Review Article

Old and New Flavors of Flame (Furnace) Atomic Absorption Spectrometry

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This paper presents some recent applications of Flame Atomic Absorption Spectrometry (FAAS) to different matrices and samples. The time window selected was from 2006 up to March, 2011, and several aspects related to food, biological fluids, environmental, and technological samples analyses were reported and discussed. In addition, the chemometrics application for FAAS methods development was also taken into account, as well as the use of metal tube atomizers in air/acetylene flame. Preconcentration methods coupled to FAAS were discussed, and several approaches related to speciation, flotation, ionic liquids, among others were discussed. This paper can be interesting for researchers and FAAS users in order to see the state of the art of this technique.

1. Introduction

Flame Atomic Absorption Spectrometry (FAAS) is one of the most successfully implemented analytical techniques. Its main characteristics are the versatility and low cost (acquisition and operation). Several AAS approaches are presented in the literature, such as those using metal tube atomizers, hydride generation, and preconcentration procedures. The main objective of this paper is to present Flame and Flame Furnace AAS applications related to food analysis, fuels, biological fluids, environmental samples and technological materials, chemometrics, and preconcentration step. Several papers were organized from 2006 to March, 2011, and its main characteristics are reported and discussed.

2. Applications to Specific Samples

2.1. Food. Most developments in the searched period dealt with simplification of strategies for sample preparation, including slurries, preconcentration, and fractionation studies. Some authors also investigated improvements in instrument performance using either simple lab-made devices,

such as Thermospray Flame Furnace AAS (TS-FF-AAS) or commercial instruments, such as High-Resolution Continuum Source FAAS (HR-CS-FAAS) and Fast Sequential FAAS (FS-FAAS). Some aspects of these developments will be highlighted with emphasis on practical approaches for obtaining fast analytical data and additional information applying proper tools for data treatment. The cited literature is not comprehensive, but represents relevant developments for improving and expanding the scope of food analysis.

Fast analytical data can be obtained by reducing the time spent in the conversion of solid samples to representative solutions which can be introduced by nebulization into the flame atomizer. Simple strategies can be based on the preparation of slurries or extractions assisted by ultrasound mechanical waves or microwave radiation. The feasibility of introduction of slurries prepared using ultrasound bath was demonstrated for determination of Mn in cassava leaves [1] and Zn in yogurt [2]. Both procedures used a 20 min sonication time, and determination was performed using conventional FAAS or HR-CS-FAAS, respectively. Bugallo et al. demonstrated the application of slurry technique for analysis of fish tissues by FAAS; however Fe was only accurately

determined when the suspension was rapidly heated by microwave radiation (i.e., 15–30 s at 75–285 W) [3]. This is expected considering the strong association of Fe and Al with matrix components in biological samples. Emulsification was also successfully applied for determination of Ca, Fe, Mg, K, Na, and Zn in egg samples by FAAS [4]. The preparation of the emulsion was carefully studied using different oily phases and surfactants. The best conditions are dependent on the element being determined. Two advantages of the developed method are the use of fewer reagents and the calibration using reference solutions prepared in water medium. Another simple procedure for analysis of a complex sample, in this case buffalo milk, was proposed by Pereira et al. using the dilution of the sample in water-soluble tertiary-amines medium [5]. Calcium, Mg, Mn, and Zn were further determined by FAAS, and no difficulties were caused by the fat content and particle size distribution of the emulsion. It should be mentioned that buffalo milk has about twice the amount of fats compared to cow milk.

Online sample digestion was proposed for determination of Mn and Zn in tea leaves [6]. The digestion was based on the electromagnetic-induced heating of a column made with polytetrafluoroethylene (PTFE) outer tube and seven compactly packed PTFE coil-coated Fe wires. Further determination was performed by FAAS, and sample throughput was 72/h. Offline sample digestion based on photooxidation with ultraviolet radiation and H_2O_2 for 30 min was applied for decomposition of wine samples followed by determination of Fe and Mn by FAAS [7].

Nowadays there is also a trend towards getting information about chemical forms and fractions. In this sense, Pohl and associates have developed fractionation procedures using successive Solid Phase Extractions (SPEs) columns for determination of Cu, Fe, and Mn in freshly ripened honeys [8], Mn and Zn in beers [9, 10], Ca, Mg, Fe and Zn in ultra-high temperature cow milks [11], and Ca and Mg [12] and Fe and Zn [13] in dietary foods and beverage products, such as bee honeys, fruit juices, and tea infusions. All developed fractionation procedures used FAAS for analytes determination and generated information about chemical forms.

A thorough discussion about sample preparation strategies for determination of metals in food analysis using spectroanalytical methods was presented by Korn et al., and a careful reading of this review is highly recommended [14].

Improvements in sensitivity for FAAS were proposed using either simple instrumental strategies, such as the use of a thermospray flame furnace for determination of Cd and Pb in complementary foods during the breastfeeding period [15], or online preconcentration columns, such as a modified Amberlite XAD-2 column for determining Cd, Co, and Ni [16] or a modified polyurethane foam for determining Cu [17] in food samples.

The analytical capability of FAAS was also expanded for indirect determination of total I in milk [18]. Milk samples were digested using an alkaline ashing procedure. Then, a flow system was used for precipitating I^- with Ag^+ and collecting the precipitate in a filter. Further, the precipitate was washed and dissolved by using diluted ammonia and thiosulfate solutions. Finally, Ag was determined by FAAS. Adopting this strategy, it was possible to circumvent one of the critical limitations of FAAS related to the determination of anions.

Another frequent limitation pointed out for FAAS is its monoelemental character. Notwithstanding, this aspect is being minimized using new instrumental arrangements. For instance, an FS-FAAS was used for the implementation of the internal standard technique for the direct determination of Cu in fruit juices [19]. Ferreira et al. demonstrated that the use of In as internal standard improved the accuracy and the repeatability for Cu determination in nondigested juice samples. Better performance for correcting matrix effects was also obtained when Co and In were used as reference elements for Mn and Fe, respectively, in wine samples [20]. Additionally, Oliveira et al. demonstrated the application of HR-CS-FAAS for determination of macro- and micronutrients in plant leaves [21, 22]. These authors exploited instrumental capabilities, such as wavelength integrated absorbance, molecular absorption bands, side pixel registration approach, least-squares background correction, and measurements at line wings, for making feasible the accurate and precise determination of macro- and micronutrients in foliar analysis.

