



FUNDAMENTALS OF EXTRACTION AND SAMPLE PREPARATION FOR PURIFICATION AND QUANTIFICATION OF ANALYTES IN FOOD MATRICES

FUNDAMENTOS DE EXTRAÇÃO E PREPARAÇÃO DE AMOSTRAS PARA PURIFICAÇÃO E QUANTIFICAÇÃO DE ANALITOS EM MATRIZES ALIMENTARES

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Resumo

O Brasil apresenta uma vasta biodiversidade de matrizes alimentícias, fontes estas que podem ser utilizadas para extração de diversas biomoléculas que podem auxiliar em suplementação de produtos, atuar como corantes alimentícios ou até auxiliar processos industriais. Desta forma, o presente estudo tem como foco abordar formas tradicionais e emergentes para extração de compostos, bem como os aprofundar os fundamentos das variadas técnicas já utilizadas pela literatura científica para purificação dos extratos.

Abstract

Brazil has a vast biodiversity of food matrices, sources that can be used for the extraction of various biomolecules that can help supplement products, act as food coloring, or even assist in industrial processes. Thus, the present study focuses on approaching traditional and emerging ways for extracting compounds, as well as deepening the foundations of the various techniques already used by the scientific literature for purification of the obtained extracts.

INTRODUCTION

Brazil has a wide diversity of food matrices. They are "living" systems that have a relative complexity, requiring numerous cares at the time of extracting the compounds, as well as in the purification step of these extracts, with numerous factors that can influence the yield of these substances, from the use of solvents to extraction methods and purification of the desired compound (COSTA et al., 2017).

The extraction of substances or compounds from food matrices has been carried out over the years to extract components from these sources that can be used, and the use of organic solvents combined with classical or conventional methods is one of the most used forms, due to the practicality of extraction, as this

technique can be applied in different matrices in which the combination of agitation, solvent and temperature facilitates the transfer of compounds (SILVA et al., 2016; RAMIREZ et al., 2017; CARVALHO et al., 2018). Allied to the extraction, the purification step has as its fundamental objective to reduce or eliminate impurities or interferences that may cause distortion in the values found, being a mandatory step for further quantification of the desired analyte content in an equipment (spectrophotometer, fluorimeter, chromatography, among other equipment).

Thus, during the extraction and purification needs of food samples, this review will aim to address some ways already published in the literature for extracting various substances, as well as the purification

of these extracts for chromatographic and spectrophotometric analysis.

EXTRACTION METHODS

The extraction process is the fundamental step to obtain the desired compound, being a unitary operation of mass transfer, where the separation of the analyte present in the sample to the solvent will occur, through physical, chemical, or mechanical processes. These extraction steps can take place in different ways, whether in solid and liquid, liquid and liquid or gas and liquid (BARBA et al., 2016; NAFFATI et al., 2017).

Among the various processes used by researchers in the food field, two groups are most relevant: conventional or traditional extraction methods that are characterized by using tools such as drag extraction, pressing, agitation and maceration, where the choice of process will depend on the laboratory infrastructure, characteristics of the samples and the compound of interest. These methods have good yields, in addition to being low cost and capital processes, as they generally use simple equipment and at temperatures close to ambient. However, conventional extraction methods have some limitations, especially for thermolabile compounds, such as in case of bioactive compounds (phenolics, flavonoids, anthocyanins, carotenoids, among others) that could undergo oxidation, isomerization, and degradation in long periods of extraction (LEVEN and SCHNÜRER, 2005; MORGANTI, 2009; CAROCHO and FERREIRA, 2013; KAKKAR and BAIS, 2014; CASAMENTI and STEFANI, 2017; KIM et al., 2017; KIM et al., 2018).

In contrast to the use of these conventional techniques, unconventional or emerging methods have been developed that have varied principles for increasing the efficiency of extraction of numerous compounds, among this group of extraction methods,

the use of assisted extraction can be highlighted. focused microwave, which presents as a principle the use of microwave energy, which is a non-ionizing radiation that results in heating by migration of ions and rotation of molecules with dipole moments, which do not cause changes in the molecular structure. This extraction processing has some advantages, as it allows for faster heating and a short extraction period, because in plant matrices, the large amount of water absorbs the energy provided by the microwave, resulting in internal heating, generating the disruption of the cell wall and, consequently, facilitating the extraction process, in addition to allowing the migration of dissolved ions, which facilitates the penetration of the solvent into the matrix and considerably increases the extraction yield (SANSEVERINO, 2002; WANG and WELLER, 2006; CRAVOTO et al. 2008; SPIGNO and FAVERI, 2009; ALUPULUI, 2012).

