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Miniaturized solid-phase microextraction of caffeine in tea samples: assessing the environmental friendliness of the methods with the GAPI tool

Abstract. Over the last few decades, there has been a significant increase in tea consumption worldwide, leading to a growing concern for the quality and nutritional value of tea. The demand for high-quality tea has necessitated the development of new analytical approaches to ensure adherence to quality standards and process control. One area of particular importance is the control of caffeine in tea, as regular consumption of caffeine in large quantities can contribute to the leaching of beneficial minerals from the human body. To address this issue, in this work have developed a rapid technique for determining caffeine in tea samples using miniaturized solid-phase microextraction (mini-SPME) combined with chromatography-mass spectrometry (GC-MS). The study included the screening of teas available in the market of Kazakhstan. In this study optimized the basic parameters of miniaturized solid-phase microextraction of caffeine from tea samples, including fiber coating, extraction temperature, extraction time, and pre-incubation time. The fiber coating used in the study was DVB/CAR/PDMS, and the optimal extraction temperature was found to be 90°C, with an extraction time of 20 minutes and a pre-incubation time of 5 minutes. The developed method is efficient and can be used for determination and control of traces of caffeine in tea samples. Furthermore, the study evaluated the environmental friendliness of the methods for analyzing caffeine in teas using the GAPI tool. The GAPI tool is a software program that assesses the environmental impact of a chemical process by considering several parameters, such as toxicity, energy consumption, and waste generation. The results of the study showed that the developed method was environmentally friendly.

Key words: miniaturised solid phase microextraction, tea, caffeine, gas chromatography, mass spectrometry.

1. Introduction

Tea is one of the most popular beverages that can be served both cold and hot due to its beneficial nutritional properties. One of the largest tea producers and exporters worldwide is China (approximately 35% of total world production) [1]. Depending on the process used, tea can be divided into several types such as black, green, yellow, and white. Each type of tea has its own unique characteristics which include taste and aroma. The quality of tea is determined by numerous factors. Some of the most important factors are variety, harvest season, soil fertility, climatic conditions and the process of direct tea production.

Green tea and black tea come from the same plant (Camellia sinensis) but are treated differently in the production process. To produce green tea, the fresh leaves are immediately steamed to give a dry crop and prevent fermentation. The steaming process removes the enzymes responsible for destroying the coloured pigments in the leaves and allows the tea to take on a green colour during the subsequent rolling and drying process [2].

Tea contains compounds beneficial to human health, such as fluoride, caffeine and minerals. Studies have shown that the presence of trace elements (metal with a high relative atomic mass) in tea is due to the cultivation of tea plants in highly acidic soils where trace elements have a high bioavailability for rooting [3].

The most important indicators of tea for its evaluation, are organic compounds such as, volatiles, alcohols, hydrocarbons, and ketones. Tea aroma is a collection of organic compounds that can be identified by various experimental methods. Tea aroma is influenced by some major organic compounds such as caffeine. To extract a particular organic compound in previous works, methods such as, solid phase microextraction (SPME), simultaneous distillation-extraction (SDE) steam distillation (SD) have been used [4-7]. The SPME method is one of the most popular and efficient extraction methods. The advantage of this method is the elimination of organic solvents, it has a low cost compared to other methods and it is easy to use for extractions. In previous scientific works, the SPME method has often been used in combination with mass spectrometric detection (GC-MS) as this combination works well for the analysis of aromatic and volatile substances. The main reason for this is the high recovery of the target analytes due to the SPME and the high accuracy, wide dynamic range and reproducibility of the GC-MS. In articles [8], [9] the aromatic compounds of different tea varieties were investigated for qualitative characteristics through sensory evaluation. HS-SPME/GC-MS was used to isolate the target volatile components.

Table 1 shows works on the determination of caffeine from various countries, where it can be seen that the predominantly widely used method of sample preparation is the SPME method. Also from the literature review, it can be seen that GC-MS, HPLC and other instruments are used to investigate and identify different volatile organic compounds in teas, particularly caffeine.

