

Focus Review Article

Review of Procedures Involving Separation and Solid Phase Extraction for the Determination of Cadmium Using Spectrometric Techniques

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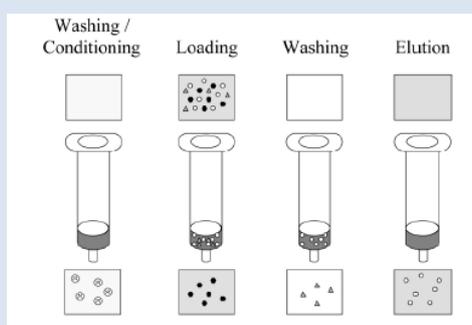
Receive Date: 26 October 2018, Revise Date: 17 November 2018, Accept Date: 09 November 2018

Abstract:

For the analysis of cadmium, the toxicity of spectroscopic methods is increasing because the measurement of the low level for detection of this element is done in various samples. This review studies the methods of separation and pre-concentration and analyzes spectroscopic methods for detecting cadmium in water samples. Considering the amount of trace cadmium ion in the analysis of aqueous samples, a suitable method should be used. From the past, chemists have been trying to find a solid phase to recover analytes from the water matrix. The experimental method of SPE is a standard method for the analysis of heavy metals such as cadmium ion in aqueous samples. Cadmium is known worldwide as a toxic metal. Therefore, it is often necessary to determine this element in environmental, biological, food and agricultural samples. However, analyses are difficult because the quantities of cadmium samples are relatively small, except for trace amounts. Measurements are made by flame atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry. For this reason, several preconcentration methods for the determination of cadmium ion, including solid phase extraction, coprecipitation and cloud point extraction, has been reviewed. A brief history of using Solid-phase extraction in the analysis of cadmium ion in water samples is presented in this paper.

Key words Solid-phase extraction; Preconcentration; Water analysis; Trace Cadmium

Graphical Abstract:



Biography:



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1. Introduction

Due to the sensitivity and selectivity of techniques such as atomic absorption spectrometers, pre-concentration must be pre-condensed, especially in water samples for cadmium ion, before measurement is trace. In addition, since high-level non-toxic components are usually accompanied by analytes, a purge step is often done. Liquid liquid extraction is a classic method to prevent the removal of metal ions and matrixes. Solid phase extraction (SPE) is another approach that offers a number of important benefits. This reduces the consumption and exposure of solution and also, the cost of disposal and extraction time to prepare the sample. As a result, in recent years, the SPE has been successfully used to isolate and identify sensitive metal ions, mainly in water samples. Following the introduction of the theory of this technique, guidelines are developed Solid-phase extraction-based methods for pre-concentration of small amounts of cadmium ions. Finally, application examples are provided[1-14].The above-mentioned techniques, with FAAS, provide low cost, high-performance, and high-end specimens. The determination of cadmium by an atomic flame spectrometer is free of interference, and this can easily be measured with compressed air-acetylene flame. In the resonance line of 228 nm, the detection limit for cadmium is 0.02 mg L^{-1} .

The analytical line is in the range of 326.1 nm to determine the concentration of Cd higher and the concentration of the characteristic is about 6 mg L^{-1} , so greater than this value should be avoided [15,16]. Cadmium measurement was difficult by ETAAS for a long time, since cadmium is an element that has volatility [17].The SPE technique is similar to the liquid fluid extraction (LLE), which consists of two phases (two incompatible solvents). However, instead of two dispersed liquid phases, as in the LLE, SPE involves partitioning between the fluid (the matrix of the sample) and a solid phase (adsorbent). This typical filtration technique provides concentration and enrichment of analytes from the solution by sorption onto a solid sorbent. Accordingly, the liquid sample is transported through a column, a cartridge, a tube, or a absorber disc that absorbs and holds the analytes. After

all the sample passes through the sorbent, the stored analytes are used then being recovered upon elution with a suitable solvent. Solid-phase extraction began for the first time fifty years ago [1,2,3]. However, numerous studies have shown that the great potential of this technique can be used for specialized studies. [18,161-177].