In addition to microwave extraction, one can mention supercritical fluid extraction using carbon dioxide as a solvent, which is based on the use of a fluid when applied pressure and temperature conditions above the critical point, becoming supercritical, of this it forms the fluid with low viscosity and high diffusion capacity, enables better drag properties of substances than liquid solvents, resulting in an increase in the analyte content in the extract (BERNA et al., 2000; ANDREO and JORGE, 2006; BASEGMEZ et al. , 2017). Instead of using carbon dioxide, some researches have used subcritical water extraction (consisting of using water at temperatures above the boiling point, however with high pressure such that it remains in a liquid state), extraction with liquids pressurized (which has as its foundation the application of high temperature and pressure in reduced time intervals) among other methods (KO et al., 2014; CORBIN, et al., 2015; LI and GUO, 2016; SILVA et al., 2016).

Finally, it can mention the extraction using ultrasound, which can extract different components, due to the use of the phenomenon called cavitation, where the effects resulting from the ultrasonic waves generate a cycle of gas bubbles and cavities in the liquid (solvent). Once the bubbles collapse, high energy waves are formed in the cavitation zone, which when it is close to the cell wall, the resulting energy exerts a strong impact on the wall surface, thus increasing the permeability, allowing the entry of the solvent for capturing the compounds. In this way, this extraction method enables the increase of

the diffusion process and reinforces the mass transfer in short periods, being a "cheaper" method in relation to the others mentioned above (PATIST and BATES, 2008; TIWARI, 2015).

Both conventional and unconventional extraction methods are used, and in many works they have focused on the yield of compounds in comparison to the extraction efficiency, evaluating several variables, such as pH, temperature, equipment power, extraction time, among other factors. Numerous analyte extraction works in the most diverse food matrices can be seen in table 01.

Table 01. Utilização de métodos convencionais e não convencionais.

Sample	Solvent	Extraction method	Analyte	Author
Conventional extraction				
<i>Opuntia ficus</i>	Methanol and Ethanol	Agitation on magnetic bar	Betalain and Phenolics	Omar et al. (2016)
<i>Vitis sp</i>	Acetone, petroleum ether, chloroform, and hexane	Maceration	Carotenoids	Stéfani et al. (2017)
<i>Cucumis melo L.</i>	Ethanol	Orbital agitation	Phenolics	Mallekpayadi et al., (2017)
<i>Carbemete sawignon</i>	Ethanol	Agitation	Terpenes and Phenolics	Pintaça et al. (2018)
Unconventional extraction				
<i>Arbutus unedo L.</i>	Ethanol	Microwave	Anthocyanins	Jiménez et al. (2018)
<i>Trigonella foenum-graecum</i>	Ethanol	Microwave	Saponins and Phenolics	Akbari et al., (2019)
<i>Lonicera caerulea L</i>	CO ₂ and water	Supercritical	Anthocyanins	Jiao (2018)
<i>Camellia oleifera Abel</i>	Water	Supercritical	Oil and saponins	Wu et al., (2018)
<i>Medicago sativa</i>	Methanol	Ultrasound	Saponins	Hadidi et al., (2020)
<i>Stenocereus pruinosus e Stenocereus stellatus</i>	Methanol and trifluoroacetic acid	Ultrasound	Betalains	García-Cruz et al., (2017)
<i>Prunus persica L. Batsh</i>	Soy oil	Ultrasound	Carotenoids	Ordoñez-Santos et al., (2019)

Although there are numerous forms of extraction of various biomolecules, the direct application of these extracts is restricted to spectrophotometry and chromatography, as the extract

has several compounds that will interfere with the results generated by the equipment, thus, previous procedures are necessary for the elimination of part of the interferents and/or the concentration of substances

present at the level of traces (PANADARE and RATHOD, 2018). As in the case of samples that are rich in chlorophylls, this compound must be removed (through a saponification), enabling the procedure of analysis of total carotenoids, since the absorption of chlorophyll overlap in relation to carotenoids, providing overestimated results, as well as when analyzing the profile of the sample's carotenoids, where when performing the saponification process in the sample, it will influence both the removal of chlorophyll and the output of fatty acids, obtaining a more accurate and reproducible chromatogram (DE CAMPO et al., 2018; MATOS et al., 2019). In this sense, the choice of the desired purification technique should consider some factors such as the polarity characteristics of the compounds, preferably being simple and fast, having a low cost, providing extracts relatively free of interferents, having high recoveries with good accuracy, precision and mainly reproducibility (JIANG et al., 2019).