The aim of this work is to develop a miniaturized and robust analytical technique based on miniaturized solid phase microextraction (mini-SPME) followed by GC-MS for the determination of caffeine in teas. For the first time a vial volume of 1.8 ml was proposed for the mini-SPME procedure using very small amounts of tea. The most important parameters (i.e. extraction temperature, type of extraction fiber, addition of NaCl) were optimised using an experimental design strategy to obtain the highest extraction efficiency. The specific tool used to assess the environmental friendliness of a method depends on the type of method and on the authors themselves. Each author can use what he/she considers most appropriate for his/her research method. The choice of GAPI as a tool to assess the environmental friendliness of the mini-SPME sample preparation method was based on the observation of survey data and sample preparation characteristics (several steps, use of different reagents, waste, etc.), whereas other tools cannot give such a comprehensive assessment. Finally, the validated method was applied to a wide range of real tea samples.

Table 1 – Previously studied works on caffeine determination from different countries

№	Target compound	Samples	Identification method	LOD	Recovery (%)	Country, reference
1	Caffeine	74 tea samples	HPLC-DAD-MS	1 ng	99.57-105.28	China [10]
2	Caffeine	Puer Tea	GC-MS	-	-	China [9]
3	Caffeine	12 green Puer teas	GC-MS	-	-	China [1]
4	Catechins, caffeine and theanine	45 samples of five fresh leaves	GC-MS, HPLC	3.92 mg/kg	-	Republic of Korea [11]
5	Catechins and caffeine	Green tea	HPLC	-	-	China [12]
6	Caffeine and catechins	Green tea	HPLC-DAD	0.03 mg/L	2.90	Saudi Arabia [13]
7	Catechins, caffeine and theanine	Green tea	HPLC	-	-	China [4]
8	Caffeine	Tea and coffee	Cyclic voltammetry (CV) AUTO-LAB	30.15 ± 0.09 µM	99.83	Iran [14]
9	Caffeine	Yinghong dark tea No. 9	GC–MS	-	-	China [6]
10	Caffeine	Jinmudan tea	GC–MS	-	-	China [8]

2. Materials and methods

2.1 Sample preparation

2.1.1 Tea samples

Various tea samples, including two types, such as black tea (BT), green tea (GT), from different manufacturers, were purchased in Almaty, Kazakhstan. The samples were purchased from various supermarkets in the city. Ten tea samples shows in Table 2 from the Kazakhstan market were analyzed. Samples were purchased in factory boxes, sealed with foil, stored at controlled temperature (20°C) and protected from light until analysis.

Table 2 – Types of tea samples analysed.

№	Name of tea	Type of tea	Addition information
1	Tess Lime	green tea	not packed
2	Piala Gold	green tea	not packed
3	Assam Classic	black tea	granulated
4	Riston Earl Gray	black tea	not packed
5	Simba Evening	black tea	granulated
6	Bayce	green tea	not packed
7	Piala Gold Classic	black tea	packed
8	Tess Lime	green tea	packed
9	Lipton Clear	green tea	packed
10	Lipton Yellow Label	green tea	packed

2.1.2 Reagents and materials

Distilled water (GOST 6709-72 distilled water), sodium chloride (NaCl 97,5 %) were purchased from Merck (Darmstadt, Germany). The caffeine used as internal standard (IS) was obtained from Merck (Teddington, UK). Individual stock solutions of caffeine (concentration about 10,000 mg L^{-1}) were prepared in boiled distilled water. Further dilutions and mixtures were prepared in distilled water. The stock solutions were stored in glass vials, protected from light, at 20°C.

Commercial 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 50/30 µm divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) and 85 µm carboxene/polydimethylsiloxane (CAR/PDMS) fibers and an SPME hand holder were from Supelco (Bellefonte, PA, USA). Before first use, the fibers were conditioned according to the manufacturer's recommendations by placing them in a GC injector under a helium stream at 250°C (PDMS/DVB), 270°C (DVB/CAR/PDMS) and 300°C (CAR/PDMS) for 30 min.

