

Review

Cloud Point Extraction in Beverage Analysis: Innovations and Applications for Trace Elements

Ingrid Hagarová *  and Martin Urík 

Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská Dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia; martin.urik@uniba.sk

* Correspondence: ingrid.hagarova@uniba.sk; Tel.: +421-2-9014-9287

Abstract: Cloud point extraction (CPE) has emerged as a highly promising method for the isolation and preconcentration of trace elements from beverages. By utilizing nonionic surfactants to form micellar structures that encapsulate analytes, CPE significantly enhances extraction efficiency and detection limits, often achieving improvements by several orders of magnitude. The optimization of CPE conditions, particularly the selection of surfactants and complexing agents, plays a crucial role in ensuring accurate analytical results. This review underscores the integration of CPE with spectrometric methods as a powerful approach for the separation, preconcentration, and quantification of numerous (ultra)trace elements across a wide range of beverages, including drinking water, wine, beer, juices, tea, and milk. The analytical potential of this integration is substantiated by the comprehensive examples listed in this paper, which include various strategies for sample preparation tailored specifically for different beverage types. While highlighting the effectiveness of conventional CPE methods, this review also emphasizes recent modifications and advancements in CPE techniques that further enhance their utility in beverage analysis. These advancements not only improve detection sensitivity but also align with the principles of green chemistry by reducing solvent consumption and energy requirements.

Keywords: cloud point extraction; elements; beverages; spectrometric methods



Citation: Hagarová, I.; Urík, M. Cloud Point Extraction in Beverage Analysis: Innovations and Applications for Trace Elements. *Beverages* **2024**, *10*, 67. <https://doi.org/10.3390/beverages10030067>

Academic Editor: Alfredo Cassano

Received: 27 June 2024

Revised: 20 July 2024

Accepted: 29 July 2024

Published: 1 August 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

It is universally acknowledged that foods and beverages provide a variety of nutrients essential for the proper functioning of living organisms. Among these nutrients, most trace minerals play critical roles in cell structure and are vital for various biochemical and physiological processes [1]. However, besides the essential elements, food and beverages can contain certain elements recognized as potentially toxic, including dissolved compounds of arsenic (As), lead (Pb), cadmium (Cd), and mercury (Hg), or nanoparticles of silver (Ag), gold (Au), titanium (Ti), and tin (Sn). These can be present at concentrations below the level of quantification or even detection when applying the most common analytical techniques. Still, their accumulation in the human body over time can lead to severe and potentially fatal diseases [2]; therefore, although challenging, their proper detection and quantification are considered necessary.

Given that beverages are one of the primary sources of trace elements through which potentially toxic elements can enter the human body, reliable quantification in these matrices is critically important. This precise analysis plays a vital role in protecting health and ensuring environmental and food safety.

To quantify trace elements, several entry-level techniques suitable for fast and reliable measurements are utilized in food analysis, including UV–visible spectroscopy (UV–Vis), flame atomic absorption spectrometry (FAAS), and electrothermal atomic absorption spectrometry (ETAAS). Although more sensitive methods, such as inductively coupled plasma mass spectrometry (ICP–MS), are available, they are generally more expensive to acquire

and maintain, especially for researchers in developing countries. However, their performance in analyzing trace elements in complex matrices is considered comparable to FAAS when appropriate sample preparation procedures are followed [3].

Using highly efficient and effective preconcentration is particularly crucial for analyzing ultratrace elements in highly complex matrices. Therefore, given the complex nature of beverage samples and strict regulations on toxic substances, continuous improvements in sample preparation procedures are essential for ensuring successful and accurate analysis.

Conventional extraction techniques, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), frequently used for the separation and preconcentration of trace elements, are not considered sufficiently efficient and environmentally friendly. Therefore, various modifications of these techniques have been developed recently that are more sustainable and less harmful to the environment while maintaining or even improving efficiency in separation. A notable advancement is a specialized form of liquid–liquid extraction that uses small amounts of nonionic surfactants instead of large quantities of harmful organic reagents, known as cloud point extraction (CPE).

Due to the fact that both extraction techniques, LLE and SPE, have undergone many modifications, in which less harmful liquid phases and highly effective solid phases are now employed, and/or miniaturized versions and various new arrangements of these two extraction techniques are established, satisfactory results are achieved in most cases. Each modification offers significant advantages, but no extraction technique is without limitations. In general, CPE is known for its efficiency in concentrating analytes from various matrices, but many new versions of extractions from both templates (LLE and SPE) can also be sufficiently efficient. CPE is generally considered cost-effective because it often requires small amounts of relatively inexpensive surfactants, compared to LLE, which uses more expensive organic solvents, or SPE, which incurs higher costs due to the purchase of disposable cartridges, syringe barrels, or microcolumns.

As mentioned earlier, from an environmental point of view, CPE is considered more environmentally friendly compared to conventional LLE due to the use of low volumes of surfactants, which are less harmful because of their non-volatility, low toxicity, and low flammability. SPE and LLE can have a higher environmental impact due to solvent usage and disposal requirements. SPE cartridges and LLE solvent phases may contribute to waste generation and environmental contamination if not handled properly.

Despite the advantages of CPE procedures, they are not without drawbacks (see Table 1).

Table 1. The advantages and disadvantages of CPE.

Advantages	Disadvantages
<ul style="list-style-type: none"> - uses small volumes of nonionic surfactants (instead of high volumes of more harmful organic solvents) - high extraction efficiency achieved (even with highly complex matrices) - significant preconcentration factors achieved (due to the small volumes of surfactant-rich phase obtained) - availability of surfactants in high-purity grades, their stability, non-volatility, low toxicity, and low flammability <ul style="list-style-type: none"> - relatively low cost - easy of instrumentation 	<ul style="list-style-type: none"> - uses relatively high energy consumption (mainly in conventional CPE procedures) - optimization is time-consuming and labor-intensive (in conventional as well as innovative CPE procedures) - requires the use of a solvent to dilute the final extract (which, inter al., leads to a decrease in the PF) - the phases must be separated with utmost precision (in order to achieve reproducible results) - developing a flow-based arrangement is not easy - even greener variants need further improvement

One significant disadvantage of CPE is the high energy consumption required to achieve the necessary temperature for cloud formation and the creation of the two isotropic phases, which contradicts the principles of green chemistry. Furthermore, the high viscosity of the resulting surfactant-rich phase necessitates dilution of the final extract for analyte quantification using a selected detection method. Consequently, to minimize energy consumption and solvent usage, greener variants of CPE have been introduced.

This article focuses on examining the procedures of conventional CPE, as well as innovative CPE procedures, which are employed for the separation and preconcentration of (ultra)trace elements in beverage samples.

2. Principle of Cloud Point Extraction for Trace Elements Analysis

Cloud point extraction (CPE) is a technique where a nonionic surfactant acts as the extraction medium. The main principle of this extraction technique is based on altering experimental conditions, usually temperature, but it can also include pressure, pH, or ionic strength, which leads to the spontaneous formation of nanoaggregates, such as micelles, at surfactant concentrations higher than the critical micellar concentration (CMC). This causes the aqueous surfactant solution to segregate into two isotropic phases: a surfactant-rich phase, which encapsulates the analyte within micellar structures, and a surfactant-poor, bulk aqueous phase.

Typically, the process for separating and preconcentrating (ultra)trace elements using CPE involves several steps [4], as depicted in Figure 1. Initially, a complexing agent is added to the solution to create hydrophobic species of the target analyte, which become trapped in the hydrophobic part of the micellar structures. Subsequently, a surfactant is introduced at a concentration exceeding its CMC. The solution is then heated, usually in a water bath, to a temperature above the cloud point temperature (CPT) to initiate cloud formation and the creation of the two isotropic phases. Separation of these phases is another step in this procedure, often expedited by centrifugation. The system is then cooled, typically in an ice bath, to increase the viscosity of the surfactant-rich phase. In the final step, the aqueous phase is removed, leaving behind a highly viscous surfactant-rich phase, which is then diluted with a solution compatible with the chosen detector, typically methanol or ethanol mixed with a mineral acid. This diluted sample is now prepared for the quantification of the target trace element.