2.2. Fuels. Fuel is any material that is capable of releasing energy and can be used to produce work. The automotive fuels most worldwide commercialized are gasoline, diesel, ethanol, and more recently biodiesel [23]. In the 1970s, during the first petrol crises, Brazil introduced the National Program of Alcohol (Programa Nacional do Álcool, Proálcool), and this fact has stimulated *flex-fuel* cars production and technological investments. As a consequence, nowadays most cars sold in Brazil are equipped with flexible fuel engines [24]. However, it is well known that transport is almost totally dependent on fossil fuels. Considering that petroleum-based fuels have limited reserves and are blamed for high emission of greenhouse gases, global warming, and climate changes, biodiesel is the best candidate for diesel fuels in diesel engines [25]; moreover, some countries or states have imposed that all diesel fuel must contain part of biodiesel.

Because of rapid industrialization and the implementation of modern economic systems, fuel is one of the highest needs for human well-being; therefore, it is necessary to develop simple, fast, and sensitive methods for its quality control. Metal contaminants are incorporated during the production processes, transport, and storage of ethanol fuel, and it may, even in low concentrations, reduce the performance of fuel and induce the corrosion of some vehicle components, as well as generate environmental pollution [26]. In 2007, a review about V determination in fossil fuel using atomic spectrometric techniques was published [27], and there were several publications using FAAS in the 1970s. However, none has been published considering direct analysis and FAAS after 2006.

Previous preconcentration steps are commonly necessary to attain the low levels required of the limit of detection (LOD), and flow-based system has been used to improve throughput of analytical procedures by FAAS. Vermicompost commonly used as a garden fertilizer was used as a

TABLE 1: Selected papers using FAAS in fuel analysis.

Sample (s)	Analyte	Remarks	Ref.
Biodiesel	Ca and Mg	Microemulsion as sample preparation	[35]
Ethanol	Cu, Fe, Ni, and Zn	Cellulose chemically modified with p-aminobenzoic groups was used for preconcentration step	[36]
Lubricating oil	Cu, Fe, Ni, Pb, and Zn	Sulphanilic acid was used to ash samples at 550°C	[37]
Lubricating oil	Cu, Fe, Ni, Pb, and Zn	ANOVA was used to show a trend of concentration increasing of metals in wear lubricating oils (samples were ashed)	[38]

biosorbent for preconcentration step for online Cd determination in ethanol fuel in μg/L range [28]. *Moringa oleifera* seeds were similarly used for Cd determination in ethanol fuel and flow and chemical parameters were optimized through multivariate designs. Limit of detection under optimized condition was $5.5\,\mu$g/L [29]. Cloud Point Extraction (CPE) also has been used for metal ions studies with further determination by FAAS. It was applied to determine Mn in saline effluents of a petroleum refinery [30].

Direct analysis of fuel samples for metal determination using FAAS presents some general problems, such as volatility, flammability, and immiscibility with water. Moreover, it produces flames that are very rich in fuel and unstable. Reduction of acetylene supply or increase of the flow rate of air is recommended to solve this problem [23]. Direct analysis of ethanol fuel by FAAS based on the use of calibrating solutions prepared in ethanol 95% v/v solvent, such as the analytical procedure proposed by Brazilian Normalizing Committee, does not consider ethanol content variations in samples making it difficult to obtain accurate results in certain cases. Thus, Silva et al. [31] proposed a flow-batch automated procedure for Fe determination using internal standard by sequential measurements. Nickel was selected as internal standard, and the procedure could improve accuracy and overcome instrumental drifts and ethanol content variation in samples.

Microemulsion has been recently reported for metal determinations in fuels instead of using organic solvents, since it allows the use of aqueous and organometallic standard solutions and it is thermodynamically stable. Microemulsion formation was optimized by phase diagram for K and Na determination by using Triton X-100 as surfactant, n-pentanol, biodiesel, and aqueous standard (KCl and NaCl) [32]. Lyra et al. [33] proposed a method for determination of Ca, Mg, Na, and K in biodiesel samples by microemulsion preparation in n-propanol medium and without surfactant use; moreover, CsCl for Na and K, and KCl for Ca and Mg were used as ionization suppressors.

Metal monitoring in lubricating oil samples is also important since some metals are added as organometallic compounds to improve some characteristics such as viscosity and corrosion inhibition properties. On the other hand, high metal concentration has been related with the friction and corrosion of the mechanical components of engines. Amorim Filho and Gomes Neto [34] studied three sample preparation procedures: microwave-assisted acid decomposition, direct dilution in kerosene, and oil-in-water emulsion

for metal determination by HR-CS-FAAS. Considering direct dilution, it was evaluated the kerosene/light mineral oil ratio to prepare standard solutions since sample and light mineral oil present different viscosities and it can cause accuracy errors. Emulsion was prepared by addition of aviation kerosene or n-hexane, Triton X-100, HNO$_3$ 50% v/v, and the volume was made up with deionized water and the resulting mixture was mixed. Calibration solutions were prepared in 1% v/v HNO$_3$, and the authors pointed out that this is one of advantages of emulsion preparation such as the reduction of the organic solvent wastes and minimization of time and analytical costs. However, the stability and homogeneity of the emulsions must be guaranteed.

Table 1 contains additional publications [35–38] about metal determinations in fuel samples using FAAS.

2.3. Biological Fluids. For human health purposes, analytical procedures for determination of trace elements in environmental and pharmaceutical samples and biological materials have been developed. Analyses of blood, serum, urine, and, most recently, human hair are used in diagnosing trace element deficiencies or to assess environmental or occupational exposure to toxic elements [39, 40]. Considering the importance of cited sample analysis in routine laboratories, direct analyses are an interesting alternative due to inherent high analytical throughput.