2.1.3 Miniaturized solid-phase microextraction (mini-SPME)

Under optimized conditions (see "Results and discussion"), 100 mg of tea was placed in a 1.8 mL glass vial. Then 2 µl hot water solution of 20 mg L^{-1} containing the internal standard (caffeine) was added to a final concentration of 200 ng g^{-1} and the sample was diluted by adding 200 µl ultrapure water. The vial was covered with an aluminum lid with partitions and the agitator was maintained at 90°C. The samples were stirred with a magnet using a tiny piece of stainless steel clamp (0.8 mm diameter, 3 mm length). After 2 min of sample equilibration, the DVB/CAR/PDMS fiber (triple) was subjected to headspace over the sample (headspace mode, HS) for 20 min. The fiber was then retracted into a syringe holder needle and immediately subjected to thermal desorption at 270°C in the GC input port for 5 min, and GC-MS analysis was performed.

2.1.4 GC-MS analysis

GC-MS analysis was performed using Agilent 7890A (GC) – 5975C inert with three-axis detector (MSD) from Agilent Technologies (Palo Alto, CA, USA). Separation was performed on a DB-35MS, 0.25 µm (30 m × 0.25 mm) capillary column from Agilent Technologies. Helium (purity 99.999%) was used as carrier gas at a constant flow rate through the column of 0.6 mL min^{-1}. The GC oven temperature was programmed from 40°C (held for 3 min) to 240°C at 10 ◦C min^{-1}. The total operating time was

30 min. Splitless mode (1 min, 75 ml min^{-1}) was used for injection. The injector temperature was set to 270°C. The mass spectrometric detector (MSD) was operated in positive electron ionisation (EI) mode (+70 eV) and the transfer line, quadrupole and ion source temperatures were set to 230°C, 150°C and 230°C respectively. Fragments with mass/charge (m/z) between 70 and 650 were monitored in full scan mode (FS). The system was operated under Agilent MSD ChemStation E.02.00.493 software.

2.1.5 Data processing

The identification of caffeine was done by their mass spectra. The caffeine retention time is usually 0.1 min longer than the true retention time, but a deviation of ± 0.1 min is acceptable. For confirmation of identification, the ratio of the peak areas of caffeine in the m/z 70 to 650 ions chromatograms should be checked. If the resulting ratio is not in this range, it is assumed that caffeine is not detected. The chromatographic peaks were identified by the ChemStation software and identified by means of the NIST 08.L MS data library and the retention indices method. The relative contents of the chromatographic peaks were determined by peak area normalization based on the total ion current. The retention index of caffeine was obtained using 1 µl of mixture under the same experimental GC-MS conditions. The data matrix was transferred to the SIMCA-P12 package (Umetrics, Umeå, Sweden) where PCA, CA and OPLS-DA analyses were performed. Duncan's multiple series tests using SPSS 17.0 software were used to test the significance of differences between different groups of Pu-Erch tea samples.

2.2 GAPI (Green Analytical Procedures Index) tool for assessing the sustainability of sample preparation

A tool for assessing the sustainability of each sample preparation step was first proposed in 2018 by the author J. Plotka-Wasylka. The GAPI tool is five pictograms consisting of fifteen individual compartments, each of which is assessed by three levels of colour scales [15]. Green indicates low environmental impact, yellow indicates medium environmental impact and red indicates high environmental impact scale. The tool evaluates each step according to the reagents used, collection and storage conditions, volume of solvents used, toxicity and flammability of each reagent according to NFPA fire safety requirements [16], also taking into account the energy consumption per sample used and how much waste ends up in the environment. The choice of the environmental assessment tool GAPI in this study is based on a literature review [18]. A review of the literature shows that all possible sample preparation methods can be evaluated with this tool. The GAPI tool allows the assessment of all steps in sample preparation, from sampling to waste. In this way, many factors affecting the environment can be taken into account. The compact and easy-to-use GAPI pictogram allows several methods to be compared simultaneously and clearly in order to select the most environmentally friendly method for a specific study [19].