1.1. Basic principles

An SPE method is always composed of three to four successive steps, as illustrated in Fig. 1.. First, a solid sorbent should be swirled with a suitable solvent (as a solvent). This step is important because it moisturizes the adsorbent and activates the adsorbent groups. In addition, the removal of possible impurities that are initially present in the sorbent is eliminated. Also, at this stage, the air contained in the column is removed and the saturated volume of the adsorbent is filled with solvent. Typically, methanol is used to activate the depleting phase (such as octadecyl-bonded silica), followed by water or a water buffer whose pH and ionic strength are similar to the sample. Care should be taken to ensure that no solids are absorbed between the two stages of elution and the passage of the adsorbent sample, otherwise the analytes will not be maintained effectively and poor results will be achieved. If the sorbent is dried for more than a few minutes, it should be re-modified.

The second step is to pass and absorb the sample through a solid absorber. Depending on the system used, the sample size can be from 1 mL to 1 L. The sample may be transmitted by gravity, pumping, vacuum or by an automatic system of adsorbent columns. The flow rate of the sample through the sorbent should be low enough to allow the adsorbent to maintain analytes efficiently. During this step, analyses enriches on the adsorbent. Even if the matrix components are retained by a solid absorber, some of them will pass, so the matrix separation is possible from sample analysis.

The third step (which is optional) may involve solid solvent washing with a suitable solvent having low tensile strength to eliminate the absorbed matrix



components. The absorbent drying step may also be recommended, especially for water matrices, to remove the effects of water absorption from solids. This eliminates the presence of water in the final extract, which in some cases may cause post-condensation concentration in the analysis with difficulty. The final step involves the removal of the desired analyte elements by a suitable solvent and without deleting the matrix components of the preservation. The volume of the solvent must be adjusted to allow quantitative recovery of the analytes by low dilution. Additionally, the stream should be properly optimized to ensure that the analyses are completely out. It is often advisable to divide the volume of the solvent into two parts and remove the analyte from the adsorbent.

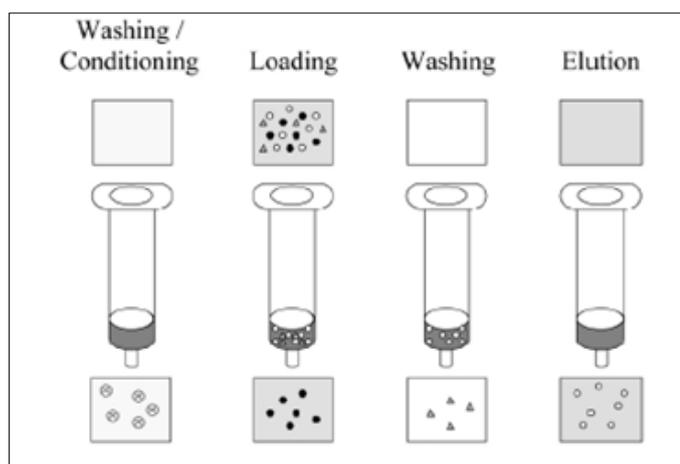


Fig. 1: . Solid-phase extraction operation steps

1.2. Maintenance and Retention of cadmium on adsorbent

Adsorption and absorption of cadmium on solid adsorbent's are necessary for preconcentration (see Fig. 2). The adsorption mechanism depends on the nature of the sorbent, and may include a simple adsorbent, chelation, or an ion exchange. Also, for the trace cadmium inhibition, ion- pair solid phase extraction can be used.

1.2.1. Adsorption.

Trace Cadmium inhibition is usually absorbed in solid phases, through the forces of water retention or hydraulic interaction. Hydrophobic interaction occurs when the solid absorbent is very non-polar (reversed phase). The most commonly used absorbent of this type is octadecyl-bonded silica (C_{18} -silica). Mostly it is activated with water-soluble oxygen, such as methanol or acetonitrile. Such interactions are usually preferred to online systems because they are not too strong .