Hair has been considered a biomonitor because the elements are permanently deposited in hair shaft as it grows and are supplied by blood [41]. Hair samples of workers exposed to welding fumes were analyzed by dynamic ultrasonic extraction of Cd and Pb using diluted HNO$_3$. Samples previously washed were placed into glass minicolumns and then immersed into a preheated ultrasound bath. Afterwards, the online extraction circuit was filled with the extraction solution (2 mL of 3 mol/L HNO$_3$), and the extraction solution was then circulated through the extraction cell under ultrasonic irradiation. After the extraction step, solution extract was homogenized through the mixing coil, the loop of the injection system was then filled with extract solution, and finally, it was injected into an ultrapure water carrier stream that transported it towards the FAAS. Variables of the system were studied by applying a Plackett-Burman design approach. According to the results, hair samples presented Cd and Pb concentrations ranged from 0.5 to $4.9\,\mu$g/g and from 10.6 to $96.2\,\mu$g/g in workers exposed to welding fumes [42]. The same system was also used for Cu, Fe, Mn, and Zn determination in human hair, and Cu, Fe, Mn, and

TABLE 2: Selected papers using FAAS in biological fluids analysis.

Sample (s)	Analyte	Remarks	Ref.
Urine	Cr	Online ultrasound-assisted sample digestion procedure exploiting the stopped-flow mode, followed by flow injection chromium preconcentration	[49]
Cosmetics	Mg and Zn	Samples were ultrasound-assisted emulsification with a probe system	[50]
Pharmaceutical products for veterinary use	Cu	Samples were mineralized in $HCl : HNO_3$ (20 : 1 v/ v)	[51]
Nile tilapia (*Oreochromis niloticus*) liver tissue	Ca, Fe, and Zn	Samples' protein spots were analyzed after mineralization in microwave oven	[52]
Aqueous waste	Ag	Evaluation of sorption potential of Moringa oleifera seeds for the decontamination of Ag(I) in aqueous solutions	[53]

Zn concentrations increased considering welder's years of profession [43]. A method based on hair sample slurries was proposed by Ferreira et al. [44] for sequential Cu and Zn determination. The hair sample slurries were prepared by cryogenic grinding followed by sonication. The analytical blank was prepared using rice flour. It should be pointed out that external calibration was effective for reaching proper accuracy [44].

The determination of trace elements in biological fluids plays an important role since it is possible to infer about the nutritional status of individuals and assessing their exposure to toxic elements [39]. Thus, Lopes et al. [45] proposed an automatic flow system to sequential determination of Cu in serum and urine by FAAS. The developed system could adjust the viscosity of serum samples, perform Cu determination in serum, and preconcentrate Cu in urine followed by its subsequent elution and determination. The analytical throughput was about 360 determinations/h for Cu in serum and 12 determinations/h for Cu in urine. A simple procedure for Pt determination by CS-FAAS was evaluated since Pt-based drugs are commonly used in cancer treatment [46]. A simple 1 + 1 v/v dilution of the urine samples with 2% v/v HCl solution was performed, and flame conditions were optimized by a multivariate D-optimal design. Limit of detection was 0.06 mg/L in the original sample.

A direct analysis of organic samples is usually difficult due to transport interferences and metal determinations have been done using matrix matching [47]. Copper determination in sugar cane spirits (cachaça) by Fast Sequential FAAS (FS-FAAS) was evaluated by using of internal standardization to reduce transport effects and variation of alcohol content in different samples. Silver, Bi, Co, and Ni were evaluated as internal standard, and Ag had the best performance for this application. Moreover, the use of internal standard approach improved precision and accuracy of the procedure [48].

Additional studies [49–53] which describe direct analyses of biological samples are presented in Table 2.

2.4. *Environmental and Technological Materials.* The high popularity achieved by FAAS as a result of its simple operation and lower costs of acquisition and maintenance has qualified it as the method of choice for metal determination in several samples. In this sense, Cuñat et al. [54] checked the accuracy of a man-portable Laser-Induced Breakdown Spectroscopy analyzer (LIBS) used for in situ determination of Pb in road sediments. The results found for both techniques agreed well being the relative error around 14% for Pb concentrations ranging from 480 to 660 μg/g. Flame AAS is also commonly applied to quality control of raw material used in industrial applications. For this purpose, Ramos et al. [55] performed XRF (X-ray Fluorescence) and FAAS analysis for Zn, Pb, and S determinations in ZnO samples used to obtain industrial ceramic enamels. A simple strategy adopted to handle samples with high Pb and Zn concentrations in FAAS determinations was to reduce the optical pathway by turning the burner to 52° or 90°, avoiding sample dilution. After comparison between FAAS and XRF results, it was concluded that FAAS exhibited better performance in terms of accuracy and precision. Antimony is regarded as an emerging contaminant due to its use as catalyst in the PET production. The migration of this toxic element to foods and beverages could be a potential source of human intake. Lopez-Molinero et al. [56] developed a novel method for Sb determination in PET bottles by volatile bromine generation coupled to FAAS. After using several multivariate statistical approaches to reach optimized conditions, the method was applied and the results were compatible with ICP OES (Inductively Coupled Plasma Optical Emission Spectrometry) standard method. Linear range from 1.0 to 17.2 μg of Sb (V) and reproducibility of 4.5 (% RSD) were obtained as figures of merit. Cespón-Romero and Yebra-Biurrun [57] exploited the good sensitivity of FAAS for Zn detection and the possibility of coupling it to FIA (Flow Injection Analysis), reducing the sample and reagents consumption, increasing the analytical throughput and minimizing sample manipulation. The method was applied to air quality assessment of workplaces detecting trace amounts of Zn in welding fumes. Good analytical figures of merit were obtained as LOD of 1.1 μg/m^3, linear range from 3.7 to 222.2 μg/m^3 for 15 min of sampling time, and an analytical throughput of 11 samples/h as well as good repeatability (1.6% of RSD).