3. Results and discussion

3.1 Miniaturization

One trend in sample preparation is the miniaturization of processes and methods. In pursuit of sustainable and high-quality results, researchers are striving to minimize preparation costs and time, as well as to obtain as few residues as possible and to develop procedures that can be easily implemented in other laboratories. In this study, the mini-SPME method was proposed for tea extraction. So far, no miniaturization of the whole process has been proposed. In most of the studies the sample amount was up to a few grams [13], [20]. In order to minimize the procedure, the extraction was carried out with 100-200 µL g of tea extract in 1.8 ml vials.

3.2 Selection of the optimal fiber coating for extraction

The type of fiber coating is one of the most important parameters of mini-SPME affecting extraction efficiency. As the target compounds have a wide polarity range, extraction efficiency was evaluated on three types of mini-SPME fibers: 65 µm PDMS/DVB (medium polarity), 50/30 µm DVB/CAR/PDMS (wide polarity range) and 85 µm CAR/PDMS (high polarity). Experiments were carried out using 1.2 g of different teas. First of all, a pre-sample preparation step was carried out by analyzing the study samples beforehand. Several tea samples were ground in a coffee grinder and sieved through a 1mm sieve. Then 1g of a homogeneous sample was measured on an analytical scale. After making 1 sample in 3 parallels, 30 ml (1:10) of boiled water at 90° C was added to 3 g of sample and allowed to stand for 15 minutes. Then 100 µl of tea extract was transferred to a 1.8 mL vial, where extraction took place accordingly. The DVB/CAR/PDMS fiber was then left to incubate in a magnetic agitator. After 30 minutes the fiber was sent for GC-MS analysis. Fiber coating plays a crucial role in the extraction efficiency of mini-SPME. The type of fiber coating affects the ability to extract target compounds, especially considering their polarity range.

The results are summarized in Figure 1. As can be seen, DVB/CAR/PDMS and CAR/PDMS fibers showed the highest chromatographic responses for caffeine. In addition, the most volatile compounds showed clearly higher results with DVB/CAR/PDMS fiber, while the use of PDMS/DVB fiber showed the lowest response for volatile compounds. The results indicate that the DVB/CAR/PDMS and CAR/PDMS fibers exhibited the highest chromatographic responses for caffeine. This suggests that these fibers were more efficient in extracting caffeine from the tea samples.

The choice of fiber coating in mini-SPME significantly impacts the extraction efficiency, particularly in terms of target compound polarity. The DVB/CAR/PDMS and CAR/PDMS fibers were found to be effective in extracting caffeine, while the DVB/CAR/PDMS fiber was particularly efficient in capturing volatile compounds. These findings highlight the importance of selecting the appropriate fiber coating for specific extraction requirements in mini-SPME analysis.