1.2.2. Chelation

Several atoms of the functional group are capable of chelating with cadmium ion in water. Atoms are often used in nitrogen (e.g. N in amines, azo groups, amides, nitriles) and sulfur (eg S in thiols, Tiocarbamate, teeth). The nature of the functional group shows the selective ligand idea of the selectivity of cadmium ion . In practice, mineral cations may be divided into 3 groups:

a) *hard ,group cations*: It reacts through electrostatic interactions (due to increase in

The entropy is due to changes in the orientation of water hydration molecules); this group consists of alkaline and alkaline- earth metals (Ca^{2+} , Mg^{2+} , K^+ , Na^+) that comprise the weakly outer crystalline complexes by only hard oxygen ligands.

b) *Boundarine, Cations*: These cations have an intermediate behavior; these groups of cations include Fe , Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+} Pb^{2+} Mn^{2+} . They have a complex for both hard and soft ligands.

c) *Soft, cations*: These cations tend to produce a medium-magnesium (N) and soft (S) ligand. Therefore, Cd^{2+} and Hg^{2+} have a strong coordinate bond with medium (N) and soft ligands (S)

For soft metals, the order of the donor atom dependence has been observed: O-N-S. A reversed covalent bond has been observed for hard cations. For a bidentate ligand, the dependence on a soft metal increases with the softness of the donor atom: (0, 0) - (0, N) - (N, N) - (N, S). This order is reversed for hard metals. In general, the competition for a one-way covalence bond of a given ligand consists essentially of the first and second group metals for sites O and metals in group two and the third group for sites N and S. The competition between the metals in group I and the third group is very weak.

Chelating chemical agents that are added directly to the sample to chelate trace cadmium loaded onto a suitable adsorbent. One method is to load the chelating group into the sorbent. finally, three different methods are available: (1) the synthesis of new sorbents containing such suitable functional groups; (2) the chemical bond with suitable functional groups on the adsorbent; (3) the physical absorption of the groups in the adsorbent by loading the solid matrix with solution containing a chemical ligand (impregnated, coated or loaded absorbers). The latter is the easiest to use in practice. The main drawback is that there is a probability that the calcite discharges from solid solvent. During the elution, it reduces the lifetime of the saturated adsorbent. Different ligands have been used on various types of solid matrices for condensation, separation and determination of successful inhibition metal ions.



Chemical groups with a hydrophobic group are stored on hydrophobic acids (such as C₁₈-silica). Also, ionic exchange resins with chemicals containing an ionexchange group, such as a sulfonic acid ditizone derivative (i.e., diphenyl tiocarbazone) (DzS), 5-sulfo-8-quinolinol, 5-sulfosalicylic acid, and tistylecyclic acid.

The metal ion cations depend on several factors for the performance of the chelate: (1) the hardness and softness, charge, and size of the metal ion; (2) the nature of the atoms of the donors in the ligand; (3) the buffer conditions that favor the metal cation extraction and bonding with the group Active chelate; (4) the main nature of the adsorbent (e.g., the degree of cross-linking for a copolymer). However, the presence of a solid sorbent may also effect and result in the formation of a complex with a different stoichiometry than that observed in Homogeneous reaction [10,11] In fact, several properties of the adsorbent should be taken into account, namely the number of active groups present in the resin phase [7,10], the resin and the ligand connected [12] Resin hole dimensions [13].

requiring air flames and acetylene [13]. Interference from aluminum and iron can be avoided by adding protective agents such as ascorbic acid, citric acid and EDTA. The technique is very low (LOD 0.02 mg L⁻¹) and is often unsuitable for low-level analysis [13]. In this sense, to determine the amount of cadmium measurement, as shown in the tables in the table below, many preconcentration and preparation methods should be performed [13].