Spectrophotometric analyzes are the most widely used due to the low operational cost and simplicity of sample preparation procedures, where the spectrophotometer can measure the concentration of a kind of analyte in a transparent fluid. In this context, analyte species must absorb light within the range of the spectrophotometer, which is typically in the vacuum wavelength range of 190-1000 nm. The limit between UV light and visible light is 380 nm, and the limit between visible light and near infrared is 780 nm, where a solution must be presented which is clear, as there is no overestimation data, since the principle of using the equipment is a result of the absorption of light by the compounds, having turbid solutions as an interference. However, simpler forms of purification can be used, such as in the case of centrifugation, addition of solvents that, due to the different polarity of the compounds, allow a two-phase formation, where the

interferents separate more efficiently from the analyte, as well as the use of solutes, enabling greater clarity of the extract, as in alkaloid analyses, where there is a fraction of the aqueous extract of the sample that contains the alkaloids and needs to go through an extraction with chloroform for complete capture, but the presence of water makes the solution of cloudy chloroform, thus requiring the addition of anhydrous solutes such as anhydrous sodium sulfate, enabling the hydration of the solute, where by performing a filtration or centrifugation, clearer extracts are obtained to determine sample concentrations (VERMA and MISHRA, 2018; GOROG, 2018)

PURIFICATION METHODS

However, despite the ease of eliminating interferents in spectrophotometric analysis, chromatographic analyzes have a greater need for purification given the greater detection sensitivity of the method, thus, other techniques are necessary for the purification of these extracts, techniques that can be used also for spectrophotometry. Therefore, the development of techniques that enabled a purification or concentration of the analyte properly from the extract can be used, among these techniques stands out the solid phase extraction (SPE), solid phase microextraction (SPME), Dispersive solid phase extraction (DSPE), the magnetic bar sorting extraction (SBSE) and printed molecular solid phase extraction (MISPE) (SPELTINI et al., 2016).

Solid phase extraction

Solid phase extraction (SPE), as shown in figure 01, is a liquid-solid separation technique, which is based on the partition between matrix analytes and a solid adsorbent, being used in compounds with low, medium, and high polarity, depending on the adsorbent used and what is to be analyzed. Cartridges or

extraction membranes (disk) packed with chemically modified silica with octyl and octadecyl groups (C-8 and C-18) or copolymers such as styrene-divinylbenzene are often used (AUGUSTO et al., 2013; ANDRADE-EIROA et al., 2016; ANDRADE-EIROA et al., 2016a).

To obtain a good selectivity in the extraction, it is necessary to elute the analytes with specific solvents, or by using specific adsorbents for a given application. Despite its relevant contribution, SPE is limited to semi-volatile compounds with a boiling temperature above the boiling temperature of the solvent (BUSZEWSKI and SZULTKA, 2012; PŁOTKA-WASYLKA et al., 2015; MAYA et al., 2018).

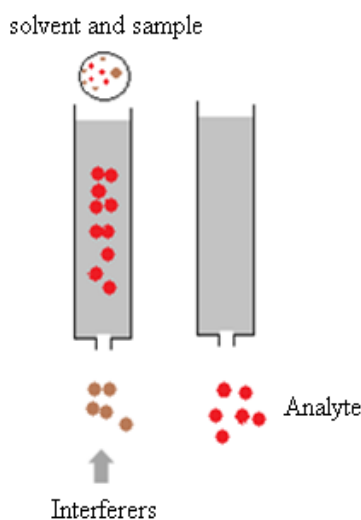


Figure 01. Representation of the SPE principle.