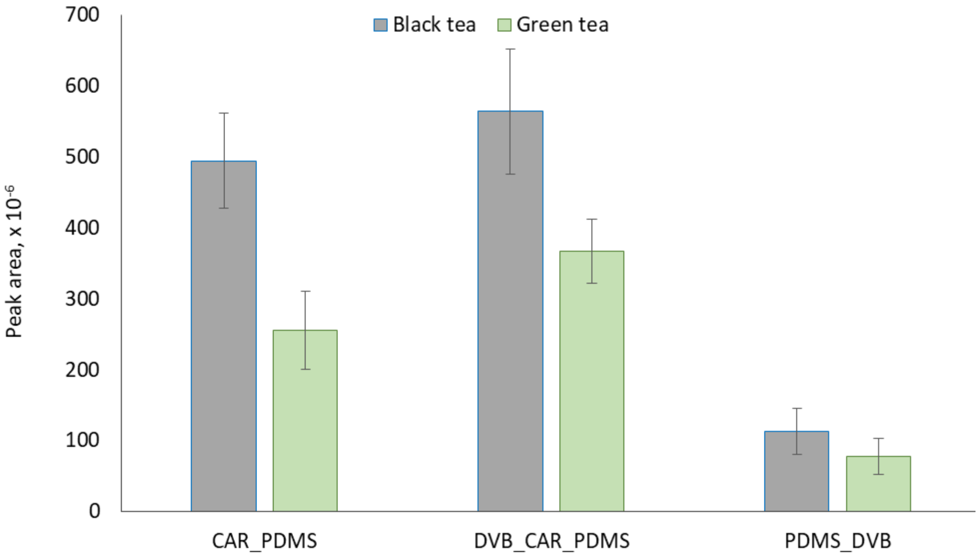


Figure 1 – Plot of fiber type versus caffeine peak area in tea samples.

3.3. Selection of the optimal extraction temperature

Temperature is also an important factor in achieving a suitable extraction as it has different effects on the mini-SPME method. As can be seen in Figure 2, performing mini-SPME extraction at the highest temperature of 90°C – gave 1,5 times higher results for organic volatile compounds, especially for caffeine, for which the results increased by a factor of 1.5 to 2. In other studies, higher temperatures than 90°C were not tested due to the possibility of metabolite formation or degradation of compounds.

Temperature is an important parameter in mini-SPME extraction. Higher temperatures, specifically up to 90°C, can lead to increased extraction yields for organic volatile compounds, including caffeine. However, caution should be exercised when exceeding this temperature range to avoid potential issues related to metabolite formation or compound degradation. Further studies may be necessary to explore the effects of even higher temperatures on mini-SPME extraction while considering the stability of the target compounds.

3.4 Selection of the optimal extraction time

In mini-SPME, the time required to reach equilibrium depends in particular on the properties of the target analytes, the sample matrix and the fiber coating. The following extraction times from 5 to 30 minutes (5, 10, 15, 20, 25, 30) were used during the optimization process. The time profile curves for caffeine are shown in Fig. 3. As can be seen, the time required to reach equilibrium depends on the caffeine compound. In general, the eluted caffeine reach equilibrium for green and black tea after

20 min of exposure, while most of the remaining compounds reach equilibrium in the time interval studied (30 min), demonstrating that the extraction process is quite fast. Because, in this study the target compound is caffeine, after reaching equilibrium after 20 min there is no point in investigating other time zones. An extraction time of 20 min seems to be optimal for the determination of a sensitive and high-performance caffeine extraction. Here also with increasing extraction time an increase of the peaks of the target analytes is observed. Therefore, in this case an optimal extraction time of 20 min was chosen. However, increasing the extraction time leads to an unstable analytical signal for caffeine, with the highest peak reached at 20 min, but the result shows that there is no big difference in peaks between 20 and 30 min. Thus, based on the data obtained, it was concluded that 20 min is the optimum extraction time, as it provides adequate detection of caffeine.

