OLIVE PITS-BASED CARBON BLACK AGGLOMERATE AS AN ADSORBENT FOR PIPETTE-TIP SOLID-PHASE EXTRACTION FOR THE DETERMINATION OF CAFFEINE IN ENERGY DRINKS

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Vegetal wastes are an interesting source for the synthesis of nanostructured carbon materials, which are potentially useful in various applications. Carbon black agglomerates (CBA) obtained from olive pits, synthesized in our previous research, had a low crystalline structure typical of this type of materials, with a pore size of 2.27 nm, confirming their micro/mesoporous structure, and with a high surface value of around 587 m^2/g. These materials were used for the extraction of caffeine in energy drinks using a green-approach micro-sample technique called pipette-tip solid-phase extraction. This microextraction technique features reduced consumption of organic solvents, of the amount of sorbent and extraction time, thus making the whole sample pretreatment process faster and greener. In this work, we proposed an analytical method for the analysis of caffeine in commercial energy drinks, using CBA with a great extraction capacity due to its high porous surface area. The developed methodology has proven to be useful from a green chemistry point of view, using only one milligram of nanostructured sorbent, minimal solvent consumption, a reduced volume of sample, as well as easy and rapid automatization for the analysis of commercial energy drinks. For the quantification of the analyte in the energy drinks, a one-point standard addition calibration was applied to correct the matrix effect. Similar caffeine concentrations per milliliter were found in the three analyzed samples, likewise, the amounts of caffeine close to those reported by the manufacturers were established for two of the samples analyzed.

Keywords: carbon black agglomerates, microextraction, pipette-tip solid-phase extraction, energy drinks, caffeine

INTRODUCTION

Olive seeds represent a waste by-product of the olive oil industry, which, without further treatment, constitutes a significant environmental problem. These wastes are generally burned or left in the field as fertilizer, causing a number of harmful effects, because of the accumulation of high organic content and of their phytotoxicity.[1-3] The use of these wastes in numerous applications[2-9] can help alleviate the negative effects on the environment. One of these applications is in biofuels, attributed to the high content of cellulose, hemicelluloses and lignin, along with the low moisture content and high heat capacity of olive pits.[10] Likewise, it is known that olive seeds present an important source of oligosaccharides, fermented sugars, and polyphenols, in addition to biomolecules, such as proteins, fibres and omega 3, which allows their

use in the production of flours to enrich the preparation of doughs in the manufacture of breads and sweets.[11,12] The application of olive seeds has been also reported for the manufacture of biocomposites used in the manufacture of circulating materials, in order to reduce the use of plastics.[13]

Likewise, olive seeds can be used as raw material for the manufacture of other value-added materials, including activated carbon black agglomerates (CBA), carbon materials with a disordered structure, low crystallinity and variable morphology, which are highly microporous.[14] These materials have been used in wastewater treatment, due to their property of adsorbing a variety of metals, organic and toxic compounds, before the discharge of the effluent into the environment.[15] The excellent electrical properties of CBA obtained from olive seeds make them suitable for use as electrode material for supercapacitors, which is due to their high surface area and electrical conductivity.[16] Moreover, these active CBA could be used for the determination and quantification of a wide variety of substances, applying environmentally friendly adsorption analytical methods. Indeed, for a complex sample matrix (such as biological and food matrices), many different compounds may interfere with the analytes of interest. Thus, a preliminary treatment step is typically undertaken to purify the sample and isolate the desired compounds. Although traditional sample treatment techniques, such as liquid-liquid extraction and solid-phase extraction (SPE), have been widely reported, the current trend in the application of microextraction techniques is in line with the principles of green analytical chemistry. A microextraction technique derived from conventional SPE is pipette tip SPE (PT-SPE), also known as disposable pipette extraction (DPX).[17,18]

This microsample pretreatment technique can be considered as a miniaturized SPE, using a pipette tip as a solid-phase extraction column to improve efficiency.[19] Some features of PT-SPE include the reduction in the consumption of organic solvent, the amount of adsorbents, and extraction time, thus making the whole sample pretreatment process faster and greener.[20] Additionally, a pipette tip is a common laboratory consumable, being low-cost and easy to obtain. An additional advantage is related to the ease of generating the motion trajectory of the sample solution, since the conical structure has a large inner diameter at the upper end and a small inner diameter at the lower end.[21] The use of novel and efficient sorbent materials represents a main parameter in the PT-SPE procedure development, focusing on improving efficiency and tuning extraction selectivity. As reported in our previous studies, the carbon black agglomerates (CBA) synthesized from olive stone by-products obtained as a raw material from the olive oil industry, have a high surface area, with a pore size of less than 3 nm, confirming the presence of a micro/mesoporous structure. Likewise, these CBA exhibit a porous structure of a predominantly microporous character, which allows them to possess important characteristics when used as a sorbent material.