Sometimes, the concentrations of the target elements are in very low levels to be directly determined by FAAS. In this sense, CPE was successfully performed for Cu determination in various matrices [58]. Several variables were

studied to attain optimized conditions such as pH, complexing agent (4-hydroxy-2-mercapto-6-propylpyrimidine), and surfactant (Triton X-114) concentrations, as well as the temperature. Simplicity, rapidity, and low analysis cost are pointed out as good features of the proposed method. Aiming the development of a method for Bi determination at low concentrations, Şahan et al. [59] proposed an online preconcentration system for Bi quantification by FAAS. A minicolumn packed with a resin containing an iminodiacetate group was used in the experiments. A linear range from 0.1 to 1.0 μg/mL was obtained with an LOD of 2.7 μg/L, repeatability of 3% (for 0.4 μg/mL of Bi), and enrichment factor of 20. Several advantages of the method were emphasized as low cost, simplicity, rapidity, and tolerance to high concentration of interferences. Coprecipitation is a simple technique based on phase separation also used for metals determination at trace levels prior to instrumental detections. Aydin and Soylak [60] proposed the separation of Au(III), Bi(III), Co(II), Cr(III), Fe(III), Mn(II), Ni(II), Pb(II), Th(IV), and U(VI) by using addition of Cu(II)-9-phenyl-3-fluorone precipitate. The LODs ranged from 0.05 to 12.9 μg/L, and the proposed procedure was applied to lake sediments analyses.

Flame AAS as any instrumental method is not free from interferences, such as those derived from sample physicochemical characteristics affecting its transport to the atomizer as well as molecular or atomic absorption that can overlap with the analytical line of the target element [61]. The Cd most sensitive line in FAAS (228.802 nm) suffers strong overlap with an As absorption line (228.812 nm). To circumvent this drawback, Waterlot and Douay [61] investigated extracts of soils contaminated with As and Cd and studied the correction of this interference using a continuum source corrector (D_2 lamp) and High-Speed Self-Reversal Method. The latter was considered the best one to overcome this interference.

In spite of that FAAS has been long recognized as a consolidated monoelement technique, a successful attempt was made to convert this technique in a high speed multielement one. That concept was reached by the proposition of the High-Resolution Continuum Source FAAS (HR-CS FAAS). Nevertheless, the typical narrow linear calibration ranges commonly addressed to FAAS are still observed in HR-CS FAAS. Thus, Raposo Júnior et al. [62] evaluated the use of secondary line and the side pixel registration strategies in HR-CS FAAS to extend its linear calibration range for the multielement determination of Cu, Fe, Mn, and Zn in DTPA soil extracts.

Noroozifar et al. [63] demonstrated the versatility of FAAS for the indirect determination of cyanide ions in an FIA-FAAS system. In this study, the authors tested four solid-phase reagents of Ag_2X (X = SO_3^{2-}, $Cr_2O_7^{2-}$, $C_2O_4^{2-}$, and CO_3^{2-}) and several parameters were optimized such as carrier flow rate, pH, loop volume, and the reactor temperature. The final optimized method exhibited good accuracy (near 100%) and precision (better than 1.2%), and it was applied for cyanide determination in well and drinking waters and electroplating wastewaters. In a novel approach for inorganic N speciation with an online FIA-FAAS system,

Noroozifar et al. [64] used Mn(IV) dioxide as an oxidant agent for conversion of nitrite to nitrate ions. In this reaction, the Mn(IV) ions in the solid phase are converted to Mn(II) ions which are measured by FAAS. Thus, the Mn absorbance is proportional to the nitrite content in the sample. Nitrate is reduced by a copperized Cd column being analyzed as nitrite. After optimization of parameters such as carrier acid concentration, reactor temperature, loop length and MnO_2 concentration, and interference studies, the method was applied to nitrite and nitrate determinations in waters and meat samples.

It is well recognized that total metal contents are poor indicators of the real menace the toxic metallic species can play in the environment. So, speciation and fractionation procedures have been proposed to assess different pools of metals and infer about bioavailability and bioaccessibility. In this sense, Frankowski et al. [65] presented a method for Al speciation in soil samples using an HPLC-FAAS (High Performance Liquid Chromatography-FAAS) hyphenated technique. The major Al species found in this study were related to 2 chromatographic peaks: the first eluted (related to AlF_2^+ and AlF_4^- species) and the second (related to AlF^{2+} and AlF_3 species). Pehlivan and Kara [66] proposed an SPE method for Fe speciation in water and sediment samples. Matos and Nóbrega [67] evaluated a method for Cr speciation in cement and cement-related materials. This determination is important because of the wide use of cement in constructions and the potential dispersion of fine powders of this material in the environment at high distances from the source. It is worth to mention the hazardous effects of hexavalent chromium to the human health. In this work, FAAS was applied to access the total concentration of Cr after a fusion step. Chromium hexavalent concentration was determined by diphenylcarbazide method after alkaline extraction. In another study of Cr speciation, Wu et al. [68] used a crosslinked chitosan-bound FeC nanoparticles as a highly selective solid-phase extractant of Cr(III) ions in water samples with subsequent determination by FAAS. Later, total Cr concentration was assessed by quantitative conversion of Cr(VI) to Cr(III) by ascorbic acid. Parameters that could affect the method performance were carefully optimized as pH, sample flow rate, and sample volume. Afterwards, column stability and interference studies were also performed. Besides simplicity, and selectivity, the high enrichment factor (100 fold) and good LOD (52.4 ng/L) are attractive characteristics of the method.

Flow injection analysis coupled to FAAS detection is a highly successful association being used in several studies. The lack of sample manipulation, high analysis throughput, simplicity, and low cost can be addressed to this combination. Mukhtar and Limbeck [69] used FIA-FAAS system to determination of water-soluble Zn in airborne particulate matters samples. When compared to the batchwise traditional system, the developed method exhibited the further above-mentioned characteristics of an FIA-FAAS and higher sensitivity. Dadfarnia et al. also applied FIA-FAAS for indirect determination of anions [70]. In the proposed method, cyanide ions were determined in waters and industrial wastewaters with good accuracy and precision.