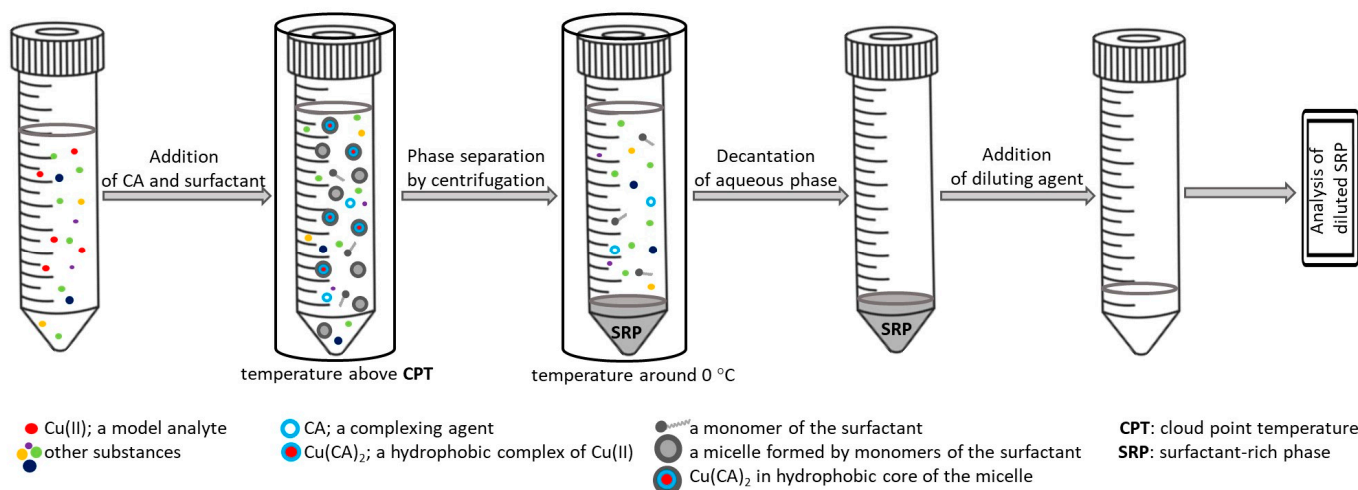


Figure 1. Schematic illustration of the cloud point extraction steps for the separation and preconcentration of trace elements, using Cu(II) as a model analyte.

To ensure a reliable procedure, optimization of the experimental conditions is necessary. This can be approached in two ways: the univariate strategy, favored for its straightforward data interpretation, and multivariate optimization strategies, which are faster, more cost-effective, and require fewer experiments [5,6]. In CPE, the choice of surfactants and complexing agents is crucial for developing an effective procedure. Nonionic surfactants, particularly polyoxyethylated alkylphenols from the Triton series, are widely used in CPE for element analysis due to their high purity, affordability, stability, non-volatility, low toxicity, and low flammability. Among these, Triton X-114 (polyoxyethylene-7.5-octylphenoxy ether) is commonly used in about 80% of studies involving CPE for the

separation, preconcentration, and speciation of inorganic analytes [7]. Hereafter, Triton X-114 will typically be abbreviated as TX-114.

From the main characteristics of surfactants (see Table 2), low CPT plays the most important role in CPE procedures. One reason is the instability of some metal chelates at higher temperatures, which leads to a significant decrease in the preconcentration factors achieved. Preconcentration factors and extraction yields in CPE using nonionic surfactants can also be influenced by the length of the alkyl chain, the presence of an aromatic group, the number of oxyethylene units, and the concentration of the surfactant. A high density of the surfactant-rich phase is also an important parameter to facilitate phase separation. The densities of commonly used nonionic surfactants are listed in Table 2 and are comparable. Other characteristics of nonionic surfactants, such as average molecular weight, hydrophilic-lipophilic balance, and aggregation number, can be found in our previous publication [8]. It can be concluded that although various studies compare different nonionic surfactants in CPE schemes, the best results are almost always achieved using Triton X-114.

Table 2. Main characteristics of selected nonionic surfactants used in CPE procedures.

Surfactant	Molecular Formula	Type	CPT (°C)	CMC (mmol/L)	ρ (g/mL)	Ref.
Triton X-114	(C ₂ H ₄ O) _n C ₁₄ H ₂₂ O, n = 7–8	Polyoxyethylene octyl phenyl ether	23–24	0.20–0.35	1.058	[9]
Triton X-100	(C ₂ H ₄ O) _n C ₁₄ H ₂₂ O, n = 9–10	Polyoxyethylene octyl phenyl ether	64–65	0.17–0.30	1.070	[9]
Triton X-45	(C ₂ H ₄ O) _n C ₁₄ H ₂₂ O, n = 4–5	Polyoxyethylene octyl phenyl ether	Disp.	136 *	1.031	[10]
PONPE 5.0	(C ₂ H ₄ O) _n C ₁₅ H ₂₄ O, n = 5	Polyoxyethylene nonyl phenyl ether	15–17	0.57	1.040	[11]
PONPE 7.5	(C ₂ H ₄ O) _n C ₁₅ H ₂₄ O, n = 7.5	Polyoxyethylene nonyl phenyl ether	5–20	0.085	1.060	[9]
Tween 20	C ₅₈ H ₁₁₄ O ₂₆	Polyoxyethylene sorbitol ester	76	0.06	1.095	[12]
Tween 80	C ₆₄ H ₁₂₄ O ₂₆	Polyoxyethylene sorbitol ester	65	0.015	1.121	[12]

* in mg/L; Disp.: dispersible; CPT: cloud point temperature; CMC: critical micellar concentration; ρ : density; Ref.: reference.

Another crucial agent for developing a reliable CPE procedure is the complexing agent. While the choice of nonionic surfactant is relatively uniform, the choice of complexing agent varies widely, from less selective to highly selective ones. Later in the text, numerous complexing agents are mentioned (see Tables 3 and 4).

For trace elements that may exist in multiple oxidation states within a sample, CPE procedures are often proposed for the selective separation of a specific oxidation state of the monitored element. For instance, in the case of selenium, where Se(IV) and Se(VI) might both be present, the experimental conditions need to be optimized to selectively separate and preconcentrate Se(IV) accurately. The total selenium content is then measured after reducing Se(VI) to Se(IV) [13].

3. Different Approaches to Sample Preparation Prior CPE Procedure Application

While numerous publications detail the preconcentration of (ultra)trace elements in drinking water samples (tap water, well water, mineral water) using CPE methodology, there is a limited number of similar studies focusing on various beverage samples. This discrepancy can be attributed to the diverse compositions of beverage samples (such as wine, beer, milk, and fruit juices), which contain a range of substances. Consequently, the pre-treatment of these samples before applying CPE procedures is more complex, often involving additional steps to ensure accurate analysis.

Drinking water samples, including tap water and bottled mineral water, are typically used for CPE procedures without any special treatment [14–17]. However, in some cases, tap water samples are filtered immediately after sampling [18–23], or occasionally, filtration is performed just before use [5,24,25]. The treatment of tap water samples may also involve acidification with HCl [26] or HNO₃ [27], followed by filtration. For filtration, a membrane filter with a pore size of 0.45 μ m is predominantly used.

From an analytical perspective, beer presents a complex matrix due to its high content of various organic compounds. These include carbohydrates and proteins, as well as

organic acids, phenolic compounds, hop derivatives, volatile esters, sulfur compounds, minerals, vitamins, nucleotides, and melanoidins. Additionally, beer is saturated with carbon dioxide. Because of this, beer is typically degassed before taking a sample for analysis to ensure its accurate volume [28]. The simplest method for degassing beer is to leave it loosely capped for at least 24 h. Alternatively, immersing a beer sample in an ultrasonic bath for a few minutes can achieve the same result effectively. Other degassing methods include using a microwave oven in a pressurized closed vessel at moderate power for several minutes or percolating an inert gas through the sample for a certain period [28].

Before conducting the CPE procedure, two degassing methods can be employed. The first approach involved adding an antifoam solution to the beer sample to prevent foaming, followed by degassing for 15 min using an ultrasonic bath [29,30]. Alternatively, a second method utilized only sonication for 30 min to achieve the same purpose [31]. Additionally, to treat the beer samples further, potassium metabisulfite can be added to destroy any proteins in the samples [30].