Caffeine is a naturally occurring alkaloid present in coffee, tea, cola drinks, and many cocoa-containing foods. In addition, this compound is an ingredient in a wide variety of pharmaceutical products. Therefore, it can be stated that caffeine is one of the most consumed stimulants of the central nervous system.[22] Belonging to the family of methylxanthines, the caffeine molecule presents high polar characteristics and low log Kow values (-0.10). Significant amounts of caffeine can be found in energy drinks, along with the presence of other stimulants, such as taurine, glucuronolactone, vitamin B, and herbal extracts. The presence of caffeine and B vitamins form an “energy mix”, used for marketing purposes.[23] Consumption of energy drinks among adolescents and young adults has increased rapidly worldwide, and according to Ares *et al*., warning labels can increase the intention to purchase energy drinks.[24] Although these products are heavily marketed to adolescents and young adults by emphasizing their effects of increasing energy, stimulation, and improving performance,[25] several papers have reported concerns about their safety when consumed by children, adolescents and young adults.[26,27] According to the available evidence, some of the negative effects of consuming these drinks include headaches, stomach aches, low appetite, sleep disturbances, cardiac arrhythmias, as well as increased hyperactivity, and inattention.[28,29]

The determination of caffeine content in energy drinks has been reported through the application of chromatographic methods, especially HPLC.[30] Other studies report the application of gas chromatography (GC-MS)[31] and UV-Vis spectroscopy,[32] with the disadvantages of using highly expensive

equipment, as well as the use of environmentally unfriendly organic solvents, respectively. HPLC methods typically involve a reverse-phase separation with UV-Vis detection,[33,34] as well as fluorescence detection.[35] Concerning the sample preparation stage, degasification is necessary to subsequently apply liquid-liquid extraction,[30] solid-phase extraction[31] or simply dilution.[36] This last strategy requires a high degree of efficiency and chromatographic resolution.

The present work details a method based on a laboratory-made PT-SPE, followed by HPLC-DAD, for the determination of caffeine in commercial energy drinks using an olive seed-based carbon black agglomerates sorbent. Certain characteristics, such as high porosity and high surface area, make this type of sorbent especially useful for the extraction of high polarity molecules, such as caffeine, from aqueous samples. Parameters such as the amount of sorbent, volume of sample in the loading step, type and volume of solvent for cleaning and elution were optimized. The resulting method presents important figures of merit, in line with the principles of green analytical chemistry.

EXPERIMENTAL

Materials

Methanol and acetonitrile HPLC-grade were supplied by J.T. Baker (Radnor, PA, USA). Purifying equipment from Thermo Scientific, model Barnstead MicroPure ST (Waltham, MA, USA) was used to obtain Type I ultrapure water. Caffeine standard was purchased from Sigma Aldrich (St. Louis, MO, USA). A stock solution was prepared at a concentration of 1 mg mL^{-1} by dissolving the exact mass in methanol. A working solution of the analyte was prepared by diluting the stock solution with the appropriate solvent. The solutions were stored at 4 °C until use. All reagents used were of analytical grade.

The synthesis and characterization of CBA were performed as detailed in the previous works.[18,37] In brief, after isolation, the solid residues from olive pits were cleaned and dried using a rotary oven at 200 °C, followed by carbonization at 700 °C and activation under steam. Then, the material was ground and a fine black powder was obtained, which was dried at 120 °C. After adding dilute H_2SO_4 and washing with abundant water, the material was impregnated with $ZnCl_2$ aqueous solution as an activating agent for 7 h. Here, the impregnation ratio was 1:4 (activating agent/initial material). The obtained material was washed, dried, and heated to 500 °C at 10 °C/min in a dynamic N_2 atmosphere at a 100 mL/min flow rate. The final temperature was maintained for 2 h. Finally, the solid was allowed to cool to room temperature in an oven under a N_2 atmosphere. Spinel was synthesized *via* mechanical activation of $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Li(CH_3COO){\cdot}3H_2O$ in the presence of polyethylene glycol polymer (PEG-400) for 1 h to adjust the particle size and shape of the particles. Further heating at 800 °C for three and a half hours produced a pure spinel with amorphous agglomerates with a pore size of 2 nm.