It is noteworthy that knowledge about the polarities of both the desired analyte and the interfering ones is essential for the application of solid phase extraction processes, because when the extracts cross the columns, if the analytes of interest are more polar than the impurities interfering, the normal chromatography phase principle (polar stationary phase and apolar mobile phase) should be chosen as the first option, and in this case an adsorbent such as silica, alumina or Florisil can be used (the separation mechanism is based on the mechanism of adsorption)

or a polar chemically bonded phase such as cyano or amino (separation mechanism is based on partition). In this way, when adding the extract containing the analyte of interest with the impurities in the polar stationary phase, the analyte will be retained, while the impurities (because they are less polar) will have greater affinity with the non-polar solvent, thus they will be eliminated together with the solvent. The analyte of interest retained in the solid phase will be removed using a more polar solvent, such as methanol, for example, enabling a good purification of the extract (SVEC, 2006; KOLKMAN et al., 2013; HERRERO-LATORRE et al., 2015; CALDERILLA et al., 2018).

It is noteworthy that the volume used in this step must be small, so that the sample is already present in the desired concentration for further analysis, so that there is no need for further concentration steps. However, it is noteworthy that if there is the opposite, that is, the analytes of interest are less polar than the impurities, a solid phase operating in reverse mode is recommended, with the solid phase consisting of silica gel chemically bonded to a nonpolar organic group, usually of the C-18, C-8, C-4 or C-2 type, will enable a good purification (AUGUSTO et al., 2013; HÁKOVÁ et al., 2018).

Solid phase microextraction

Another method of purification is solid phase microextraction (SPME) which has been used to isolate and concentrate analytes to adequate levels and obtain a level of sample cleanliness that does not compromise chemical analysis where its steps create the link between the chemical matrices and analytical instruments, being particularly interesting for gas chromatography. The basic SPME device consists of retaining the analytes by means of a capillary fiber combined with a polymer that can be polydimethylsiloxane (PDMS), polyacrylate (PA) or carbowax (Cwx) or a solid adsorbent (Carboxen =

microparticulate active carbon), with subsequent thermal desorption in the injector of a chromatograph (GHAEMI et al., 2014; PIRI-MOGHADAM et al., 2016; PIRI-MOGHADAM et al., 2017; REYES-GARCÉS et al., 2017).

The sequence of procedures to perform extraction and desorption in the chromatograph injector is shown in figure 02.

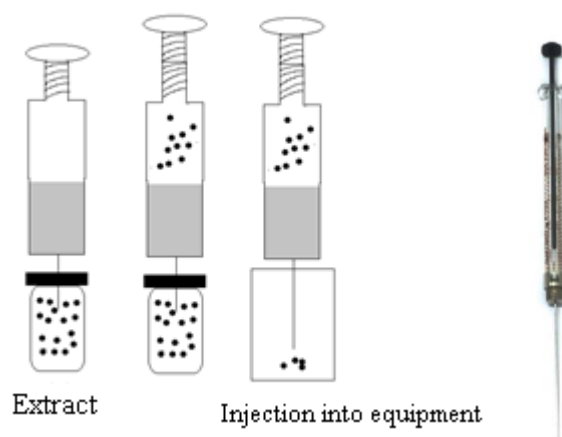


Figure 02. Representative scheme of SPME extraction

Magnetic bar sorting extraction

Magnetic bar sorting extraction (SBSE), as shown in figure 03, was developed by Baltussen et al. (1999), based on some SPME principles, using instead of fibers, a stir bar coated with polydimethylsiloxane (PDMS). In a simplified way, the procedure can be described as follows: the magnetic bar is inserted in the aqueous phase to be analyzed and the

extraction/concentration of the compounds of interest takes place during the stirring process. After a certain period, this is removed from the aqueous solution and the compounds are extracted and then analyzed. This stir bar comprises a magnet inserted into a glass tube, which is covered by a layer of PDMS (NOGUEIRA, 2015; ROCÍO-BAUTISTA et al., 2017).