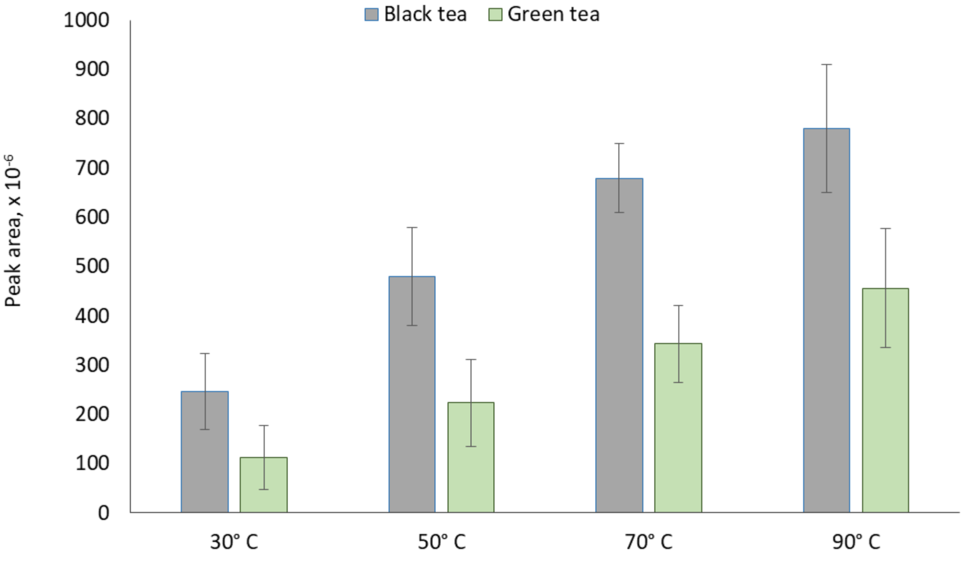


Figure 2 – Temperature versus peak area graph for caffeine in tea samples.

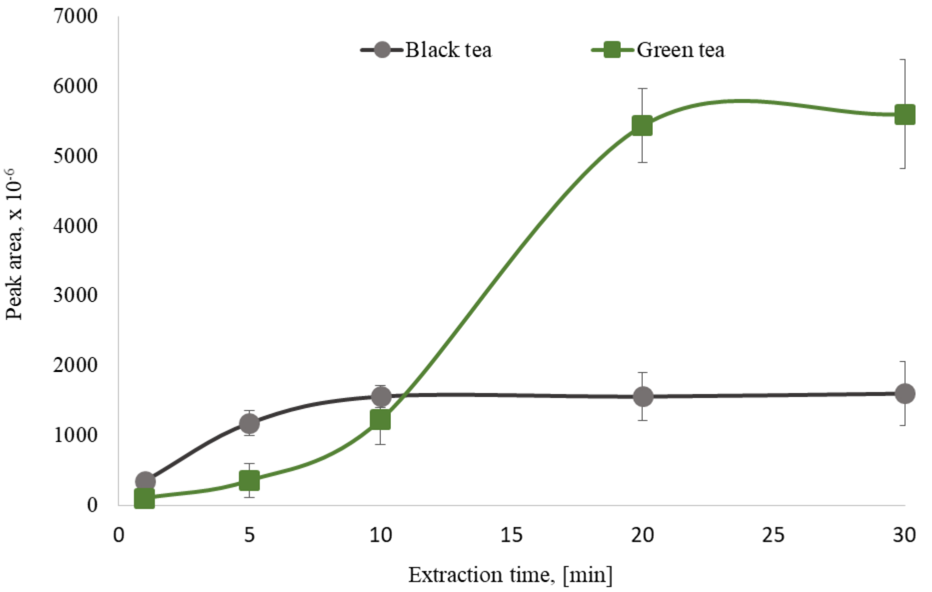


Figure 3 – Plot of extraction time versus peak area of caffeine in tea samples.

3.5 Selection of the optimal salt concentration

The method used to enhance the extraction of organic analytes from tea samples is to add a strong electrolyte that increases the ionic strength of the solution.

To determine the effect of ionic strength on the extraction of caffeine, 0.1, 0.2, 0.3 g sodium chloride was added to a mini-SPME-GC-MS tea extract without addition. The results of the experiment are shown in Fig. 4. Experimental results showed that increasing the concentration of sodium chloride led to a decrease in caffeine response for most samples. The highest response was recorded in the analysis of tea samples added 0.2 g of sodium chloride.

Thus, 0.2 g sodium chloride is most appropriate for increasing the caffeine response in tea samples. In the case of tea samples containing significant amounts of dissolved salts, it is necessary to supplement the quantitative method with a standard additive or internal standard method.