PT-SPE device preparation

PT-SPE devices were prepared, using a small piece of 20 µm porosity polyethylene (PE) frit (Merck, Darmstadt, HE, Germany), which was placed at the bottom of a 1 mL capacity pipette tip. This type of frit allows the solvent to pass through while the sorbent material remains in the tip. Subsequently, the amount of CBA was weighed on an analytical balance and placed inside the pipette tip to close the upper part of the tip with paraffin paper. The amount of the sorbent was carefully weighed, to obtain the least deviation in the devices, and consequently in the replicate analyses of the standard solutions and samples.

Adsorption studies

For the development of the adsorption studies and analysis of the commercial samples, the following equipment was used: centrifuge for 50 mL capacity tubes, LW Scientific brand, model C5 (Lawrenceville, GA, USA), an ultrasonic bath, BransonTM brand, model C5, CPX2800 (Ferguson, MO, USA), a mechanical stirrer from KoolLab, model KS-VM-1000 (Miami, FL, USA), and a vacuum pump from Millipore, model WP6111560 (Burlington, MA, USA). Standards, reagents, and CBA were weighed on an OHAUS Explorer Pro model analytical balance (Parsippany, NJ, USA). The extraction procedure was performed on an Agilent Technologies (Santa Clara, CA, USA) solid-phase extraction chamber. For the spectroscopic studies, a double beam spectrophotometer, Shimadzu model UV-1800 (Nakagyo-ku, Kyoto, Japan) was used, equipped with a deuterium lamp and a tungsten filament lamp. 10-mm quartz cells of optical path length were used for measurements. Acquisition and data treatment was made through the software UVprobe version 2.7 (Shimadzu).

The extraction study was conducted using a solution of caffeine at a concentration of 0.01 mg mL^{-1} prepared in ultrapure water. In the first test, it was evaluated if the extraction percentage was affected by the amount of agglomerates used, for which PT-SPE devices with 1 and 5 mg of the sorbent were prepared. For this, two aliquots of 1 mL of the standard solution were passed through two extraction devices, one containing 1 mg and the other containing 5 mg of CBA. Each aliquot was collected and diluted with 2 mL of water to obtain the absorption spectrum and corresponding absorbance values. A third aliquot of

equal volume was diluted with 2 mL of water and measured directly in the spectrophotometer.

The chromatographic studies were carried out in a Shimadzu liquid chromatograph, Prominence model (Nakagyo-ku, Kyoto, Japan), equipped with a DGU-20A5 degasser, an SIL-20A automatic injector, a CTO-A20 column oven, and an LC20-model pump, as well as AT, a CMB-20Alite control system, and an SPD-M20A diode array detector. For the data acquisition and analysis, the EZstart software version 7.4 (Shimadzu) was used. A 15-cm C18 XDB column with an internal diameter of 4.6 mm and a particle size of 5 μm from Agilent (Santa Clara, CA, USA) was used for the chromatographic separation. The mobile phase consists of a mixture of water (A) and methanol (B) (80:20, v/v) in gradient elution mode: 20% B at 0 min, held for 2 min, then until 50% at 5 min. Subsequently, this percentage was maintained for 2 min to decrease to 20% in 2 min. Finally, the initial conditions were obtained in 2 min. The total analysis time was 11 minutes, and the caffeine signal appeared at 6 minutes. The flow of the mobile phase was 1 mL min^{-1}, with an injection volume of 10 μL for the standard and sample solutions, and the analyses were carried out at room temperature. The maximum absorption of the caffeine signal was recorded at 275 nm.

Method validation

Although the guidelines of the International Council on Harmonization Q2(R1)[38] are commonly applied for method validation, some works in the literature point out the importance of carrying out this process differently from other standardization methods when standard addition is applied.[39,40] Therefore, specificity, linearity, precision, and accuracy parameters were evaluated. For the calculations of these parameters, Microsoft Excel software was used, using internally developed spreadsheets that have been previously validated.