Graphite furnace atomic absorption spectroscopy (GF-AAS) is a good alternative to determining the small amount of cadmium in several samples for sensitivity [13]. However, in some cases, the steps before and after the isolation are performed before the GF-AAS analysis measurements. Using a modifier, fixes cadmium, and allows measurement without effect Matrix and interference species. The Pd-Mg modifier is one of the most commonly used ones, since it produces the best results. This modifier allows for the use of temperatures in the range of 1200 °C to 1400 °C, which can further distribute the disturbing elements [13-17]. The stabilizer effect of this modifier also improves its atomic temperature to 2000 °C [13]. Ammonium phosphate is another modifier that is often used to determine cadmium by the GF-AAS, which allows its atomic temperature to be reduced to 1600 °C and reaches a detection limit of 15 pg[13,18].

2.2. Inductively coupled plasma optical emission spectrometry (ICP OES)

An induced optical-optical optical spectrometry is an appropriate analytical method that is often used to determine most heavy metals such as cadmium in different types of specimens [19]. However, the small amounts of cadmium in many samples are below the detection limit of this technique. Almost all photomultiplier-based ICP spectrometers use the analytical line Cd 220.353 nm, despite the high background interference and interference between the elements of 220.4 nm alpha and the background change due to iron (Hg). The direct interference of the overlap due to iron in the analytical lines was found to be 226.0 and 284.8 nm[20,21]. Therefore, preconcentration and separation methods are designed to measure the cadmium content in complex matrices using ICP OES. Several tables shown in this paper summarize the use of separation techniques such as liquid liquid extraction, solid phase extraction, cloud extraction, as a preparation for cadmium determination using ICP OES.

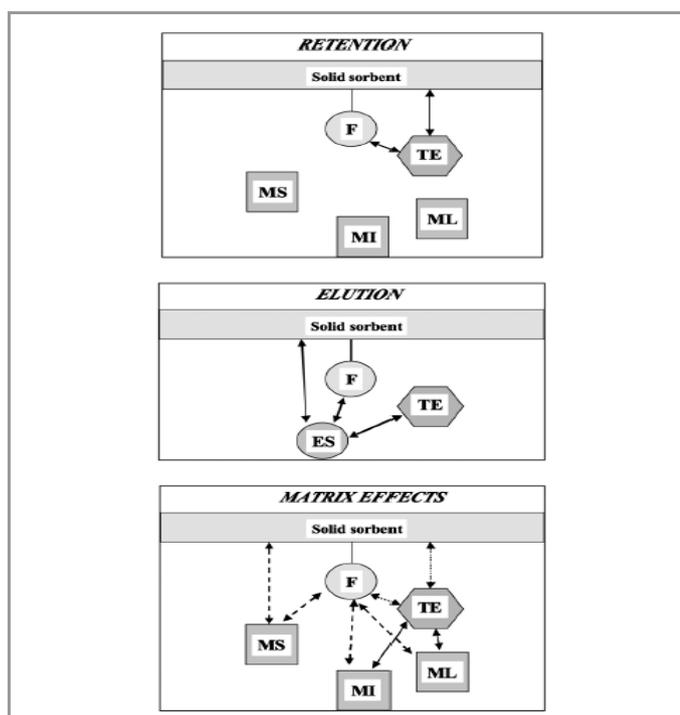


Figure 2. Interactions occurring at the surface of the solid sorbent. F, functional group; TE, trace element; MS, matrix solvent; MI, matrix ions; ES, elution solvent.

2. Measuring cadmium

2.1. Atomic Absorption Spectroscopy (AAS)

The determination of cadmium by the Flame Atomic Absorption Spectrometer (FAAS) is virtually intact,

3. Separation and pre-condensation of cadmium

Separation techniques [23,50], liquid liquid extraction [57-60], solid phase extraction [69-134], and cloud extraction [139-146,150-160] have been successfully



used. Each technique has advantages and disadvantages and should be selected according to the analytical problem.

3.1. Coprecipitation

One of the most efficient separation and enrichment methods for heavy metal ions is also coprecipitation. In this technique, the collector should be easily separated from the matrix solution. This can be done by filtering, centrifuging and depositing. The advantages of this technique is its simplicity. Inorganic or organic collector used as efficient collectors of fine elements. However, this process is slow [22]. This technique is used to determine the cadmium samples in water. For cations such as aluminum, gallium, cerium (IV), erbium, iron (III), magnesium, samarium and zirconium hydroxide, they have been widely used and successfully applied to trace amounts of cadmium ions used [23,50]. In Table 1, several methods for determining cadmium in many samples are described using coprecipitation as a separation and preconcentration method.