The principle of the method is the use of a minicolumn of Salen [N,N′-bis(salicylidene) ethylenediamine] on sodium dodecyl sulfate-coated alumina saturated with Ag^+ ions. The liquid sample is passed through the column, and its cyanide ions eluted the Ag^+ ions as cyanide Ag complexes, which are determined by FAAS. The Ag absorbance is proportional to the cyanide content in the sample.

As is mentioned above, FAAS is commonly applied for metal determinations in several environmental matrices. A sequential extraction procedure based on the BCR scheme was applied for metal fractionation in Chilean soils [71] before and after incubation for 60 days with a biosolid material. In this study, FAAS and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) were used, and Zn was the element with the highest concentration in the biosolid among the studied analytes (Cu, Cr, Ni, Pb, and Zn). Moreover, it was demonstrated that biosolid application enriched the soils with metals, and the largest pool of metals was in the residual fraction. This fraction is regarded as the most resistant to extraction and exhibited the lowest availability to plants uptake. Sediments and soils are labeled as sinks of pollutants in natural ecosystems being used in various environmental monitoring studies. Silva-Filho et al. [72] analyzed leachate pond sediments from the southeastern Brazil in relation to their contents of Hg, Zn, Fe, and Mn. Mercury was analyzed by Cold Vapor AAS (CV-AAS) and the remaining elements by FAAS. Higher element concentration in the upper layers of the sediment cores is consistent with the early development of the Brazilian economy notably after the 1990s with an increasing pattern of metals contamination. Additionally, proposition of analytical strategies to speed up and simplify procedures for metals extraction in environmental matrices is of special relevance. In this sense, Remeteiová et al. [73] used ultrasonic-assisted extraction to reduce the analysis time in the fractionation of gravitation dust sediments. Flame AAS was elected as analytical technique to determine Cu, Pb, and Zn in the extracts obtained with the conventional and the proposed method. Raposo Júnior et al. [74] evaluated the concentration of metals in 9 lichen species of the South-Mato Grossense Savannah. The dilution factor applied (1 g of sample to final volume of 50 mL) and the concentration range of the analyzed samples (Co, 10.08–24.81; Cr, 18.24–44.26; Cu, 3.23–7.57; Fe, 248.41–1568.01; Mn, 98.50–397.33; Zn, 14.62–34.79 mg/kg) allowed the adequate application of FAAS. Average concentrations of Cr, Mn,and Co were higher than samples from nonpolluted areas of Kenya, Nepal, and Italy which may indicate a contribution of anthropogenic sources and accumulation by these organisms. Mosetlha et al. [75] evaluated the use of microdialysis sampling for Cu and Ni determination in plant materials. Strong linear correlation between the total concentration of these elements and the concentration in the dialyzed were observed, qualifying this technique as a powerful predictor of metal content in plant tissues without the need of mineralization. In this study, FAAS was applied to access the total concentration of metals, and GF AAS determinations were performed for Cu and Ni quantification after the microdialysis procedure. In large urban areas, where vehicles are intensively used for transportation, the neighborhoods of roads and streets suffer severe diffuse contamination by heavy metals coming from fossil fuel burning, tire wears, oil residues, and other related sources as biological powdered material by traffic. Faiz et al. [76] determined Cd, Cu, Ni, Pb, and Zn concentrations by FAAS in road dust from a heavily anthropogenic impacted highway in Islamabad, Pakistan. These authors calculated some indexes to infer about the pollution, and all of them led to the conclusion that the area has low or middle level of pollution.

3. Flame Furnace and Hydride Generation

Since the youth of FAAS, three negative aspects of this technique limit its sensitivity. One is the relatively low efficiency of the pneumatic nebulizer, the second is the short residence time of analyte atoms in the measurement zone, and the third one is the dilution of the atom cloud in the flame gases. Although less sensitive, FAAS is so simple, straightforward, and inexpensive in terms of instruments and running costs that researchers have made great efforts during the last years to develop novel sensitive flame atomization systems.

By arranging a flame furnace over the burner head of a FAAS spectrometer, Gáspár and Berndt [77] and Davies and Berndt [78] improved the sensitivity of FAAS by 2-3 orders of magnitude for 17 volatile/semivolatile elements (Ag, As, Au, Bi, Cd, Cu, Hg, In, K, Pb, Pd, Rb, Sb, Se, Te, Tl, and Zn). This arrangement, named thermospray flame furnace AAS (TS-FF-AAS), requires a peristaltic pump, an injector, a ceramic capillary, and a Ni tube. The applications of TS-FF-AAS found in the literature focus mainly on biological, environmental, and food samples.

The typical sensitivity reached by FAAS does not allow determinations of Cd, Cu, and Pb in beverages because these elements are usually present in these types of samples at $\mu g/L$ levels. For this reason, Schiavo et al. [79] developed a procedure aiming the direct determination of Cd, Cu, and Pb in wines and grape juices by TS-FF-AAS, and quantification was based on the standard additions method (SAM). Wine samples were measured after simple dilution, and grape juice samples were analyzed without any pretreatment. The LODs obtained for Cu, Cd, and Pb were 12.9, 1.8, and 5.3 $\mu g/L$, respectively.

The concentration of Se in most samples is usually below FAAS limits of quantification. One alternative to overcome this problem was developed by Rosini et al. [80] when the authors evaluated Se behavior in TS-FF-AAS and determined this element in biological samples. The SAM was applied for Se determination in biological materials and the LOD attained was 95 times lower than that typically reached by FAAS.

In TS-FF-AAS the introduction of a greater sample volume into the atomizer implies in a higher amount of concomitants being inserted together with the analyte and, as a result, elevated background signals are obtained. For this reason, Miranda et al. [81] used background signals and multivariate calibration as a procedure to assess the total concentration of concomitants in TS-FF-AAS. Background signals of 29 solutions containing Cd ($25 \mu g/L$), Pb ($500 \mu g/L$), and four concomitants (Ca, K, Mg, and Na) were recorded at 228.8 nm

for Cd and 283.3 nm for Pb. A pharmaceutical sample containing a total of 3 g/L of Ca, K, Mg, and Na was analyzed, and 3% was the relative error.

