAS) [16,18–20].

Recently, Bagheri et al. developed a methodology where they used for first time a sorbent based on CNTs in a NTD for microextraction of polycyclic aromatic hydrocarbons from aquatic media [21]. The use of NTCs as NTD sorbents has generated great interest in the scientific community, which is related to their unique properties, such as chemical stability, durability and corrosion resistance [22]. In addition, these materials have a high surface area and can be easy to process. It should be noted that the preferential use of MWCNTs as sorbents is evident, which may be due to the fact that SWCNTs present more resistance to acid treatments [23]. Thus, the acid oxidation conditions required for functionalization are less aggressive for the MWCNTs [24]. Furthermore, MWCNTs have superior physical properties such as increased strength and thermal and electrical conductivity.

In the present work a method was developed to analyze selenium in grape pomace samples by integrating MW-AD, HG and NTD in a FI system. Selenium hydrides were micro-preconcentrated on oxidized MWCNTs (oxMWCNTs) with ETAAS determination. The study of the different variables affecting the system was performed by a multivariate experimental design. After optimization of these variables, the analytical results as well as the validation studies on grape pomace samples were successfully evaluated.

2. Experimental

2.1. Standard and reagents

All reagents used were of analytical grade, and no presence of Se was detected in the working range. The MWCNTs were obtained from Sigma-Aldrich (St. Louis, USA). A standard stock solution (100.0 mg L^{-1}) of Se was prepared by dissolving an appropriate amount of Na_2SeO_3 (Sigma, St. Louis, USA) in 5% HNO_3. The diluted working solutions were prepared daily by serial dilutions of the stock solution. A solution of 1% (*w*/*v*) sodium tetrahydroborate (Aldrich Chemical Co., St. Louis, USA, 98%) was prepared in 0.5% (w/v) sodium hydroxide solution and filtered through filter paper Whatman No. 42 to remove undissolved solids. This solution was prepared daily. H_2SO_4, HNO_3, H_2O_2, HCl used for the functionalization of MWCNTs as well as the digestion and treatment of samples were from Merck, Darmsdat, Germany.

2.2. Apparatus/instrumentation

Determination of Se concentration was carried out on a Shimadzu Model AA-7000 atomic absorption spectrometer (Tokyo, Japan) equipped with a background correction system employing a continuum source, a GFA-EX7 electrothermal atomizer, and an ASC-7000 auto sampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. A selenium hollow-cathode lamp (Hamamatsu, Photonics K.K., Japan) was employed as radiation source at 196.0 nm with a slit of 1.0 nm. The ETAAS instrumental and operating conditions are listed in Table 1.The graphite tubes were pre-treated three times with the iridium modifier as follows: 50 μL of 1000 g L^{-1} Ir stock solution were injected into the graphite tube and heated according to the temperature program given in Table S1 (Supplementary material) [25]. The temperature of pyrolysis was optimized from 0 °C to 700 °C.

Table 1
Experimental conditions for Se determination in grape pomace.

Parameter	Value
Sample amount	100 mg
HNO_3 digestion solution concentration	2.4 M
HNO_3 digestion solution volume	2.5 mL
H_2O_2 concentration	30%
H_2O_2 volume	2.5 mL
HCl concentration	6 M
HCl volume	1 mL
$NaBH_4$ concentration	1%
$NaBH_4$ volume	2.3 mL
$NaBH_4$ flow rate	2.5 mL min^{-1}
Elution volume	30 μL

A domestic microwave oven Samsung model G245C (Seoul, South Korea) of 2450 MHz frequency and operating at a maximum exit power of 1500 W was employed for MW-AD. For validation, a digestion was carried out in a laboratory microwave digestor (Milestone, Sorisole, Italy). Digestion was performed according to the manufacturer indications: 0.5 g of pomace samples were weighed and placed in individual microwave reactors. The aliquots were treated with 7 mL concentrated HNO_3 and 1 mL H_2O_2. Reactors were placed in the digestor at a ramp temperature of 10 min up to 200 °C and hold for 10 more minutes. The employed microwave power was up to 1000 W.

Gilson Minipuls 3 peristaltic pumps (Villiers, Le-Bell, France) and Tygon-type pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel sample, eluent and reagents. Headspace vials (20 mL) and accessories were obtained from Perkin Elmer (Thornhill, Canada). These vials were used for sample digestion, as well as for HG. All unions were sealed to avoid gas losses.

The Design Expert® 7.0 software package (Stat-Ease Inc., Minneapolis, USA) was used for experimental designs, data analysis and response surfaces.

2.3. MWCNTs oxidation

To achieve CNTs functionalization, 0.1 g of MWCNT were weighed and placed in a 500 mL balloon. Then, 200 mL of oxidizing mixture H_2SO_4: HNO_3 (3: 1) were added and covered with a detachment tube. After this, the balloon was placed in an ultrasonic bath and was sonicated for 1 h. Then the mixture was placed in a thermostatized bath (55 °C) for 1 h. Then 200 mL of Milli-Q water were added and the mixture was allowed to cool at room temperature. By centrifugation at 4000 rpm, the acid was removed and washed with pure water, until neutral pH is reached. Finally, oxidized MWCNTs were dried at 70 °C for 12 h and weighed. OxMWCNTs were chosen for Se hydride retention according to previous works were these show a higher hydride retention efficiency [16,17].

2.4. NTD preparation

The NTD was built using a stainless steel bevel needle with a length of 40 mm and an internal diameter of 0.5 mm. To avoid sorbent losses, the needle was pre-conditioned by placing glass wool in the needle bevel, applying heat to partially fuse the glass wool to generate a porous stopper. The needle was filled by preparing an aqueous suspension with 4 mg of oxMWCNT, which was introduced into the syringe using the FI system. Thus, the porous stopper retained CNTs, allowing the packaging. Finally glass wool was placed in the upper side of the needle (Fig. 1).