3.2. Methods by Liquid-liquid extraction

Solvent extraction is one of the most extensive methods of preparation and separation to determine the small amounts of heavy metals. Its feature is simplicity, convenience, wide scope and, etc.. In this method, the metal is between two non-intermixing liquid phases (usually the water and organic phase). After a complex reaction, the metal ion is extracted from the water solution to the organic phase. To measure, the extracted metallic cation can be measured directly in the organic phase and usually acid is performed [51-53]. Separation and preconcentration methods using solvent extraction generally result in high concentration because of the difference in the volume of water and organic phases. This method is time consuming and retains a large amount of potentially toxic organic solvents as waste. This single operation can be done with a flow injection system (FI) and / or a sequential injection (SI), which, in addition to reducing sample consumption and solvent consumption, automatically manipulates the enclosed [54].

Methods in flow injection systems for separation and pre-concentration using solvent extraction to determine metals such as cadmium and lead are widely discussed in literature [55, 56]. Table 2 shows several analytical systems for separating cadmium and pre-condensation using solvent extraction and determining cadmium by flame atomic spectrometry techniques.

3.3. Methods by Solid phase extraction

The solid phase extraction method is based on the partition between a liquid containing a sample matrix

and a suitable solid phase (sorbent). The method is based on the contact of a homogeneous liquid sample through a column, a flask, a cartridge, a tube, or a disc containing a selective absorber holds cadmium ions. After this step, recovered cadmium is eluted by a proper solution with a suitable solvent [68]. Sorbents used for pre-concentrate and determining cadmium can be loaded with complex reactions by suitable reagents. Reagents suitable for loading these sorts adsorbents include: activated carbon, natural adsorbents, Amberlite XAD resins [71-75],

polyethylene [76] and others [77]. Many reactants have been used to store cadmium ions, which include: 2-(2-thiazolylazo)-*p*-cresol (TAC) [85], 2-propylpiperidine-1-carbohydrate [86], 2- (2 Benzotriazole-*zo*) -2-*p*-cresol (BTAC) [80,87], red periglolol [81], 1- (2-pyridylazo) -2-naphthol (PAN), [88], dithizone [89,90], and 2- (5-Bromo-2-pyridylazo) -5-diethylaminophenol (5-Br-PADAP) [91]. Reagents can also be used with chemical reactions, which are potent inhibitors for the pre-concentration of cadmium.

Supports includes the Amberlite XAD Series [92,93], Silica Gel [94-96] and Cellulose [97,84]. Several methods for the separation and pre-concentration of cadmium have been proposed using the solid phase extraction method shown in Table 3.

3.4. Automation and on-line analysis

The solid phase extraction isolation technique can be easily automated [123-124]. Also, a larger sample size can be analyzed. In addition, a smaller sample size can also be used. However, in the case of complex specimens, off-line SPE should be used because of its greater flexibility, as well as the possibility of analyzing the same extraction using various techniques to apply.

3.4.1. On-line coupling to liquid chromatography.

On-line systems mainly use a micro-column. On-line systems have been reported with several detectors, such as ultraviolet detectors or plasma mass spectrometers (ICP-MS), which have been inductively coupled, with detection limits in the range of 0.05-50 ppm. Using a photodiode fluorescent detector, detection with a maximum absorption wavelength can reduce the detection limit to 0.50 ppb [125].