From a chemical standpoint, wine is a complex mixture of water and ethanol, encompassing a diverse array of both organic and inorganic substances [32]. Non-volatile organic compounds usually include low-volatile alcohols, sugars, organic acids, and their conjugated salts, which can negatively affect the application of CPE procedures. Additionally, wine contains minor quantities of amino acids, polyphenols, flavonoids, and similar substances. In terms of the inorganic fraction, wine is enriched with salts of Cl^- , PO_4^{3-} , SO_4^{2-} , and SO_3^{2-} . The principal counter ions (major elements) in both inorganic and organic salts are related to grape physiological processes, including K, Ca, Na, and Mg. Trace elements, typically present in concentrations ranging from 0.1 to 10 mg/L, include Al, B, Cu, Fe, Mn, Rb, Sr, and Zn. Ultratrace elements, such as Se, Pb, and Cd, are found in even lower concentrations below 0.1 mg/L [32].

Despite this intricate composition, wine samples are occasionally analyzed immediately after collection without extensive pre-treatment, often through simple dilution [14,31]. Alternatively, they are typically stored at 3–4 °C, followed by filtration to remove sediments and precipitates. Degassing is performed for sparkling wines prior to any other treatment. In certain instances, wine samples undergo initial de-alcoholization [33].

Before employing a CPE procedure, wine samples were de-alcoholized at 80 °C using a reduced-pressure evaporator [29]. To prevent foaming, 1-octanol was added to the wine samples, which were then degassed for 5 min using an ultrasonic bath [34]. Similar to treatments for beer samples, another step for wine samples involves breaking down organic substances, which includes the addition of potassium metabisulfite [34].

To obtain a clear solution, both beer and wine samples are typically digested. This process can be carried out using closed-vessel microwave-assisted systems or open-vessel systems, most commonly on a hot plate. Various mixtures of chemical reagents are used for this purpose, with HNO_3 being the predominant choice. The most frequently used mixture is HNO_3 combined with H_2O_2 [27,29,30,34–37]. Alternatively, satisfactory results have also been achieved using combinations of two mineral acids, such as HNO_3 and HClO_4 [29,34,36], or HNO_3 and HCl [27,38]. After obtaining a clear solution, an aliquot of the sample is used in an optimized CPE procedure to preconcentrate the element of interest.

A specialized treatment process for wine and beer samples involves passing the diluted samples through an HLB cartridge, followed by a cation exchange column. After washing with water, the cationic species are eluted from the exchanger using HNO_3 and then diluted to an exact volume. Aliquots of these treated solutions were subsequently subjected to the CPE process [39].

Fruit juices are recognized as a rich source of a wide range of physiologically and nutritionally important compounds, including carbohydrates, proteins, vitamins, carotenoids, pectins, flavonoids, glucarates, coumarins, monoterpenes, limonoids, triterpenes, phenolic acids, as well as macroelements and microelements [40]. Fruit juices are heterogeneous solutions with high concentrations of organic matter and dissolved solids, making the

direct quantification of (ultra)trace elements nearly impossible. To remove particles and solid deposits that could interfere with spectrochemical measurements, juice samples can be centrifuged and/or filtered. However, this process may lead to the loss of information regarding element concentrations present in the pulp (in the case of pulpy fruit juices). For obtaining the total concentration of a selected element, wet digestion in open-vessel or closed-vessel systems is more suitable. These digestion procedures lead to the destruction of the organic matrix and the release of elements into solution as simple ions. Such a form of the element is essential because the proposed CPE procedures are specifically designed for the ionic forms of the monitored elements. Similar to beer and wine samples, various mixtures of chemical reagents are used for this purpose. A mixture of HNO₃ and H₂O₂ is predominant [19,35,41–45]. Other mixtures such as HCl and H₂O₂ [42], HNO₃ and HClO₄ [36,43], HNO₃ and HCl [38], or HNO₃, HCl, and H₂O₂ [41,46] have also been described in the published literature.

Table 3. Summary of conventional CPE procedures used for separation and preconcentration of (ultra)trace elements in beverage samples.

Sample	Analyte	Complexing Agent	Surfactant	Detection Method	LOD (µg/L)	RSD (%)	Recovs. (%)	Ref.
Fruit juices, wine, beer	As(V)	AOH ⁺ /TA	TX-114	UV-Vis	1.14	5.7	95–100	[25]
Fruit juices, wine, beer	Sb(V)	VPB ⁺	TX-114	FAAS	0.25	4.2	97–104	[36]
Fruit juices, wine, beer, milk	Sb(V)	Pyronin B	TX-114/SDS	FAAS	4.28	6.1	97–99	[38]
Fruit juices, wine, beer, milk	Sb(III)	Pyronin B	TX-114/SDS	FAAS	1.68	6.0	97–99	[38]
Fruit juices, wine, beer	Sb(III)	VPB ⁺	TX-114	FAAS	5.15	4.5	98–103	[36]
Fruit juices, wine, beer, milk	Sb(III)	Azomethine-H	TX-114/CPC	FAAS	0.15	5.9	95–98	[30]
Fruit juices	Sn(IV)	Celestine blue/TA	TX-114/SDS	UV-Vis	1.3	5.3	97–103	[45]
Fruit juices, wine, beer	Sn(IV)	GC ⁺ /glycine	Tween20/CPC	FAAS	0.33	6.2	96–104	[36]
Fruit juices, wine, beer	Cu(II)	Sudan II	TX-114/SDS	UV-Vis	0.085	3.9	99–101	[29]
Orange juices	Cu(II)	BIYPYBI	TX-114	FAAS	1.4	1.1	104	[47]
Orange juices	Ni(II)	BIYPYBI	TX-114	FAAS	1.9	1.1	103	[47]
Wine, beer	Co(II)	CCA	TX-114/CPC	FAAS	0.20	5.7	92–104	[27]
Fruit juices	Cd(II)	VBB ⁺ /KI	TX-114	UV-Vis	0.34	4.6	97–101	[43]
Fruit juices, wine, beer	Zn(II)	PBHA	TX-114	FAAS	0.42	3.2	99–100	[29]
Orange juices	Zn(II)	BIYPYBI	TX-114	FAAS	1.0	1.0	103	[47]
Beer	Fe(II)	5-Br-PADAP/EDTA	TX-114	UV-Vis	0.80	1.0	100–102	[48]
Orange juices, milk	Fe(III)	Ferron	TX-114	FAAS	0.40	1.3	102–103	[49]
Orange juices	Fe(III)	BIYPYBI	TX-114	FAAS	2.2	0.8	104	[47]
Fruit juices, wine	Mo(VI)	VPB ⁺ /KSCN	TX-114/CPC	FAAS	2.18	3.2	97–102	[44]
Fruit juices, wine, beer, milk	B(III)	Azomethine-H	TX-114/CPC	FAAS	0.75	4.0	95–98	[30]

LOD: limit of detection; RSD: relative standard deviation (indicating better precision than the value shown); Recovs.: recoveries; Ref.: reference. Complexing agents: AOH⁺: arcidine orange; TA: tartaric acid; VPB⁺: Victoria pure blue BO; GC⁺: galloycyanin; BIYPYBI: 2-(6-(1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1H-benzo[d]imidazole; CCA: calcon carboxylic acid; VBB⁺: Victoria blue B; PBHA: N-phenylbenzohydroxamic acid; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Surfactants: TX-114: Triton X-114; SDS: sodium dodecyl sulfate; CPC: cetylpyridinium chloride.

From a chemical viewpoint, milk can be seen as a complex suspension of proteins and fats (primarily casein and saturated fatty acids) in an aqueous medium, with cow's milk containing approximately 87% water. It also has a high content of carbohydrates, mainly lactose, which makes up about 5% (*m/v*) of cow's milk, along with various elements bound to organic compounds, such as P and Ca bound to proteins. Milk is also a significant source of important macronutrients, including Ca, Mg, and K, as well as micronutrients like Cu, Fe, Mn, and Zn [50].

Regarding sample pre-treatment steps before utilizing a CPE procedure, the published literature mentions two primary methods. One approach is direct wet digestion using a mixture of HNO₃ and H₂O₂, followed by heating on a hot plate [16,51], or using a mixture of HNO₃ and HCl, followed by heating in an ultrasonic bath [38]. In the other approach, trichloroacetic acid is added first to deproteinize and defat the milk samples, followed by

wet digestion, predominantly using a mixture of HNO_3 and H_2O_2 [30,41,52]. However, a combination of three reagents, such as HNO_3 , HCl , and H_2O_2 , has also been employed for this purpose [41].

Tea extracts are complex solutions that vary depending on the type of tea and the extraction process used. They are rich in polyphenols, alkaloids, amino acids, vitamins, minerals, volatile compounds, carbohydrates, lipids, pigments, and other bioactive compounds. These constituents contribute to the tea's health benefits, flavor, and aroma.