In order to bring information about variations in surfaces, shapes, and compositions of tube atomizers, Petrucelli et al. [82] compared the performance of metal tube atomizers composed of Cr, Fe, Mo, Ni, Ti, and W and ceramic tubes before and after being used for determinations of Cd, Cu, Mn, Pb, and Zn by TS-FF-AAS in aqueous solutions, food and environmental samples. Nickel tube atomizers presented good performances for Cd, Cu, Pb, and Zn determinations and their lifetimes seemed to be long. Titanium tubes presented excellent results for Cu determination, but their lifetime was extremely short, due to the fast formation of a TiO_2 layer.

Due to the fact that Ti tubes presented good results for Cu determination, Pereira-Filho [83] evaluated the combination of Ni and Ti tubes to increase the Ti atomizer lifetime. The new arrangement combining both tubes increased the sensitivity approximately four times compared to single Ni or Ti tubes. It was possible to use the Ni/Ti tube for more than 13 h (around 500 determinations) without a loss of performance. The LOD obtained using a Ni/Ti tube atomizer was $2\,\mu g/L$ for Cu. A useful and informative review article by Arruda and Figueiredo [84] describes the recent developments in the application of metallic atomizers to FAAS.

Ultrasonic nebulizers (USNs) became popular with ICP OES and ICP-MS. In order to extend the benefits of USN from ICP instruments to flame furnace AAS, Ribeiro et al. [85] proposed the coupling between USN and flame furnace. A significant improvement in the detection power was achieved with the USN-flame furnace AAS system which, according to the authors, is mostly due to the longer residence time of the analyte inside the atomizer and to the absence of dilution by the flame gases as it would occur in FAAS. The LODs obtained by USN-flame furnace AAS for Cd, Cu, Pb, and Zn were 36, 4, 39, and 30 times lower than those typically reached by FAAS with pneumatic nebulization.

A sound strategy for online atom trapping was developed by Wu et al. [86] for preconcentration purposes. The analyte solution was introduced via a pneumatic nebulizer into the flame-heated furnace by a flow of Ar and the middle part of the flame furnace where the carrier gas impacts was cooled by the sample aerosol. A stainless steel plate was put on the top of the flame burner in the middle to lower the temperature of the flame furnace to facilitate the atom trapping process. Cadmium was selected as the analyte element. With 10 s preconcentration time, a sensitivity enhancement factor of 730 was achieved and the LOD of the proposed method was 15 ng/L.

A novel method of CPE involving two steps was developed by Wu et al. [87] for the determination of trace Ag in complex matrices by TS-FF-AAS. Firstly, Cu ion reacts with diethyldithiocarbamate (DDTC) to form Cu-DDTC before it is extracted; secondly, after removing the aqueous phase, a sample or standard solution containing Ag ion is added and another CPE procedure is carried out. Potential interference from coexisting transition metal ions with lower DDTC complex stability was largely eliminated. The LOD obtained was $0.2\,\mu g/L$ with a sample volume of 10 mL.

A sensitive method for the determination of trace Cd in rice and water by using flow injection online precipitation-dissolution in a knotted reactor (KR) as a preconcentration procedure for TS-FF-AAS was developed by Wen et al. [88]. Sample solution and the precipitating reagent were mixed online in a KR. Then, the resultant precipitate of Cd hydroxide was eluted with 1 mol/L HNO_3 and the eluant analysed by TS-FF-AAS. The LOD was $0.04\,\mu g/L$ with a sensitivity enrichment factor of 34 using a sample volume of 4 mL.

Using a fast sequential FAAS and a Ni flame furnace, Pereira-Filho [89] performed the sequential determination of Cd, Cu, Pb, and Zn. A significant improvement in the analytical throughput of TS-FF-AAS was obtained. Limits of detection obtained for Cd, Cu, Pb, and Zn were 0.3, 7.5, 4.4, and $0.3\,\mu g/L$, respectively.

A review article by Bezerra et al. [90] covers the recent developments and applications in the production of thermosprays into flame furnaces to improve the analytical sensitivity in atomic absorption. Principles, characteristics, and instrumentation of TS-FF-AAS are discussed.

Significant improvements in the LODs of FAAS may also be achieved by chemical vapor generation, mostly using hydride generation and in-atomizer trapping for the determination of As, Bi, Cd, Ge, Hg, In, Pb, Sb, Se, Sn, Te, and Tl. Since in situ trapping technique allows a significant enhancement in sensitivity, Matusiewicz and Krawczyk [91] evaluated the analytical performance of a coupled volatile species generation-integrated atom trap atomizer FAAS system for the determination of Cd and Pb in reference materials. Vapors of PbH_4 and Cd^0 were atomized in an air-acetylene flame-heated integrated atom trap. A significant improvement in LOD was achieved (0.05 and 0.40 ng/mL for Cd and Pb, resp.) compared with other existing arrangements (water-cooled single silica tube, double-slotted quartz tube, and "integrated trap"). The research group of Matusiewicz also used this device for the determination of In and Tl [92], Te [93], Sb [94], Bi [95], As and Se [96], Ge and Sn [97], Hg [98], As, Bi, Cd, In, Pb, Se, Te and Tl [99], and Ni [100].

An atom trapping approach was used by Ertas et al. [101] to determine Pb by hydride generation FAAS. Lead hydride, generated online by reacting Pb in hydrochloric acid-potassium ferricyanide medium with $NaBH_4$, was trapped on the interior walls of a slotted T-tube. Atomization was achieved by aspirating 50 mL of methyl isobutyl ketone. The LOD obtained was $0.075\,\mu g/L$ for 7.8 mL of blank solution. Then, the method was successfully applied to determine Pb in certified reference materials.

Online atom trapping inside a Ni flame furnace using chemical vapor generation for sample introduction was successfully applied by Wu et al. [102] for the determination of trace Cd in high-salinity water samples by FAAS. Volatile species were generated upon reaction with potassium borohydride and then trapped into a flame furnace using N_2 as the carrier gas. The LOD was 20 ng/L.