3.4.2. Determinates of cadmium with Online coupling to Atomic Absorption

Online spectroscopy in atomic absorption for heavy elements [126] Olsen et al and Fang et al [127,128] were presented for the first time. Then, an absorption extraction system, which was coupled with the GF-



Table 1: Preconcentration procedures using coprecipitation for the determination of cadmium

Sample	Collector	Technique	LOD(μgL^{-1})	R.S.D. (%)	Reference
Ground water	MnO ₂	FAAS		3.3-8.3	[23]
Natural water	MnO ₂	FAAS			[24]
Rain water	MnO ₂	FAAS			[25]
Sea water	MnO ₂	FAAS			[26]
Zinc and zinc ~aluminum	MnO ₂	ICPOES			[27]
River waters	MnO ₂	ICPOES	3.2	5.0	[28]
Sea waters and mineral	Aluminum hydroxide	FAAS	16	2.0-3.0	[29]
Sea waters	Cerium(IV) hydroxide	FAAS	7	8	[30]
Tap water	Erbium hydroxide	FAAS	0.Z4	1-9	[31]
Sea water	Gallium hydroxide	ICPOES	0.IS		[32]
Sea water	Gallium hydroxide	ICPOES	0.IS		[33]
Sea water	Iron hydroxide	ETAAS			[34]
Sodium tungstate	Lanthanum hydroxide	ICPOES	I.JI	3.1-5.5	[35]
Dialysis concentrate	Magnesium hydroxide	ETAAS			[36]
Sea water	Magnesium hydroxide	ICP-MS	2.7.10 ⁻⁴		[37]
Urine, sediment	Copper	EAAS	24.0	5.0	[38]
Natural water	Zirconium hydroxide	E,AAS	4.2.10 ⁻⁴	<10	[39]
Infant formulas and milk	Ammonium Pyrrolidine	ETAAS	0.04		[40]
Cupric sulfate	Ammonium Iron sulfate	ICPOES		4.4-5.8	[41]
Natural water	Bismuth dithyldithiocarbamate	ETAAS			[42]
Natural water	Copper dithyldithiocarbamate	FAAS	1.5	4.4	[43]
Natural water	Copper dithyldithiocarbamate	FAAS	3.2	2.0	[44]
Cobalt sulfate	Cerium phosphate	FAAS	55.9		[45]
Water	Lanthanum phosphate	ICPOES		1.6	[46]
Sea water	Palladium	ETAAS		3.8	[47]
Natural water	Sodium dithyldithiocarbamate	ICPOES			[48]
River water	Sodium dithyldithiocarbamate	ICPOES	10.0		[49]
Sea water	Sodium sulphide	ICPOES		1.9	[50]

**Pg/mL ^a ng/g

AAS coupling, was proposed for small amounts of cadmium [129]. Since then, numerous articles have been reported by FI. The selected programs are shown in Table 4. This sorbent should be used for rapid analysis of antibiotics in FI systems [130]. In practice, the C₁₈-silica adsorbent is widely used. Selection of the appropriate reactant based on their rapid reaction with metals, such as diethyldithiocarbamate (DDTC) and Ammonium pyrrolidine dithiocarbamate (APDC) [131,132]. Also, both reactants are soluble in water and not absorbed in C₁₈- silica so that they are not loaded with their reactants. However, these reagents are public and non-selective. Although the C₁₈-silica is often used sorbent for preconcentration of flow injection analyses, other sorbents are used for some applications as reported in Table 4, such as reactive activated carbon [134], polyurethane foam PUF) [134] or PTFE rotation [133]. A small reactor (KR) has recently been found which includes a long spiral tube, usually made of PTFE.

3.4.3. Cadmium ion determinates in coupling with ICP-AES or ICP-MS.

The first preconcentration report of FI in line with the ICP-atomic emission spectrometry (AES) appeared about 25 years ago [130]. Since then, numerous studies have been carried out to measure heavy metals, including cadmium, using various adsorbents such as modified ZrO₂ or modified silica gel [136].

3.4.4. On-line coupling of cadmium by spectrophotometry

The benefits of spectrophotometry are cheap and very common tools. In addition, by choosing a redundant reaction, it is possible to determine the number of metal cations [123].