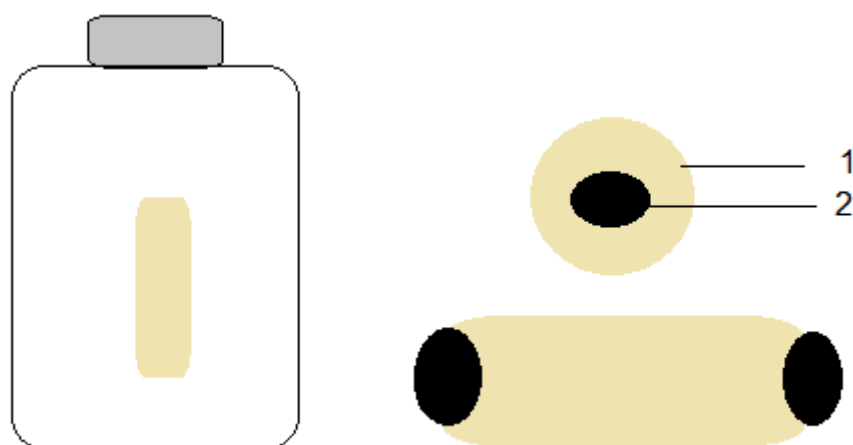


Figure 03. SBSE representation; where 1 (Polymer) and 2 (Magnetic bar).

It is noteworthy that SBSE has numerous characteristics that favor the use of this process, as the analytes are not retained on the active surfaces of the extracting material as strongly as in the case of common adsorbents but are partitioned or dissolved in the polymeric film retained throughout its span and thickness. As this dissolution or association process is relatively weak, the degradation of unstable analytes is significantly less or absent in PDMS when compared to associations with phases such as silica, alumina or Florisil®. Based on the weak interactions with the analyte, these can be removed at moderate temperatures, minimizing losses of thermolabile analytes. In addition, PDMS film degradation fragments are easily recognized by a selective mass detector, and in theory, the holding capacity of PDMS for certain compounds is not influenced by the presence of large amounts of water or other analytes, as they are all the solutes have their own partition equilibrium in the polymeric phase and the displacement does not occur, causing many researchers to choose the use of SBSE (CAMINO-SÁNCHEZ et al., 2014; NOGUEIRA, 2015).

Dispersive solid phase extraction

Another purification technique that can be mentioned is D-SPE, which is the dispersive solid phase extraction, as shown in figure 04, with a quick and simple procedure, allowing to obtain cleaner extracts for multi-residue analyses. D-SPE generally involves the use of one or more sorbents, together with anhydrous magnesium sulfate, in a centrifuge tube to remove co-extracts from the organic extract. It is used to clean extracts in both plant and animal samples, based on the so-called QuEChERS method, which means fast, easy, cheap, effective, resistant and safe (ISLAS et al., 2017; KHEZELI and DANESHFAR, 2017; CHISVERT et al., 2018; COLLINS et al., 2019).

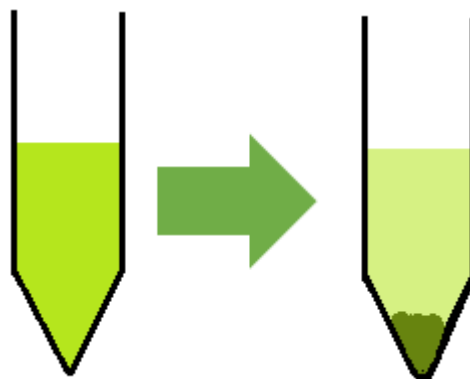


Figure 04. Representation of D-SPE purification using sorbent and magnesium sulfate.

The D-SPE proposed by Anastassiades et. al., (2003) is based on a quite simple method to clean the sample intended for the chromatographic analysis of residues and food contaminants. In this way, being considered one of the cheapest purification methods, when compared to the others.

Molecular solid phase extraction

The printed molecular solid phase extraction (MISPE) was based on the concept proposed by Pauling (1940), where an antigen was used as a template molecule to originate a polypeptide chain of antibodies. Based on this information, Dickey, in 1949, carried out several tests, which promoted a technique that, through specific adsorbents with memory inherent to a given compound, with the ability to specifically bind with the mold molecule, promoted a greater selectivity in the extraction of compounds.

The synthesis of these materials occurs as a function of a template molecule by non-covalent or covalent bonds, enabling the formation of a complex between the desired substance and the functional monomer (standard), having in this process the polymerization by means of a radical agent, which it will propagate and form the complexes that will be fixed through cross-linking reactions of the polymers, in this way, the molded molecules are extracted from the

polymer matrix, resulting in a highly selective and specific polymer with the mold formed (ALVES et al., 2015; SARAFRAZ-YAZDI and RAZAVI, 2015; MADIKIZELA et al., 2018).