In a study on green tea and selenium content [53], two types of samples were prepared: water leachates to measure the water-extractable selenium fraction and decomposed samples to quantify the total selenium content. The total selenium content was approximately 3–5 $\mu\text{g/g}$, of which the water-extractable fraction ranged from 25% to 35%. This value is relatively high, likely due to the unusual preparation method for the water-extractable fraction, which involved placing a beaker with tea samples into boiling water for 2 h. Although there are many ways to prepare green tea, boiling the leaves in water for such an extended period is quite uncommon. Therefore, achieving such a high selenium intake from green tea consumption seems improbable.

In another study aimed at quantifying As(V) and total arsenic, tea infusions were prepared by immersing one tea bag (green, black, or herbal) in hot water for 10 min, allowing it to stand for 5 min, followed by filtering and neutralization using NaOH [42]. An aliquot of the sample solution was then diluted to an exact volume with water. These prepared sample solutions were used for total matrix digestion. After that, an optimized CPE procedure was applied for the selective separation and preconcentration of As(V) through an ion-association reaction with acridine red (ARH^+) in the presence of pyrogallol and Triton X-45. The final results showed that As(V) concentrations ranged from 3.9 to 6.4 $\mu\text{g/L}$, and total arsenic ranged from 5.8 to 9.9 $\mu\text{g/L}$. It seems that these results consider the sensitivity enhancement factor of 115, and the detected values need to be divided by this factor to estimate the arsenic intake from drinking tea.

From the information stated above, it is evident that the primary limitation of CPE when applied to complex beverage matrices is the complexity of the matrices themselves. Beverages such as wine, beer, fruit juices, and milk contain a variety of components (e.g., sugars, organic acids, proteins) that can interfere with the extraction of target elements. Even though simple pre-treatment steps like dilution, filtration, or centrifugation can help reduce matrix complexity before CPE, it is not unusual for a decomposition step to be incorporated as a pre-treatment step. In this process, more complex organic molecules (which, among other things, can contain trace elements of interest) are converted to simpler compounds, such as CO_2 and H_2O , and the target element is present in its simple ionic form. After that, an optimized CPE can be reliably used.

The aforementioned beverages have been primarily analyzed to quantify (ultra)trace concentrations of various elements using conventional CPE procedures. The main goal was to enhance analytical sensitivity, especially when using less sensitive detection methods such as UV-Vis and FAAS (see Table 3). These methods, combined with optimized extraction procedures, enabled the reliable quantification of (ultra)trace concentrations of target elements with high accuracy and precision. Innovative CPE procedures will be discussed in more detail in the following subsection.

4. Innovative CPE Procedures for the Separation and Preconcentration of Trace Elements in Beverage Samples

Developing an accurate and effective CPE procedure requires a significant investment of time and effort. Optimization of experimental conditions is always conducted using model solutions. After validating the proposed procedure by analyzing certified reference materials, it is typically applied to the samples of interest.

The following text will now focus on recent modifications in CPE procedures, highlighting the future direction of this scientific field. We will start by discussing faster procedures, followed by energy-efficient and greener CPE methods that minimize the

use of organic agents required for dissolving the surfactant-rich phase. Lastly, we will explore state-of-the-art nanoparticle-assisted CPE techniques. All these variations have been employed for the separation and preconcentration of (ultra)trace elements in liquid matrices, including drinking water samples and some beverage samples.

Table 4. Summary of innovative CPE procedures used for separation and preconcentration of (ultra)trace elements in drinking water and beverage samples.

Sample	Analyte	CPE Modification	Complexing Agent	Surfactant	Detection Method	LOD (µg/L)	RSD (%)	Recovs. (%)	Ref.
Drinking water, fruit juices, wine, beer	As(V)	UA-CPE	NRH ⁺ /PG	PONPE 7.5	FAAS	0.45	4.2	98–104	[35]
Tap water, pulp fruit juices	Sb(III)	UA-CPE	NRH ⁺	PONPE 7.5/CTAB	HG-AAS	0.0036	5.3	93–107	[19]
Tap water, Nescafe, fruit juices, wine	Sb(III)	UA-CPE	Morin	PONPE 7.5/CTAB	FAAS	0.03	5.2	97–104	[34]
Fruit juices, wine, beer, milk	Sb(III)	UA-CPE	TAR	Tween 80/SDS	FAAS	0.13	3.2	98–103	[30]
Fruit juices, wine, beer, milk	Sb(III)	UA-CPE	TAC	Tween 80/SDS	FAAS	0.28	3.5	98–103	[30]
Tap water, mineral water	Se(IV)	UA-CPE	Dithizone	TX-114	UV-Vis	0.30	3.2	93–102	[24]
Tap water, pulp fruit juices	Se(IV)	UA-CPE	NRH ⁺	PONPE 7.5/CTAB	HG-AAS	0.00245	5.1	93–107	[19]
Tap water, Nescafe, fruit juices, wine	Sn(IV)	UA-CPE	Morin	PONPE 7.5/CTAB	FAAS	0.03	5.4	97–104	[34]
Milk	Mo(VI)	UA-CPE	Nile Blue A	PONPE 7.5	FAAS	0.86	2.4	96–102	[51]
Fruit juices, milk, vinegar	V(V)	UA-CPE	Safranin T/PG	TX-114	UV-Vis	0.58	4.6	95–98	[41]
Milk	V(V)	UA-CPE	Nile Blue A	PONPE 7.5	FAAS	1.55	2.2	96–102	[51]
Fruit juices, milk, vinegar	Cu(II)	UA-CPE	Safranin T/PG	TX-114	UV-Vis	0.60	4.4	93–98	[52]
Drinking water, fruit juices, tea samples	As(V)	VA-CPE	ARH ⁺ /PG	TX-45	UV-Vis	0.25	3.7	96–103	[42]
Tap water, milk	Mo(VI)	RT-CPE	DHDPhB	TX-100	UV-Vis	2.3	4.5	97–106	[16]
Tap water, mineral water	Se(IV)	RS-CPE	Dithizone	TX-114	UV-Vis	0.20	4.3	95–105	[24]
Tap water	Hg(II)	M-CPE	PAR	TX-114	UV-Vis	13.1	6.4	108–115	[54]
Tap water	Zn(II)	M-CPE	PAR	TX-114	UV-Vis	51.7	4.7	93–113	[54]
Tap water	Cu(II)	M-CPE	PAR	TX-114	UV-Vis	9.8	5.9	93–98	[54]
Tap water, mineral water	Hg(II)	IL-CPE	TPPP	TEGII	Fluorimetry	80	2.4	100–101	[55]
Tap water	Hg(II)	IL-CPE	HECAT	TX-114	UV-Vis	0.5	1.5	95–96	[56]
Drinking water, mineral water, fruit juices	Hg(II)	MA-CPE-DSPE	CdFe ₂ O ₄ NPs/DBH	TX-114	FS-FAAS	5.0	4.2	91–100	[46]
Tap water, mineral water, wine, beer	Cu(II)	CPE-DSPE	AgNPs/MESNA	TX-114	ETAAS	0.0024	4.3	95–105	[39]
Tap water, well water, mineral water	Cu(II)	CPE-DSPE	Al ₂ O ₃ NPs *	TX-114	ETAAS	0.0026	4.9	96–106	[57]
Tap water, mineral water, wine, beer	Ni(II)	CPE-DSPE	AgNPs/MESNA	TX-114	ETAAS	0.0021	4.3	95–106	[39]
Tap water, well water, mineral water	Ni(II)	CPE-DSPE	Al ₂ O ₃ NPs *	TX-114	ETAAS	0.0028	5.6	96–104	[57]
Tap water, well water, mineral water	Co(II)	CPE-DSPE	Al ₂ O ₃ NPs *	TX-114	ETAAS	0.0025	6.5	96–104	[57]
Tap water	Zn(II)	CPE-DSPE	TiO ₂ NPs *	TX-100	Colorimetry	0.33	1.8	100–102	[58]
Tap water, well water	Pb(II)	CPE-DSPE	ZrNO ₂ NPs/cation	TX-114	ETAAS	0.0022	3.5	95–99	[59]
Tap water, mineral water	Cr(III)	CPE-DSPE	GONPs *	TX-45	ETAAS	0.005	5.2	98–103	[60]
Tap water, mineral water, wine, beer	Cr(III)	CPE-DSPE	AgNPs *	TX-114	ETAAS	0.002	4.3	95–105	[31]
Tap water, mineral water, beer	V(IV+V)	CPE-DSPE	GONPs *	TX-114	ETAAS	20	4.7	96–105	[61]