Its coupling with FI analysis is well suited for regulatory purposes, and examples are shown in Table 4 [123]. Solid phase spectrophotometer (SPS) is also provided with FI systems due to its simplicity and low detection limits. Solid sorbents are commercially



available or customizable. FI extraction methods have several advantages: an increase in sample size (with an increase of 1 to 2 times), the consumption of the prototype and the indicator is reduced two to three times, the relative standard deviation of the standard decreases by about 1-2%, low pollution And the method will be automated quickly and easily.

3.5. Cloud Point Extraction (CPE)

The cloud point phenomenon occurs when a non-ionic or amphoteric surfactant react above the critical concentration of micelle (CMC) causes the metal cation or the main solution to be analyzed in two steps, when the temperature specified in the thermometer is called the super-spot cloud Gets At the top of the cloud point, the micelles form the surfactant molecules that act as an organic solvent in the extraction of the liquid liquid, and the analytes are divided between the micelles and the water phase [135-137]. Therefore,

metal cation can be trapped and dispersed into a rich phosphorus phase, which is hydrophobic. The nucleus of the micelle is formed in the form of an accumulated hydrophobic, which is formed between the metal ion and a proper chalky agent in the proper conditions.

Partition evaluate, So the coefficients of the ligands and surrounding complexes create a peripheral Surfactant that changes the ratio of the reaction, the position of the equilibrium, and the parameters of the analysis [140], for example, the cadmium determined prior to centrifugation in a micellar phase of Triton X-114 phase And is determined by GF-AAS using appropriate modifiers. Therefore, at a higher pyrolysis temperature, the removal of the surfactant matrix is achieved prior to the cadmium atomization step without risking the loss of the analite and preventing the absorption of the background. Table 5 shows some of the new CPE methods for determining cadmium and heavy metals.

Table 2 : Preconcentration methods by solvent extraction for determination of cadmium

Sample	Technique	Complication Solvent agents	Enrichment factor	Reference
Table salt	FAAS	Dithizone MIBK ^a	99	[57]
Waste Water	FAAS	HBDAP ^b HNO ₃ /HCl		[58]
Estuarine water	GFAAS	APDC ^c and DDC ^d		[59]
Urine and CRF	ICP-MS	APDC MIBK/HNO ₃	23.3	[60]
High Purity aluminum	ICPOES	APDC HNO ₃ /H ₂ O ₂		[61]
Natural water	FAAS	Dithizone Xylene		[62]
Natural water	FAAS	Dithizone HNO ₃	543	[63]
Aragonite	ET AAS	NaDDC MIBK		[64]
water	FAAS	APDC MIBK		[65]
Seawater	ICP-MS	DOC		[66]
Drinking water	FAAS	CMPQ ^e		[67]

^a Methylisobutyl ketone

^b NN-bis(2-hydroxy-5-bromo-benzyl)-1-

^c Ammonium Pyrrolidinedithiocarbamate

^d Dithionitrothiocarbamate

^e 5-(2-Cabomethoxyphenyl)azo-8quinolinol



Table 3: Off-line procedures for Cadmium preconcentration using solid phase extraction

Sample	Enrichment factor	Technique	LOD(μgL^{-1})	R.S.D. (%)	Reference
Sea water	-	FAAS	-	3.3	[71]
Environmental sample	-	FAAS	-	-	[72]
Sea water	150	FAAS	-	-	[73]
Waste water	100	FAAS	0.001	-	[81]
Tap water	-	FAAS	2.00	2.2	[82]
River waters	-	FAAS	5.0	5.1	[83]
Sea waters	12000	FAAS	0.005	2.1-3.2	[88]
Tap water	200	FAAS	-	1.9	[90]
River waters	-	FAAS	4.06	2.9	[92]
River waters	-	FAAS	-	5.0	[93]
Sea water	-	GF-AAS	4.0	8.0	[95]
Tap water	-	FAAS	3.3	3.9	[98]
Sea water	40	ICPOES	53.0	4.2	[99]
Sea water	100	GF-AAS	0.20	5.0	[100]
Natural water	500	ICPOES	0.15	<10	[101]
soil	200	FAAS	2.50	2.4-3.2	[103]
River waters	-	FAAS	-	2.9	[104]
Natural water	250	FAAS	4.00	4.4	[105]
Natural water	375	FAAS	0.25	2.5	[106]
Water	129	FAAS	0.20	-	[107]
Waste water	130	FAAS	6.10	1.6	[108]
Waste water	-	FAAS	15.0	2.8	[109]
Natural water	-	FAAS	-	3.0	[110]
River water	100	GF-AAS	0.04	4.9	[111]
Water sample	-	FAAS	0.70	1.9	[112]
Sea water	50	FAAS	0.10	-	[113]
Sea water	-	FAAS	0.03	2.8	[115]
Sea water	-	FAAS	-	2.0	[116]
Water sample	294	FAAS	3.0	2.78	[117]
Water sample	-	FAAS	0.017	-	[118]
Tap water	115	FAAS	1.0	2.2	[120]
Sea water	-	FAAS	-	1.9	[121]