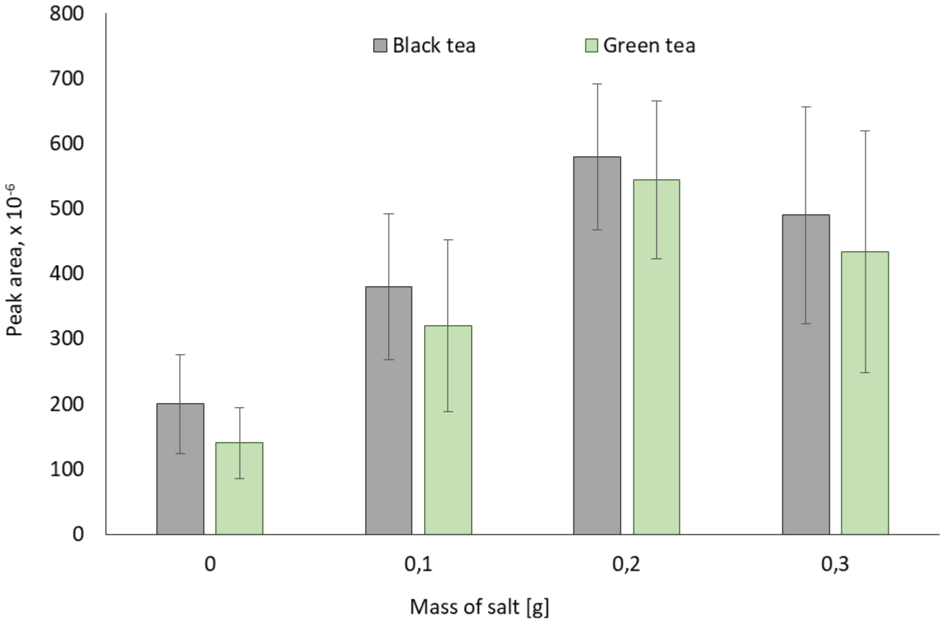
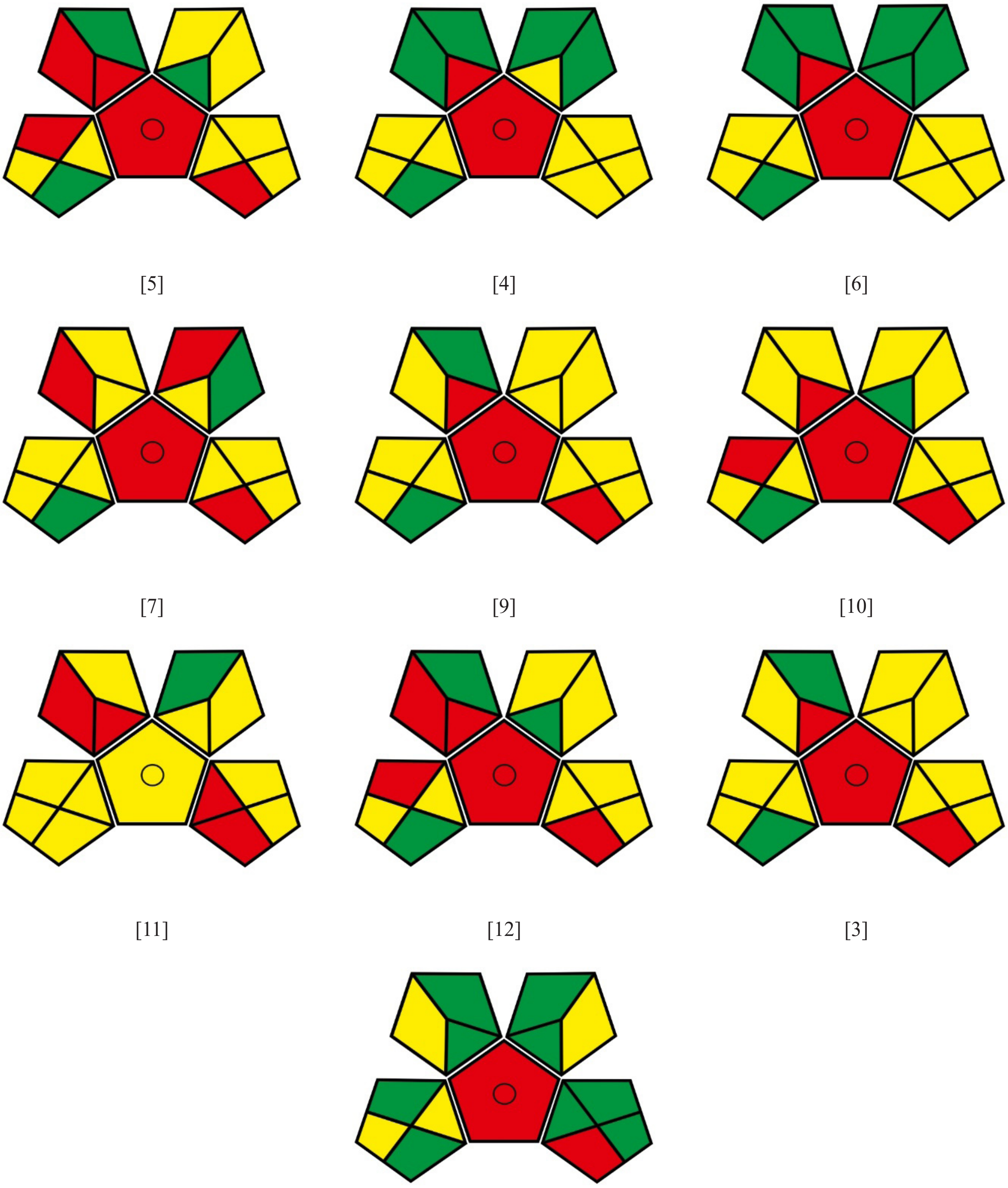