* no complexing agent used; LOD: limit of detection; RSD: relative standard deviation (indicating better precision than the value shown); Recovs.: recoveries; Ref.: reference. CPE modifications: UA-CPE: ultrasound-assisted CPE; VA-CPE: vortex-assisted CPE; RT-CPE: room temperature CPE; RS-CPE: rapidly synergistic CPE; M-CPE: micro CPE; IL-CPE: ionic liquid supported CPE; MA-CPE-DSPE: microwave-assisted CPE combined with dispersive solid-phase extraction; CPE-DSPE: CPE combined with dispersive solid-phase extraction. Complexing agents: NRH⁺: 3-amino-7-dimethylamino-2-methylphenazine hydrochloride; PG: pyrogallol; TAR: 4-(2-thiazolylazo)resorcinol; TAC: 2-(2-thiazolylazo)-p-cresol; ARH⁺: acridine red; DHDPhB: 6,7-dihydroxy-2,4-diphenylbenzopyrylium perchlorate; PAR: 4-(2-pyridylazo)resorcinol; TPPP: 5,10,15,20-tetra-(4-phenoxyphenyl)porphyrin; HECAT: 3-(2-hydroxy-5-ethoxycarbonylphen-1-ylazo)-1,2,4-triazole. Nanoparticles: CdFe₂O₄NPs/DBH: nanoparticles of CdFe₂O₄ modified with (2 N'-(4-diphenylamino)benzylidene)hydrazinecarbothiohydrazide); AgNPs/MESNA: silver nanoparticles functionalized with the sodium salt of 2-mercaptoethanesulfonic acid; Al₂O₃NPs: alumina nanoparticles; TiO₂NPs: titania nanoparticles; ZrO₂NPs/cation: zirconia nanoparticles modified with 1-(4-nitrophenyl)-3-(4-phenylazophenyl)triazene; GONPs: graphene oxide nanoparticles; AgNPs: silver nanoparticles. Surfactants: CTAB: cetyltrimethylammonium bromide; SDS: sodium dodecyl sulfate; TX-114: Triton X-114; TX-45: Triton X-45; TX-100: Triton X-100; TEGII: tetraethyleneglycol-bis(3-methylimidazolium)diiodide. Detection methods: FAAS: flame atomic absorption spectrometry; HG-AAS: hydride generation atomic absorption spectrometry; UV-Vis: spectrophotometry; FS-FAAS: fast sequential flame atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry.

In conventional CPE, heating in a water bath is typically used to achieve the cloud point phenomenon. This can also be accomplished using ultrasound energy in ultrasound-assisted CPE (UA-CPE) or microwave irradiation in microwave-assisted CPE (MA-CPE),

both of which are considered faster than conventional CPE, with UA-CPE being used more frequently (see Table 4).

In UA-CPE, ultrasound accelerates the clouding process by increasing the intensity and rate of interaction between the surfactant and the aqueous phase. This significantly improves the extraction efficiency of target analytes, as documented in several studies on the analysis of (ultra)trace elements in beverage samples, such as Hg(II) [26], Se(IV) [24], and Se(IV) and Sb(III) [19].

In MA-CPE, microwaves provide rapid and uniform heating of the sample, which accelerates the extraction process, enhances extraction efficiency, and reduces both solvent consumption and extraction time [46].

Vortex-assisted CPE (VA-CPE) was also developed to speed up the extraction process. In VA-CPE, the mixture is vigorously shaken using a vortex agitator for a set period, leading to the formation of fine droplets. These fine droplets, formed during the preconcentration process, extract the target analyte more quickly due to their shorter diffusion distances and larger specific surface area [42].

An energy-efficient CPE procedure, termed room temperature CPE (RT-CPE), was optimized for the quantification of Mo(VI) in tap water and milk samples [16]. The clouding phenomenon was achieved immediately after the addition of an appropriate concentration of sodium salicylate and a 0.1 M H₂SO₄ solution, despite Triton X-100 being used as the extracting agent (whose cloud point temperature can range from 60 to 65 °C, depending on the experimental conditions).

Another variant of CPE procedures that can be performed at ambient temperature is rapidly synergistic CPE (RS-CPE). In this approach, certain alcohols, such as n-octanol and n-pentanol, act as synergistic reagents. This allows for a significant reduction in the cloud point temperature of the nonionic surfactant, enabling the preconcentration step to be conducted at room temperature without the need for heating. A major advantage of this method is that the extraction can be accomplished rapidly through manual shaking for just 1 min. Using RS-CPE, where octanol served as both a cloud point depressant and a synergistic reagent for extraction, tap water samples and bottled mineral water samples were analyzed to quantify ultratrace concentrations of Se(IV) [24]. While selenium concentrations of around 3 µg/L were detected in tap water, no selenium was found in the bottled mineral water samples.

A greener variant of CPE, known as micro-cloud point extraction (M-CPE), was introduced to minimize solvent usage typically required to reduce the viscosity of the surfactant-rich phase formed after extraction. When very small volumes of the final extract are obtained (tens of microliters), reduced amounts of organic solvent are needed compared to conventional CPE methods. In this scenario, due to the extremely low volumes, accessories such as micro cuvettes (used in spectrophotometry) must be utilized. This adaptation of CPE has been effectively applied to the quantification of Hg(II), Cu(II), and Zn(II) in tap water samples [54]. An additional advantage of the developed method is that M-CPE can be performed at room temperature due to the salting-out effect in the presence of Na₂SO₄.

Longer procedures compared to conventional CPE have been proposed to address issues with organic solvents, which are typically used to reduce the viscosity of the surfactant-rich phase. This approach is known as dual CPE (d-CPE). In d-CPE, two extraction steps are involved. The first step is usually conventional CPE, where analytes are separated into the surfactant-rich phase. This is followed by a second extraction step, where analytes are re-extracted into an aqueous solution. The second extraction commonly employs mineral acids such as HNO₃ or HCl. The advantage of this longer procedure is its effective elimination of organic solvents, which can cause potential interferences in some detection methods. This extraction technique was specifically developed for the quantification of Hg(II) in tap water and bottled mineral water samples before ETAAS analysis [17]. While the efficiency of the procedure is well established, it raises a question: why was such a lengthy d-CPE process necessary, especially when ETAAS quantification does not usually encounter issues

with the analysis of acidic methanol or ethanol solutions, which are the most commonly used agents for dissolving the surfactant-rich phase? However, interesting results were obtained: while no Hg(II) was detected in bottled mineral water samples, two out of three tap water samples contained this heavy metal, with concentrations of $0.48 \pm 0.08 \mu\text{g/L}$ and $0.63 \pm 0.03 \mu\text{g/L}$ [17].

Currently, various supramolecular systems utilizing ionic liquids (ILs) and deep eutectic solvents (DESs) have been proposed for LLE procedures. This trend has also influenced CPE techniques.

For instance, a room temperature ionic liquid (RTIL) such as tetraethyleneglycol-bis(3-methylimidazolium)diiodide (TEGII) was used as a surfactant, and 5,10,15,20-tetra-(4-phenoxyphenyl)porphyrin (TPPP) as a complexing agent for the separation and pre-concentration of Hg(II) from tap water and mineral water samples before spectrofluorimetric quantification [55]. Another study describes an ionic liquid-based CPE (IL-CPE) approach combined with spectrophotometry [56]. In this approach, a mixed-micellar system employing 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] as the IL, Triton-X114 as the extracting agent, and 3-(2-hydroxy-5-ethoxycarbonylphen-1-ylazo)-1,2,4-triazole (HECAT) as the complexing agent was utilized. An optimized procedure was developed for the quantification of Hg(II) in tap water and mineral water samples. All analyzed samples showed no detectable mercury, and recovery tests demonstrated no interference from different co-existing species after spiking samples at two concentration levels.

DESs exhibit similar physicochemical properties to commonly used ILs but have the advantages of being significantly cheaper, easier to prepare, and less impactful on the environment [2]. Additionally, they can be tailored to be target-specific. Recently, a rapidly synergistic deep eutectic solvent cloud point extraction (RS-DES-CPE) method for aluminum ions was developed [62]. In this method, aluminum ions were first chelated using 2-hydroxy-5-p-tolylazobenzaldehyde (HTAB), followed by the addition of appropriate amounts of Triton X-114 and a DES. After mechanical shaking for a specified duration, the solution turned cloudy at room temperature, indicating the formation of a micellar system. Compared to conventional CPE, the developed RS-DES-CPE method required less time. Finally, both CPE procedures were utilized for the separation and preconcentration of aluminum in bottled beverage samples.