Since organic solvents are recognized as interferents in the determination of hydride forming elements, Karadjova et al. [103] investigated the interference effects of various

organic solvents miscible with water on As determination by hydride generation AAS employing two types of flame atomizers: miniature diffusion flame and flame in flame. The best tolerance to interferences was obtained by using flame in flame atomization together with higher Ar and H_2 supply rates and elevated observation heights.

The traditional monoelement hydride generation AAS with a quartz tube atomizer is mainly applied for single element measurements which greatly increase analysis time and reagent consumption. In order to enhance the analytical throughput, Guerra et al. [104] successfully employed a fast sequential FAAS and hydride generation AAS to sequentially determine As and Sb in bottled mineral waters. Adequate sensitivity, high throughput and minimization of reagents, and sample consumption are the attractive features of the developed method. Limits of detection obtained for As and Sb were 0.15 and 0.14 μg/L, respectively.

4. Chemometrics Applications

Chemometrics combines the use of mathematics and statistics in chemistry, and its application is devoted to extract the maximum of information from a chemical system. The use of optimization strategies for methods development is useful because few experiments are needed and it is possible to identify the interaction among the investigated variables. Santos et al. [105], for instance, applied simplex approach to optimize an automated online preconcentration system for Mn determination. The authors observed an LOD of 2.0 μg/L.

Khajeh et al. [106] used a Doehlert design to optimize a microwave-assisted extraction for Cu and Zn determination in cereal samples using FAAS. The best work conditions were observed with 110°C, 176 W, and 16 min. In another study Khajeh and Sanchooli [107] used a Box-Behnken design to optimize microwave-assisted extraction for Fe and Zn determination in celery. The best conditions achieved were 80°C, 105 W, and 9 min. A microwave-assisted acid digestion method was also investigated by Rojas et al. [108] for metals determination in biomorphic ceramic samples. The authors used a 3^3 full factorial design, and three variables were studied: volumes of HNO_3 and HF and digestion time. Microwave-assisted leaching was studied by Soriano et al. [109] for Cu, Fe, Mn, and Zn determination in multivitamin/multimineral supplements.

Mixture design was used by Bezerra et al. [110] to optimize a method for Mn and Zn determination in tea leaves employing slurry sampling. The method was tested in certified reference samples, and the best results were obtained with a mixture composed by 2.0 mol/L HNO_3, 2.0 mol/L HCl, and 2.5% v/v Triton X-100 in the proportions of 50%, 12%, and 38% v/v, respectively. A combination of sorbent material and flow injection was used by Anthemidis et al. [111] for Pb determination, and the experimental variables were optimized using factorial design. Santelli et al. [112] optimized a digestion procedure using a focused microwave system for Fe, Mn, and Zn determination in food samples. The best conditions were 12 min, 260 W, and 42% v/v of H_2O_2.

A full factorial design was used by Kenduzler et al. [113] to study the preconcentration variables for Cr(III) determination. The solid phase was composed by an Amberlite 36 resin. In another strategy, Portugal et al. [114] used CPE for Cd and Pb determination in drinking water. The variables were studied using two-level factorial design and Doehlert design. Dutra et al. [115] developed an online preconcentration system for Zn determination in biological samples. The authors used a minicolumn filled with silica gel and chemically modified with Nb(V) oxide (Nb_2O_5-SiO_2). In addition, the variables were investigated with full factorial and Doehlert designs. Ferreira et al. [116] developed a preconcentration procedure for determination of Cu and Zn in food samples by sequential multielement FAAS. The optimization step was performed using a Box-Behnken design and three variables investigated: solution pH, reagent concentration, and buffer concentration.

Moreda-Piñeiro et al. [117] investigated systematic errors when using FAAS and ETAAS (Electrothermal AAS) to analyze biological materials. The authors combined experimental design and PCA (Principal Component Analysis) and concluded that the use of slurry sampling technique in ETAAS and FAAS and the determination of high element concentrations by ETAAS have led to poor precision.

There are several publications applying chemometric methods for treatment of data obtained by FAAS itself or FAAS associated with ICP OES and ICP-MS. For instance, Amorim et al. applied PCA and hierarchical cluster analysis (HCA) for classifying green and roasted coffee and demonstrated that the main elements for discrimination were Ca, Cu, Fe, Mg, K, and Na [118]. Similarly, Madejczyk and Baralkiewicz applied cluster analysis for FAAS and ICP-MS data and showed that the source of honey samples correlated with their chemical composition [119]. Similar approaches were applied for Brazilian coffees cultivated by conventional and organic agriculture [120], for *Salvia fruticosa* [121] and traditional Chinese medicine formula [122]. All these works demonstrated that analytical information may be expanded when associating reliable results obtained by FAAS or other spectroanalytical methods and chemometry.

5. Applications Based on Preconcentration Step

5.1. Speciation. From recent developments in analytical techniques, it is well known that the determination of the total concentration of elements does not provide enough information on important parameters such as mobility, toxicity, bioavailability, and essentiality. Thus, a more detailed analysis usually requires a study of chemical speciation, which according to IUPAC is the analytical activity which is able to identify and/or measure the amounts of one or more chemical species present in the sample [123–125].

In the literature, several methods are utilized in elemental determinations, including sample preparation and preconcentration steps prior to detection. Some preconcentration methods such as SPE, CPE, coprecipitation, liquid-liquid extraction, and ion exchange are used for speciation and separation of the different species. Pena-Pereira et al. described

an overview of three miniaturized methods that have been applied to preconcentrate and extract different inorganic analytes in various matrices. Several drawbacks which make liquid-liquid extraction time consuming and expensive such as large volume of samples and reagents and the consequent generation of large amounts of residues were also discussed. New methods capable of minimizing such drawbacks like single-drop microextraction (SDME), in which only a small fraction of the analyte is preconcentrated, hollow fiber liquid-phase microextraction (HF-LPME), used to extract and preconcentrate analytes from complex samples, and dispersive liquid-liquid microextraction (DLLME), a simple, fast microextraction based on the use of an appropriate extractant, were presented. Relevant applications in trace metal determinations for each of these methods were also presented and discussed [126].