RESULTS AND DISCUSSION

Initial extraction study

From an analytical point of view, the application of CBA synthesized from olive pits for the extraction of caffeine in aqueous media requires optimization of the amount of sorbent. In this sense, a low amount of sorbent is desirable, to avoid elimination problems and to ensure a more cost-effective method.[41] However, it is appropriate to think that the greater the amount of sorbent, the greater the retention percentage of the molecule in the PT-SPE device. Figure 1 shows the absorption spectra obtained, where the unextracted solution (upper) presents a higher absorbance signal, whereas the solution extracted with 5 mg (lower) presents the lowest signal and the caffeine dilution extracted with 1 mg of CBA (middle) has an intermediate signal. According to these results, it is possible to establish that the greater the amount of absorbent material, the greater the percentage of caffeine extraction will be. However, a greater amount of sorbent will generate greater retention of impurities and interferences present in the real samples, increasing the matrix effect, as observed in previous studies.[18]

Optimization of PT-SPE parameters

Before optimizing the different PT-SPE extraction parameters, chromatographic separation was achieved using the procedure reported by Ponce-Rodríguez *et al*.,[42] with some modifications, and obtaining the chromatographic signal of caffeine before 6 minutes. The compound was determined by comparing the resulting absorption spectrum with the theoretical absorption spectrum of caffeine. Based on the results of the extraction studies, initial tests were performed using 5 mg of CBA in the pipette tip. For this, a standard aqueous solution of caffeine with a concentration of 10 μg mL^{-1} was extracted and analyzed in the liquid chromatograph. The same unextracted solution was analyzed and the comparison of the signals showed an extraction percentage above 50%. When repeating the experiments using 1 mg of the sorbent material, the recovery percentage was 35%, following the same behavior of the initial extraction studies. Before proceeding to optimize the cleaning and elution steps, a commercial energy drink sample was extracted by pipetting 100 μL and passing it through the PT-SPE device. The resulting chromatogram showed an increase in the caffeine peak signal (Fig. 2). This may be due to the high interference retention of the sample in the nanostructured material, that is, a matrix effect.

The matrix effect is usually an issue in PT-SPE[18,43], thus a common strategy to reduce it is to minimize the sample volume. We tested passing from 100 μL to 50 μL of energy drink sample, since the smaller the sample, the less interference will be present. Here, a positive effect was obtained, reflected in a decrease in the caffeine signal, without compromising the detection limit required in the analysis, due to the high amounts of the analyte commonly found in this type of sample. The next strategy for reducing the matrix effect was to use a cleaning solvent capable of eliminating or at least reducing interferences, without affecting the amount of retained caffeine. However, the high polarity of caffeine limits the

use of solvents with high elution strength, such as acetonitrile. Accordingly, a low amount of methanol (100 µL) was used to reach a compromise between reducing interferences and limiting the loss of the analyte.

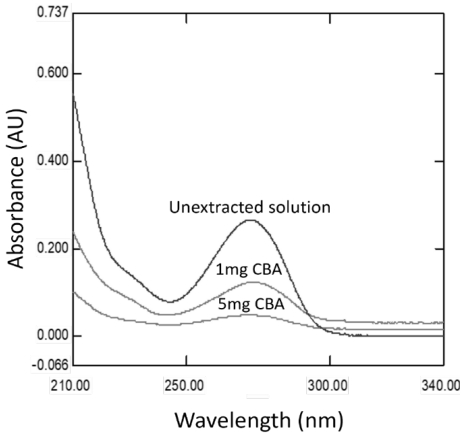

Figure 1: Extraction study (unextracted solution (upper), extracted solutions with 1 mg (middle) and 5 mg (lower) of CBA)

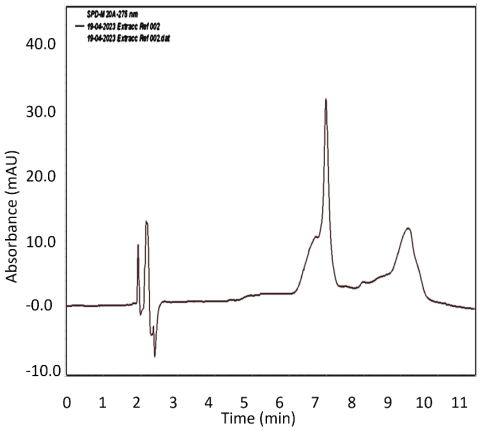

Figure 2: Chromatogram of the analysis of the energy drink with the presence of the matrix effect

Finally, the type and volume of eluting solvents represent crucial parameters in PT-SPE[44,45]. Therefore, the use of acetonitrile as an elution solvent was evaluated to achieve the desorption of the caffeine retained in the nanostructured material. For this purpose, tests were carried out with different amounts of the solvent, as well as the split of portions of the total volume. This last strategy has been reported to be especially beneficial for the elution of caffeine in SPE procedures, increasing the recovery percentage.[46] In this work, the best results were found when applying the elution with two portions of 300 µL of acetonitrile. The final volume of 600 µL was then collected in a vial to finally add 400 µL of water. This last step was necessary to avoid the tailing factor in the chromatographic separation, due to the polarity differences between the mobile phase and the elution solvent.