The combination of two extraction approaches, dispersive solid-phase extraction (DSPE) and cloud point extraction (CPE), is a current trend in developing new separation procedures. By integrating the advantages of both methods, more efficient processes can be achieved. Recent literature provides a comprehensive review of solid materials used in DSPE for separating a wide range of inorganic substances from complex matrices. Among these materials, nanoparticles (NPs) of various origins and compositions are frequently studied and utilized due to their unique physicochemical properties, including high surface area, high chemical activity, high adsorption capacity, rapid adsorption dynamics, and excellent mechanical and chemical stability [63]. However, using NPs in DSPE can present challenges, such as slow sedimentation and difficulty in separating them from large aqueous sample volumes. To address these issues, NPs can be suspended in a surfactant medium and employed in CPE procedures for the separation and preconcentration of target analytes. The literature describes various terms for procedures where nanoparticles are used to carry the target element into a surfactant-rich phase. Some of these terms include combination of cloud point extraction and solid-phase extraction [58,64], combination of cloud point extraction and dispersive solid-phase extraction [46], microextraction based on suspended nanoparticles [57,59], cloud point microextraction involving nanoparticles [61], cloud point extraction assisted by nanoparticles [39], or cloud point extraction in the presence of nanoparticles [31]. For those unfamiliar with extraction terminology, this variety of names can be confusing. Despite the different terms, Table 2 lists these procedures under the common abbreviation CPE-DSPE. This combined approach is predominantly used for the separation and preconcentration of (ultra)trace elements in various drinking water

samples [39,46,57–60,64], as well as in more complex matrices such as wine, beer [31,61], and fruit juices [46].

5. Concluding Remarks and Future Perspectives

This paper discusses cloud point extraction (CPE) as an environmentally benign alternative procedure for separating (ultra)trace elements from beverage samples in greater detail. This technique is considered environmentally friendly because it uses small amounts of nonionic surfactants as extracting agents instead of large volumes of harmful organic reagents, aligning with the principles of green analytical chemistry. Once all experimental conditions are optimized, developed CPE procedures can offer high extraction efficiency, significant preconcentration factors, low cost, and enhanced safety. High efficiency and preconcentration factors are crucial parameters for (ultra)trace analysis of complex matrices. Given the complexity of beverage samples and stringent limits for various toxic substances, continuous improvement of current sample pre-treatment procedures for analysis is essential.

For trace elements, the ability to use commonly available but less sensitive spectrometric methods (e.g., UV-Vis, FAAS) in conjunction with CPE procedures is advantageous for laboratories using such instrumentation. CPE preconcentration can significantly improve detection limits across all spectrometric methods used, sometimes by several orders of magnitude. The integration of CPE procedures with spectrometric methods demonstrates considerable analytical potential for separating, preconcentrating, and quantifying numerous (ultra)trace elements in various types of beverages, including drinking water, wine, beer, juices, and milk, as extensively documented by examples reviewed in this paper.

As mentioned earlier, despite the advantages of CPE procedures, they are not without drawbacks. The high energy consumption in conventional CPE schemes, which contradicts the principles of green chemistry, has led to the development of energy-efficient procedures such as room temperature CPE (RT-CPE), rapidly synergistic CPE (RS-CPE), and rapidly synergistic deep eutectic solvent CPE (RS-DES-CPE). Procedures that operate at room temperature without the need for heating systems contribute to greener practices by reducing energy consumption.

Furthermore, the high viscosity of the resulting surfactant-rich phase necessitates dilution of the final extract for analyte quantification using a selected detection method. To minimize solvent usage typically required for this step, a greener variant of CPE known as micro-cloud point extraction (M-CPE) was introduced. When very small volumes of the final extract are obtained, reduced amounts of organic solvent are needed compared to conventional CPE methods.

At the end of this concluding section, it is important to mention the combination of two extraction techniques, dispersive solid-phase extraction (DSPE) and cloud point extraction (CPE), where nanoparticles are employed to transfer the target analyte into the surfactant-rich phase. This combination has been predominantly used for the separation and preconcentration of ultratrace elements in drinking water samples, followed by the quantification of these elements using electrothermal atomic absorption spectrometry (ETAAS). The integration of CPE-DSPE with ETAAS has achieved the lowest detection limits, in the range of 2–5 ng/L, compared to other reviewed methods. Combining two extraction techniques allows for the cumulation of their advantages, leading to the development of highly efficient procedures. Given that nanoscience and nanotechnology are rapidly growing fields, with new nanomaterials (including nanoparticles) continually being developed and tailored for specific applications, it is expected that new combinations of DSPE and CPE will emerge. These new proposed combinations of DSPE and CPE will likely incorporate advanced nanomaterials to develop analytical procedures that enhance the potential of detection methods even further.

Recent advancements in CPE clearly align well with the principles of green chemistry. What could be more helpful in the future is incorporating CPE procedures into online arrangements with suitable detection methods. This remains a significant challenge. Au-

tomating the entire analytical procedure is essential for saving time and energy, potentially paving the way for the development of new flow-based setups.

Further improvements could involve selecting biodegradable and completely environmentally benign surfactants.

In summary, a CPE procedure using a biodegradable surfactant designed to operate at room temperature in a flow-based setup can represent a highly environmentally friendly alternative for this effective extraction technique.

In the end, it can be concluded that while innovative CPE procedures, which represent a more efficient and greener alternative to conventional CPE procedures, have primarily been applied in the analysis of drinking water samples thus far, it seems likely that over time, these procedures will increasingly find application in the analysis of more complex matrices, including various beverages of different origins and compositions.

Author Contributions: Conceptualization, methodology, validation, investigation, and resources, I.H.; writing—original draft preparation, I.H.; writing—review and editing, M.U.; funding acquisition, I.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences under the contract VEGA 1/0135/22.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. El Hosry, L.; Sok, N.; Richa, R.; Al Mashtoub, L.; Cayot, P.; Bou-Maroun, E. Sample preparation and analytical techniques in the determination of trace elements in food: A review. *Foods* **2023**, *12*, 895. [[CrossRef](#)] [[PubMed](#)]
2. Luján, C.E.; Lemos, A.A.; Oviedo, M.N.; Llaver, M.; Wuilloud, R.G. Deep eutectic solvents as a green alternative for trace element analysis in food and beverage samples: Recent advances and challenges. *Talanta* **2024**, *269*, 125451. [[CrossRef](#)] [[PubMed](#)]
3. Mogwasi, R.; Onyancha, M.E.; Mobegi, E.; Nyabaro, O. Inductively coupled plasma-mass spectrometry versus flame atomic absorption spectrophotometry for the analysis of Fe, Cu, Zn, Mn and Cr in medicinal plants: A comparison study. *Adv. Transl. Med.* **2023**, *2*, 1–15. [[CrossRef](#)]
4. Hagarová, I.; Urik, M. New approaches to the cloud point extraction: Utilizable for separation and preconcentration of trace metals. *Curr. Anal. Chem.* **2016**, *12*, 87–93. [[CrossRef](#)]
5. Ghambarian, M.; Yamini, Y.; Saleh, A.; Shariati, S.; Yazdanfar, N. Taguchi OA16 orthogonal array design for the optimization of cloud point extraction for selenium determination in environmental and biological samples by tungsten-modified tube electrothermal atomic absorption spectrometry. *Talanta* **2009**, *78*, 970–976. [[CrossRef](#)] [[PubMed](#)]
6. Wang, M.; Zhong, Y.Z.; Qin, J.P.; Zhang, Z.H.; Li, S.; Yang, B.Y. Determination of total selenium in food samples by d-CPE and HG-AFS. *Food Chem.* **2017**, *227*, 329–334. [[CrossRef](#)] [[PubMed](#)]
7. Hagarová, I.; Nemček, L. Recent advances in speciation analysis of trace antimony in environmental and biological samples based on cloud point extraction and spectrometric methods. In *Sustainable Agriculture Reviews*; Lichtfouse, E., Ed.; Springer Nature: Cham, Switzerland, 2021; Volume 52, pp. 49–77.
8. Halko, R.; Hagarová, I.; Andruch, V. Innovative approaches in cloud-point extraction. *J. Chromatogr. A* **2023**, *1701*, 464053. [[CrossRef](#)] [[PubMed](#)]
9. Quina, F.H.; Hinze, W.L. Surfactant-mediated cloud point extractions: An environmentally benign alternative separation approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 4150–4168. [[CrossRef](#)]
10. Wang, Z.L.; Xu, H.H.; Zhang, W.Z.; Zhuang, B.H.; Qi, H.S. Cloud point of nonionic surfactant Triton X-45 in aqueous solution. *Colloids Surf. B-Biointerfaces* **2008**, *61*, 118–122. [[CrossRef](#)]
11. Hinze, W.L.; Pramauro, E. A critical review of surfactant-mediated phase separations (Cloud-point extractions)—Theory and applications. *Crit. Rev. Anal. Chem.* **1993**, *24*, 133–177. [[CrossRef](#)]
12. Wan, L.S.C.; Lee, P.F.S. CMC of Polysorbates. *J. Pharm. Sci.* **1974**, *63*, 136–137. [[CrossRef](#)] [[PubMed](#)]
13. Hagarová, I.; Nemček, L. Reliable quantification of ultratrace selenium in food, beverages, and water samples by cloud point extraction and spectrometric analysis. *Nutrients* **2022**, *14*, 3530. [[CrossRef](#)] [[PubMed](#)]