Figure 4 – Plot of salt addition versus caffeine peak area in tea samples.

3.6 Assessing the sustainability of tea analysis methods with the GAPI tool

In this study the environmental friendliness of sample preparation methods from previous caffeine analyses was evaluated, and the environmental friendliness of the proposed work in this study was also evaluated. As shown in Fig. 5, the collection, preservation, transportation and storage required for the samples are the same for most of the SPME methods, this can be seen in the pictograms of the lower right pentagon. In these methods, however, the difference in green and yellow can be seen in the upper right pentagon pictograms. Because the volume of organic solvent and the degree of sample preparation required for the method are slightly higher.

When comparing the mini-SPME method developed in this paper with other methods that have been done previously, the difference for these methods is that the extraction in the former occurs in a microvolume and in the latter in a macrovolume. The other methods require slightly more additional sample processing steps, whereas mini-SPME requires only a small sample volume for extractions, incubations and extractions. This difference can be seen in the upper left pentagon, in which one compartment shows the additional procedures. Thus, the mini-SPME method is the most environmentally friendly sample preparation method for the extraction of caffeine as well as other organic compounds from black and green tea samples.



[5] [4] [6]

[7] [9] [10]

[11] [12] [3]

mini-SPME

Figure 5 – Environmental assessment of sample preparation methods

Conclusion

The identification of total caffeine content in tea samples is of great interest to the tea industry, as consumers increasingly demand high-quality tea products with accurate labeling. In this study, a new method for the determination of total caffeine content in tea samples using gas chromatography-mass spectrometry (GC-MS) combined with miniaturized solid-phase microextraction (mini-SPME) was developed for the first time. The sensitivity of the method was optimized for green and black tea samples, and trace amounts of caffeine were determined. In this work established the following optimum parameters: fiber coating 50/30 µm divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS), extraction temperature 90°C, extraction time 20 min, with 0.2 g salt (sodium chloride) added. The developed method was successfully applied to detect traces of caffeine in teas and its general screening. The study demonstrated the high sensitivity and selectivity of the method, as well as its accuracy and precision. In this study also evaluated the environmental friendliness of the sample preparation using the Green Analytical Process Index (GAPI) tool. The GAPI tool assesses the environmental impact of an analytical method by considering factors such as toxicity, energy consumption, and waste generation. Based on the results of the environmental assessment, the developed and optimized method was found to be safe for both the environment and the operator. The study provides a new and reliable method for the determination of total caffeine content in tea samples, which can be used to ensure the quality and safety of tea products. The method can be further developed and applied to the analysis of other natural products, such as herbs and spices, in the food industry.

Acknowledgments

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