Despite the application of the strategies described above, an important matrix effect continued to be observed in the analysis of samples. Therefore, it was decided to apply one-point standard addition calibration for the analysis of commercial energy drink samples. This type of calibration excels at correcting matrix effects, due to the sample being part of the calibration solution.[47] The standard procedure involves the addition of very small volumes of highly concentrated aliquots of the compound to the sample,[48] therefore, in the proposed method, we decided to take a 25 µL aliquot of the energy drink sample and fortify it with 5 µL of a standard caffeine solution, whose concentration was 1000 µg mL^{-1}, and subsequently the PT-SPE was carried out with the previously optimized conditions. A second aliquot of the 50 µL sample, called "unfortified", is extracted in a PT-SPE device, in the same way as the first. Finally, the calculation of the caffeine concentration in the samples is obtained using the equations reported in the literature.[48,49] Figure 3 shows the PT-SPE procedure used for the determination of caffeine in energy drinks.

Method validation

The specificity and selectivity of the method were established by the analysis of spiked samples and the visual comparison of the absorption spectra obtained in the chromatogram of the standard solution and sample analysis. Linearity was determined using a 5-point standard addition calibration curve. In detail, five aliquots of 25 µL were taken from one of the energy drink samples and fortified with the standard solution in the range from 10 to 25 µg mL^{-1}. The theoretical concentration of the 25 µL aliquots, based on what was reported on the sample label, was 5 µg mL^{-1}. The calibration curve was prepared on 3 different days (n = 15). Regression analysis for calibration curve data indicates a linear relationship over the concentration range evaluated, with a determination coefficient equal

to 0.9911, and the regression equation was Y = 2381.7X – 38663, where Y is the peak area value and X is the concentration of caffeine. For intra-assay and inter-assay repeatability evaluation, the experiments included the analysis of one sample of energy drink, with n equal to 5, on two different days. From these experiments, the relative standard deviation (%RSDs) was calculated at the real concentration of the caffeine preexisting in the samples, and the values were less than 6%. Table 1 summarizes the results of the validation process.

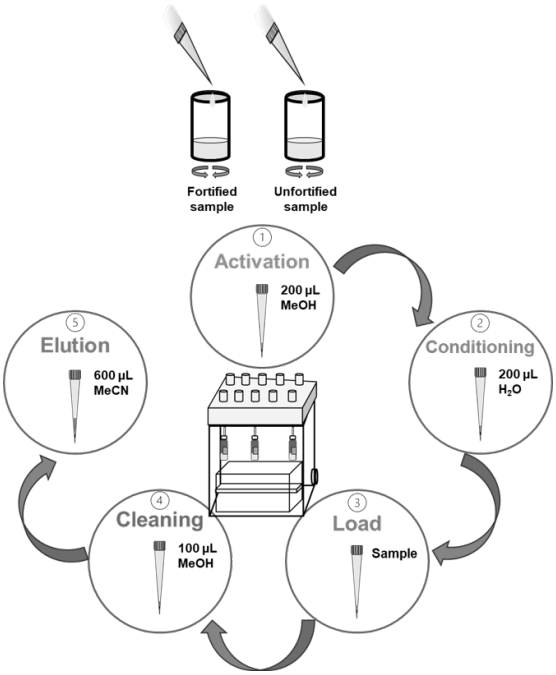

Figure 3: Scheme of the PT-SPE procedure optimized for the analysis of commercial energy drinks

Table 1
Results obtained in the evaluation of the performance of the method

Parameters	Values
Linearity range (µg mL^{-1})	0 – 25
Determination coefficient	0.9911
Slope	2381.7
Confidence interval of slope[1]	2246.86 – 2516.58
Standard error of slope	62.42
Intercept	38663
Standard error of intercept	1025.74
Intra-day precision (n = 5) (%RSD)	3.85
Inter-day precision (n = 10) (%RSD)	5.12