14. Depoi, F.D.; Pozebon, D. The use of cloud point extraction and hydride generation for improving the Sb and Se limits of detection in ICP OES. *J. Braz. Chem. Soc.* **2012**, *23*, 2211–2221. [[CrossRef](#)]
15. Biata, N.R.; Mashile, G.P.; Ramontja, J.; Mketi, N.; Nomngongo, P.N. Application of ultrasound-assisted cloud point extraction for preconcentration of antimony, tin and thallium in food and water samples prior to ICP-OES determination. *J. Food Compos. Anal.* **2019**, *76*, 14–21. [[CrossRef](#)]
16. Snigur, D.; Barbalat, D.; Chebotarev, A.; Synievyd, A.; Bevziuk, K. A rapid cloud point extraction of Molybdenum(VI) with 6,7-dihydroxy-2,4-diphenylbenzopyrylium perchlorate prior to its spectrophotometric determination. *Chem. Pap.* **2021**, *75*, 1823–1830. [[CrossRef](#)]
17. Thongsaw, A.; Sananmuang, R.; Udnan, Y.; Ross, G.M.; Chaiyasith, W.C. Dual-cloud point extraction for speciation of mercury in water and fish samples by electrothermal atomic absorption spectrometry. *Spectrochim. Acta Part B-At. Spectrosc.* **2019**, *160*, 105685. [[CrossRef](#)]
18. Chen, B.B.; Hu, B.; He, M. Cloud point extraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for the speciation of inorganic selenium in environmental water samples. *Rapid Commun. Mass Spectrom.* **2006**, *20*, 2894–2900. [[CrossRef](#)] [[PubMed](#)]
19. Altunay, N.; Gürkan, R. Separation/preconcentration of ultra-trace levels of inorganic Sb and Se from different sample matrices by charge transfer sensitized ion-pairing using ultrasonic-assisted cloud point extraction prior to their speciation and determination by hydride generation AAS. *Talanta* **2016**, *159*, 344–355. [[CrossRef](#)] [[PubMed](#)]
20. Ulusoy, H.I.; Gürkan, R.; Ulusoy, S. Cloud point extraction and spectrophotometric determination of mercury species at trace levels in environmental samples. *Talanta* **2012**, *88*, 516–523. [[CrossRef](#)]
21. Niazi, A.; Momeni-Isfahani, T.; Ahmari, Z. Spectrophotometric determination of mercury in water samples after cloud point extraction using nonionic surfactant Triton X-114. *J. Hazard. Mater.* **2009**, *165*, 1200–1203. [[CrossRef](#)]
22. Afkhami, A.; Madrakian, T.; Siampour, H. Highly selective determination of trace quantities of mercury in water samples after preconcentration by the cloud-point extraction method. *Int. J. Environ. Anal. Chem.* **2006**, *86*, 1165–1173. [[CrossRef](#)]
23. de Wuilloud, J.C.A.; Wuilloud, R.G.; Silva, M.F.; Olsina, R.A.; Martinez, L.D. Sensitive determination of mercury in tap water by cloud point extraction pre-concentration and flow injection-cold vapor-inductively coupled plasma optical emission spectrometry. *Spectrochim. Acta Part B-At. Spectrosc.* **2002**, *57*, 365–374. [[CrossRef](#)]
24. Wen, X.D.; Zhang, Y.Y.; Li, C.Y.; Fang, X.; Zhang, X.C. Comparison of rapidly synergistic cloud point extraction and ultrasound-assisted cloud point extraction for trace selenium coupled with spectrophotometric determination. *Spectrochim. Acta Part A-Mol. Biomol. Spectrosc.* **2014**, *123*, 200–205. [[CrossRef](#)] [[PubMed](#)]
25. Gürkan, R.; Mr, U.; Altunay, N. Development of a simple, sensitive and inexpensive ion-pairing cloud point extraction approach for the determination of trace inorganic arsenic species in spring water, beverage and rice samples by UV-Vis spectrophotometry. *Food Chem.* **2015**, *180*, 32–41. [[CrossRef](#)] [[PubMed](#)]
26. Liu, J.L.; Han, Q.; Hu, E.Y.; Yang, C.; Yin, M.M. Determination of trace mercury in water samples by cloud point extraction coupled with atomic fluorescence spectrometry. *J. Anal. Chem.* **2023**, *78*, 303–309. [[CrossRef](#)]
27. Ulusoy, H.I.; Gürkan, R.; Demir, Ö.; Ulusoy, S. Micelle-mediated extraction and flame atomic absorption spectrometric method for determination of trace cobalt ions in beverage samples. *Food Anal. Methods* **2012**, *5*, 454–463. [[CrossRef](#)]
28. Pohl, P. Determination and fractionation of metals in beer: A review. *Food Addit. Contam. Part A-Chem. Anal. Control Expo. Risk Assess.* **2008**, *25*, 693–703. [[CrossRef](#)] [[PubMed](#)]
29. Gurkan, R.; Altunay, N. A reliable method of quantification of trace copper in beverages with and without alcohol by spectrophotometry after cloud point extraction. *Quim. Nova* **2013**, *36*, 1146–1154. [[CrossRef](#)]
30. Altunay, N.; Gürkan, R. Simultaneous determination of antimony and boron in beverage and dairy products by flame atomic absorption spectrometry after separation and pre-concentration by cloud-point extraction. *Food Addit. Contam. Part A-Chem. Anal. Control Expo. Risk Assess.* **2016**, *33*, 271–281. [[CrossRef](#)]
31. López-García, I.; Vicente-Martínez, Y.; Hernández-Córdoba, M. Non-chromatographic speciation of chromium at sub-ppb levels using cloud point extraction in the presence of unmodified silver nanoparticles. *Talanta* **2015**, *132*, 23–28. [[CrossRef](#)]
32. Grindlay, G.; Mora, J.; Gras, L.; de Loos-Vollebregt, M.T.C. Atomic spectrometry methods for wine analysis: A critical evaluation and discussion of recent applications. *Anal. Chim. Acta* **2011**, *691*, 18–32. [[CrossRef](#)] [[PubMed](#)]
33. Pohl, P. What do metals tell us about wine? *Trac-Trends Anal. Chem.* **2007**, *26*, 941–949. [[CrossRef](#)]
34. Altunay, N.; Gürkan, R.; Yildirim, E. A new ultrasound assisted-cloud point extraction method for the determination of trace levels of tin and antimony in food and beverages by flame atomic absorption spectrometry. *Food Anal. Methods* **2016**, *9*, 2960–2971. [[CrossRef](#)]
35. Altunay, N.; Gürkan, R.; Kir, U. Ultrasound assisted-cloud point extraction combined with flame atomic absorption spectrometry for selective preconcentration and determination of As(v) in selected water and beverage samples. *Anal. Methods* **2015**, *7*, 6629–6639. [[CrossRef](#)]
36. Gürkan, R.; Altunay, N. Determination of total Sn in some canned beverages by FAAS after separation and preconcentration. *Food Chem.* **2015**, *177*, 102–110. [[CrossRef](#)] [[PubMed](#)]
37. Filik, H.; Aksu, D. Determination of vanadium in food samples by cloud point extraction and graphite furnace atomic absorption spectroscopy. *Food Anal. Methods* **2012**, *5*, 359–365. [[CrossRef](#)]