Table 4: Applications of SPE to FI on-line preconcentration systems

Matrix	Sorbent	Eluent	Analysis method	Recovery%	Preconcentration	Matrix	Sorbent
Certified	C18-silica	IBMK	F-AAS	99.2–101%	60–189	3000	[132]
biological,	C18-silica	EtOH	F-AAS	--	4–1000	300–3000	[134]
vegetable	C18-silica	MeOH	F-AAS	--	14–60	4000-10000	[130]
samples	PTFE turnings	IBMK	F-AAS	95–102	330	800	[133]
Standard	PUF	EtOH	F-AAS	--	4–1000	300–3000	[134]
solutions	Lewatit TP807'84 PAPH	HCl	Spectrophotometry	80–120	50	2000-5500	[123]



Table 5 : CPE applications for cadmium preconcentration and determination

Sample	Analysis method	LOD($\mu\text{g}\cdot\text{mL}^{-1}$)	RSD(%)	Reference
vegetable	F-AAS	0.3		[139]
blood	GF- AAS	0.08		[140]
River waters	FAAS	1.10	3.5	[141]
Human hairs	F-AAS	2.86	1.39	[142]
Tap water	ICP-OES	0.077	4.2	[143]
Waters	ICP-MS	0.004		
Waste waters	GF- AAS	0.08	4.8	[144]
			2.8	[145]
Biological sample	GF- AAS	0.040		[146]

Table 6 : preconcentration of cadmium ions using knotted reactors

Sample	Analysis method	Enrich factor	LOD($\mu\text{g}\cdot\text{mL}^{-1}$)	RSD(%)	Reference
Tap water	FAAS	37	7.5	2.9	[150]
Water,tea	FAAS	57	8.0	1.30	[151]
Water and Biological sample	FAAS	58	0.2	3.30	[152]
Blood and liver	F-AAS	20	2.0	2.60	[153]
Water samples and soil	GF- AAS	99	1.6	2.70	[154]
Biological s and environmental samoples	GF- AAS	125	4.8	2.0	[155]
Water sample	GF- AAS	142	5.0	4.8	[156]
Blood	GF- AAS	99	1.60	2.8	[157]
Biological samople, Urine	ICP-OES	140	0.2	2.70	[158]
Urine	ICP-MS	34	4.7	2.65	[159]
Seawater	ICP-MS	28	0.028	-	[160]

4. Conclusions

The trace of cadmium ions is toxic and carcinogenic. Trace of cadmium ions in various samples pre-concentrated methods are used by separation techniques such as liquid liquid extraction, solid phase extraction, deposition, and cloud extraction. However, each method has its own advantages and disadvantages and should therefore be selected according to the type of sample. Most proposed methods are performed using solid phase extraction. In recent years, online systems have become more important.

5. Acknowledgment

The author gratefully acknowledge department of chemistry, Varamin(Pishva) branch Islamic Azad University, Varamin.

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How to cite this manuscript: Ali Moghimi*, Mohamma Yari. Review of procedures involving separation and Solid Phase Extraction for the determination of cadmium using spectrometric techniques. *Journal of Chemical Reviews (J. Chem. Rev.)*, 2019, 1(1), 1-18.