[1]95% confidence limit

Analysis of real samples

Three different brands of energy drink samples were purchased at a local store. Before analysis, the samples were placed at room temperature and degassed in an ultrasonic bath for 5 minutes, to ensure the accuracy of the volume measured. Each sample was analyzed in triplicate, following the procedure shown in Figure 3 and subsequently, the amount of caffeine was calculated. In the case of those samples that report the amount of caffeine present, the percentage obtained was calculated. Table 2 shows a summary of the results, indicating that ED 1 and ED 3 contained 91.82% and 91.08%, respectively, of the reported amount of caffeine on their labels. The percentage of caffeine found in sample ED 2 was not calculated because the label of this sample did not detail the theoretical amount added to this energy drink. Finally, it can be established that the caffeine concentrations per milliliter

found were in a range of 0.18 to 0.24 mg mL^{-1}. Moreover, Figure 4 shows representative chromatograms of the sample analysis. Figure 4A shows the analysis of sample ED 1 without fortification, while the analysis of the same fortified sample is shown in Figure 4B. Both chromatograms exhibited similar signal intensities for the caffeine peak.

Table 2
Results of the analysis of energy drink samples

Sample	Total volume of sample (mL)	Reported amount of caffeine (mg)	Caffeine found (mg) ± SD (n=3)	Caffeine percentage
ED 1	355	71	67.61 ± 2.11	91.82
ED 2	600	No reported	111.35 ± 4.24	NA
ED 3	296	76.8	69.95 ± 3.75	91.08

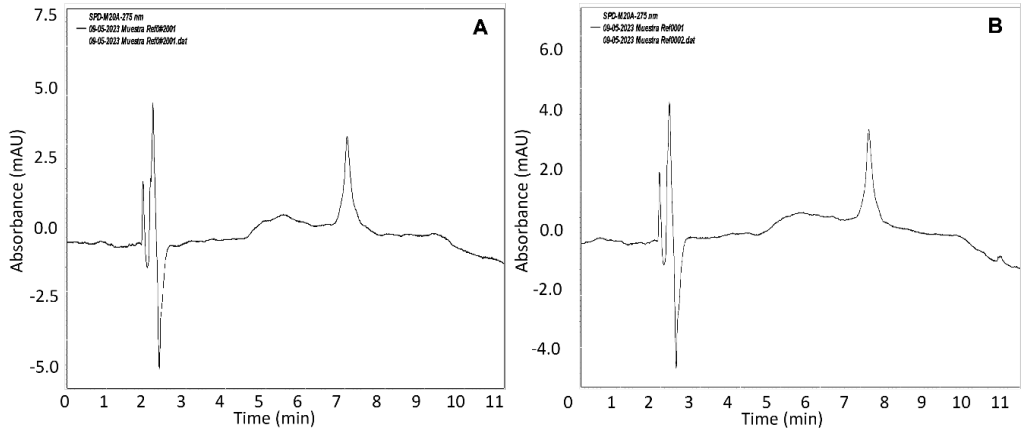

Figure 4: Representative chromatograms of: (A) ED 1 sample without fortification, (B) ED 1 sample fortified

CONCLUSION

Through a quick and simple process using as raw material a by-product of the olive oil industry – olive pits, we obtained carbon black agglomerates characterized by a low crystalline structure, micro/mesoporosity with a low pore size, and a high surface value. This porous material demonstrated a high capacity to extract the caffeine contained in energy drink samples. In this study, a novel and eco-friendly microextraction technique, known as PT-SPE, was used for the determination of caffeine present in these samples. The results were satisfactory for the extraction of the caffeine molecule, with high extraction percentages greater than 90% in the initial studies by UV-Vis spectroscopy. The developed PT-SPE procedure proved to be simple and economical, using only 1 mg of the nanostructured material and less than 2 milliliters of solvents; besides, the amount of sample required for one analysis was 50 µL, and the extraction time less than 5 min. Despite all these advantages, the high retention of impurities in the CBA produces a high matrix effect, which is difficult to eliminate, which is why it is necessary to apply the standard addition method. To avoid the laborious and exhaustive procedure of the standard addition method with multiple points, it was decided to apply the one-point standard addition calibration, simplifying the determination of caffeine in energy drink samples. Three samples of energy drinks were analyzed using the proposed procedure, and similar caffeine concentrations per milliliter were established for all of them.

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