MISPE is a technique, which takes advantage of synthesized polymers that have specific sites of interaction with the compound of interest, being used as a stationary phase for purification and/or concentration. It is noteworthy that the use of these printing polymers has numerous advantages, as it has high selectivity, because these polymers have specific sterically molded sites coming from a molecule or analyte of interest, resulting in retention in the polymer of the desired component, having the use of these polymers already applied to various techniques such as capillary electrochromatography, solid phase extraction, liquid chromatography, selective adsorbents in chemical sensors, among others (MOHAJERI et al., 2010; YANG et al., 2014; SARAFRAZ-YAZDI and RAZAVI, 2015; NCUBE et al., al., 2019).

Thus, depending on the purification needs of the sample, there are numerous existing methods that can be used to carry out an adequate purification, examples of these methods in foods can be seen in table 02.

Table 02. Evaluation of works that use different extraction and purification principles.

Ice Cream	Technique	Matrice	Analytes	Instrumental	Author
Polyurethane/pyrocatechol	SPE	Foods	Cobalt, copper and nickel	Flame Atomic Absorption Spectrometry	Lemos et al., (2007)
VBADB	SBSE	Milk and swine urine	β -Agonist	HPLC-MS/MS	Huang et al., (2013)
Stearic acid	MEPS	Multiple samples	Pb (II)	FI-FASS	Dadfarnia et al., (2006)
MIP- vanillin	SPE	Vanilla fragrans and beer	Vanilla	UV e HPLC	Wang et al., (2006)
MIP	MSPE	Honey	Cloranfenicol	LC-MS/MS	Chen and Li (2014)
Silica gel/MIP	SPE	water, soil and wheat	Dufulin	HPLC	Miao et al., (2014)
Immobilized ionic liquid-silica	SPE	Foods	Acrilamida	HPLC	Zhao et al., (2014)
Solica-Nb ₂ O ₅	SPME	Aqueous solution	Álcoois e fenóis	CG/FID	Oliveira et al., (2005)
MTMOS-TEOS	DSPE	Foods	Acrilamidas	CG-MS	Omar and Ibrahim (2014)
C18	SPE	Avocato	Abamectinas	HPLC-FL	Borges et al., (2007)
C18	MEPS	Beer	Prenilflavonoides	UHPLC	Gonçalves et al., (2013)
C8	MEPS	Wine	Componentes fenólicos	UHPLC/PDA	Gonçalves et al., (2012)
Fe ₃ O ₄ -SiO ₂ – MIP	SPE	Eggs, powdered milk and pig feed	Dimetridazol	HPLC-UV	Ji et al., (2009)
ZIF-8	SPE	water and milk	Tetraciclina	HPLC	Khajeh and Golzary (2014)
BaSO ₄ -APRB	DSPE	Residual Waters	POPs	ICP-OES e IC	Ding et al., (2010)
MWCNTs	DSPE	Vegetables	Pesticidas	CG	Perez et al., (2010)
MWCNTs/P2AT	SPE	Fish and sediment	Cd(II) e Pb(II)	AA	Ren et al., (2011)
MWCNTs	SPE	Water	Agrotóxicos	PLS	Zhao et al., (2012)
Methacrylic acid monomer	MISPE	Canned food	Bisphenol	LC-ESI/MS	Alnaimat et al., (2019)
rGO/AuNPs	D-SPE	Fried foods	acrylamide	LC-MS/MS	Cheng et al., (2019)
Sephadex G-150	SPE	Miscellaneous foods	Íons de crómio	Potenciostato	Filik and Avan (2019)
PDMS	SBSE	Coffee & baby food in a jar	Furan	GC-MS	Ridgway et al., (2010)
PDMS	SBSE	Beer	52 volatile compounds	GC-MS	Ruvalcaba et al., (2019)

CONCLUSIONS

The solid phase extraction technique (SPE) is the most used technique in the process of purification and/or concentration of analytes, being the most versatile, as it presents numerous possibilities to use the most different solid phases, enabling different methods of purification of the sample.

Generally, SPE and its types (SPME, D-SPE, SBSE, r-DSPE) are not very recent techniques, but currently they are used in new differentiated matrices that demonstrate their versatility, in addition to the possibility of their improvement (automation), makes these techniques widely used in sample preparation, which often lead to different results when compared to other extraction methods.

For a chromatographic and spectrophotometric analysis to present good results, the sample extraction and preparation step is of great relevance, where for each analyte of interest without interfering there will always be a sorbent and a suitable extraction method, with which the best results were found purification and extraction.

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