38. Altunay, N.; Gürkan, R. A simple, inexpensive and convenient procedure for determination of inorganic Sb species in milk and beverage samples in PET containers by flame atomic absorption spectrometry. *Anal. Methods* **2015**, *7*, 9850–9860. [[CrossRef](#)]
39. López-García, I.; Vicente-Martínez, Y.; Hernández-Córdoba, M. Determination of very low amounts of free copper and nickel ions in beverages and water samples using cloud point extraction assisted by silver nanoparticles. *Anal. Methods* **2015**, *7*, 3786–3792. [[CrossRef](#)]
40. Szymczycha-Madeja, A.; Welna, M.; Jedryczko, D.; Pohl, P. Developments and strategies in the spectrochemical elemental analysis of fruit juices. *Trac-Trends Anal. Chem.* **2014**, *55*, 68–80. [[CrossRef](#)]
41. Temel, N.K.; Gürkan, R. Preconcentration and determination of trace vanadium(V) in beverages by combination of ultrasound assisted-cloud point extraction with spectrophotometry. *Acta Chim. Slov.* **2018**, *65*, 138–149. [[CrossRef](#)]
42. Altunay, N.; Gürkan, R.; Kir, U. Spectrophotometric determination of low levels arsenic species in beverages after ion-pairing vortex-assisted cloud-point extraction with acridine red. *Food Addit. Contam. Part A-Chem. Anal. Control Expo. Risk Assess.* **2016**, *33*, 259–270. [[CrossRef](#)] [[PubMed](#)]
43. Gürkan, R.; Altunay, N. Determination of trace cadmium in nonalcoholic beverages by coupling cloud point extraction with spectrophotometry. *Pol. J. Food Nutr. Sci.* **2013**, *63*, 253–260. [[CrossRef](#)]
44. Gürkan, R.; Aksoy, Ü.; Ulusoy, H.I.; Akçay, M. Determination of low levels of molybdenum (VI) in food samples and beverages by cloud point extraction coupled with flame atomic absorption spectrometry. *J. Food Compos. Anal.* **2013**, *32*, 74–82. [[CrossRef](#)]
45. Altunay, N.; Gürkan, R. An inexpensive and sensitive method for speciative determination of Sn(IV), Sn(II), and total Sn as Sn(IV) in selected beverages by micellar improved spectrophotometry. *Food Anal. Methods* **2015**, *8*, 994–1004. [[CrossRef](#)]
46. Seyedmohammadi, P.; Taheri, A.; Rezayatizad, Z. Extraction and determination of mercury from spring water, beverage and rice samples using combined microwave-assisted cloud point and dispersive-solid phase extraction in micellar media. *Water Environ. J.* **2023**, *37*, 729–739. [[CrossRef](#)]
47. Ghaedi, M.; Niknam, K.; Niknam, E.; Soylak, M. Application of cloud point extraction for copper, nickel, zinc and iron ions in environmental samples. *J. Chin. Chem. Soc.* **2009**, *56*, 981–986. [[CrossRef](#)]
48. Filik, H.; Giray, D. Cloud point extraction for speciation of iron in beer samples by spectrophotometry. *Food Chem.* **2012**, *130*, 209–213. [[CrossRef](#)]
49. Ghaedi, M.; Shokrollahi, A.; Mehrnoosh, R.; Hossaini, O.; Soylak, M. Combination of cloud point extraction and flame atomic absorption spectrometry for preconcentration and determination of trace iron in environmental and biological samples. *Cent. Eur. J. Chem.* **2008**, *6*, 488–496. [[CrossRef](#)]
50. Soares, S.; Moraes, L.M.B.; Rocha, F.R.P.; Virgilio, A. Sample preparation and spectrometric methods for elemental analysis of milk and dairy products—A review. *J. Food Compos. Anal.* **2023**, *115*, 104942. [[CrossRef](#)]
51. Gürkan, R.; Korkmaz, S.; Altunay, N. Preconcentration and determination of vanadium and molybdenum in milk, vegetables and foodstuffs by ultrasonic-thermostatic-assisted cloud point extraction coupled to flame atomic absorption spectrometry. *Talanta* **2016**, *155*, 38–46. [[CrossRef](#)]
52. Temel, N.K.; Gürkan, R. Application of ultrasound-assisted cloud-point extraction and spectrophotometry for preconcentration and determination of trace amounts of copper(II) in beverages. *J. Anal. Chem.* **2019**, *74*, 1174–1183. [[CrossRef](#)]
53. Wen, S.P.; Zhu, X.S.; Wei, Y.X.; Wu, S.B. Cloud point extraction-inductively coupled plasma mass spectrometry for separation/analysis of aqueous-exchangeable and unaqueous-exchangeable selenium in tea samples. *Food Anal. Methods* **2013**, *6*, 506–511. [[CrossRef](#)]
54. Ghasemi, E.; Kaykhani, M. Determination of zinc, copper, and mercury in water samples by using novel micro cloud point extraction and UV-Vis spectrophotometry. *Eurasian J. Anal. Chem.* **2017**, *12*, 313–324. [[CrossRef](#)]
55. Bozkurt, S.S.; Ocaoglu, K.; Merdivan, M. Separation and preconcentration of mercury in water samples by ionic liquid supported cloud point extraction and fluorimetric determination. *Microchim. Acta* **2012**, *177*, 47–52. [[CrossRef](#)]
56. Garoub, M.M.; Gouda, A.A. An efficient ionic liquid-based cloud point extraction to preconcentrate mercury in environmental samples and hair of occupational workers before spectrophotometric detection. *Bull. Chem. Soc. Ethiop.* **2022**, *36*, 767–778. [[CrossRef](#)]
57. Dadfarnia, S.; Shakerian, F.; Shabani, A.M.H. Suspended nanoparticles in surfactant media as a microextraction technique for simultaneous separation and preconcentration of cobalt, nickel and copper ions for electrothermal atomic absorption spectrometry determination. *Talanta* **2013**, *106*, 150–154. [[CrossRef](#)] [[PubMed](#)]
58. Pourreza, N.; Naghdi, T. Combined cloud point-solid phase extraction by dispersion of TiO₂ nanoparticles in micellar media followed by semi-microvolume UV-vis spectrophotometric detection of zinc. *Talanta* **2014**, *128*, 164–169. [[CrossRef](#)] [[PubMed](#)]
59. Shakerian, F.; Dadfarnia, S.; Shabani, A.M.H.; Esfahani, G.S. Preconcentration and determination of lead(II) by microextraction based on suspended cation covered zirconia nanoparticles in a surfactant media. *Microchim. Acta* **2013**, *180*, 1225–1232. [[CrossRef](#)]
60. López-García, I.; Muñoz-Sandoval, M.J.; Hernández-Córdoba, M. Cloud point microextraction involving graphene oxide for the speciation of very low amounts of chromium in waters. *Talanta* **2017**, *172*, 8–14. [[CrossRef](#)]
61. López-García, I.; Marín-Hernández, J.J.; Hernández-Córdoba, M. Graphite furnace atomic absorption spectrometric determination of vanadium after cloud point extraction in the presence of graphene oxide. *Spectrochim. Acta Part B-At. Spectrosc.* **2018**, *143*, 42–47. [[CrossRef](#)]

62. Abdulhussein, N.M.; Muslim, N.M.; Hussien, M.A.; Azooz, E.A.; Al-Mulla, E.A.J. Green preconcentration procedures for the determination of aluminium in bottled beverages prior to electrothermal atomic absorption spectroscopy: A comparative study with environmental assessment tools. *J. Iran. Chem. Soc.* **2024**, *21*, 1203–1212. [[CrossRef](#)]
63. Hu, B.; He, M.; Chen, B.B. Nanometer-sized materials for solid-phase extraction of trace elements. *Anal. Bioanal. Chem.* **2015**, *407*, 2685–2710. [[CrossRef](#)] [[PubMed](#)]
64. Nekouei, S.; Nekouei, F.; Ulusoy, H.I.; Noorizadeh, H. Simultaneous application of cloud point and solid-phase extraction for determination of Fe(III) and Cu(II) ions by using SnO₂ nanopowder in micellar medium. *Desalination Water Treat.* **2016**, *57*, 12653–12662. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.