Dispersive LLME combined with FAAS was applied for speciation of Cr in water. After optimizing important parameters, such as time, type of solvent, salinity, pH, and amount of chelating agent, enrichment factors of 275 and 262 and LODs of 0.07 and 0.08 μg/L for Cr(VI) and total Cr were obtained, respectively [127].

The determination of Cr species is important in analytical chemistry and toxicological studies because the oxidation state significantly affects the metal toxicity. It is well known that Cr(III) is considered essential while Cr(VI) is toxic to humans. Tokalioğlu et al. developed a method for indirect speciation of Cr applying SPE with a new chelating resin (poly N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonis acid-co-divinylbenzene). Some parameters such as eluent type, effect of pH, sample volume, sample solution flow rate, and effect of interfering ions on Cr(III) preconcentration were studied. This specie was separated from Cr(VI) and preconcentrated using a column containing the new resin. The Cr(VI) concentration was estimated indirectly by subtracting the Cr(III) values determined. Total Cr was determined after reducing Cr(VI) to Cr(III) [128].

Long et al. proposed a novel and miniaturized microsequential injection bead-injection lab-on-valve (μSI-BI-LOV) for determination of bioavailable Cr(VI) in soil with detection by ETAAS. The proposed method offers several advantages as immediate separation between concomitant preconcentration and released chromate, minimization of interconversions, and enhanced accuracy. The method accuracy was evaluated using spikes with water-soluble Cr(VI) salts at different concentration levels and applied for high levels of bioavailable chromate in soils [129].

Speciation of As is necessary due to the different levels of toxicity of its species: inorganic ions are more toxic than organic species. Tian et al. [130] developed a method for As speciation based on interfacing solid phase preconcentration, liquid chromatography with gradient separation, and hydride generation-quartz FAAS (SI-HPLC-GHG-QFAAS). A MnO_2 minicolumn was used to preconcentrate As species, and tetramethylammonium hydroxide (TMAH) was used as eluent. Arsenium(III) was converted to As(V) via oxidation by MnO_2 and the As(III)-PDC complex formed by the reaction with ammonium pyrrolidine dithiocarbamate

(APDC) was selectively adsorbed by the cellulose fiber minicolumn. Finally, As(III) was quantified by GFAAS. Enrichment factors of 17, 16.7, 14, 19.2 and LODs of 0.33, 0.39, 0.62, 0.019 μg/L were obtained for As (V), MMA, DMA, and As(III), respectively [130]. Table 3 shows more applications [131–134] of preconcentration and speciation.

5.2. Cloud Point Extraction. Despite the intrinsic selectivity of AAS, matrix interference is a critical aspect in trace metal determinations. A wide range of sample preparation methods have been proposed to reduce such effects on the analytical signal by simply destroying the matrix [135], but problems related to soluble, nonvolatile concomitants still remain a challenge for determinations at low concentration levels. In FAAS, the most critical aspects limiting sensitivity are the low sample introduction efficiency, the analyte dilution in the combustion mixture, and the atomic cloud short residence time in the observation zone [136, 137]. Considering these two aspects, that is, matrix interferences and FAAS relatively high LODs, several methods have been proposed to separate the analytes from their original matrix and simultaneously improve FAAS detection power. Electrodeposition [138], preconcentration on polymeric membranes [139], and SPE [140] are some examples of successful procedures used in recent years.

In this context and due to characteristics such as simplicity, low cost, efficiency, use of less toxic reagents, and production of low volumes of residues, CPE has become one of the most popular extraction/preconcentration methods in FAAS determinations [141–150]. Introduced in 1978 by Watanabe and Tanaka [151], CPE is based on the property of some surface-active agents (surfactants or detergents) of being able to aggregate in aqueous solution to form colloidal-sized clusters known as micelles. These surfactants are typically amphiphilic organic substances that present a long hydrophobic chain and either a small charged group or several neutral groups of polar (hydrophilic) nature. The micelle aggregation and phase separation occur when the solution presents a minimum surfactant concentration (so-called, critical micelle concentration, CMC). By carefully changing the solution conditions, for example, temperature, pressure, or ionic strength, the surfactant molecules become large aggregates (surfactant-rich phase) which can dissolve metal complexes and are eventually separated from the bulk aqueous solution (surfactant-poor phase) [152–154]. Probably due to characteristics such as low toxicity, versatility, and typically low cloud point temperatures, nonionic surfactants are by far the most used in CPE methods [141–150]. Among those, the most popular is α-[p-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxylpolyoxyethylene (Triton X-114), with a cloud point temperature in the 23–25°C range and a CMC of 0.17–0.30 mmol/L [152]. In order to extract metals from aqueous solutions into hydrophobic surfactant aggregates, a complexing agent is usually required. A wide range of reagents is available and APDC is one of the most commonly used [155–157]. On the other hand, the possibility of using just the surfactant in a CPE-FAAS procedure has been demonstrated by Candir et al. [158]. In this work, polyethylene glycol

Table 3: Selected papers using FAAS in chemical speciation and associated to preconcentration strategies.

Sample (s)	Analyte	Remarks	Pre concentration factor	LOD (μg/L)	Complexing agent	Ref.
Tap water, lake water, river, water, seawater, fruit juice, cola, molasses	Fe (III)	The Fe(III)–AMPC was extracted into methyl isobutyl ketone(MIKB) phase in the pH range 1.0–2.5	*	0.24	4-Acetyl-5-methyl-1-phenyl-1H-pyrazole-3-carboxylic acid (AMPC)	[131]
River water, lake water, seawater, SRM 2109, CRM 1643d	Cr(VI) and Pb	Use of the hydrophobic poly-chlorotrifluoroethylene (PCTFE)-beads as on-line preconcentration system	94 for Cr(VI) and 220 for Pb	0.4 and 1.2	Ammonium pyrrolidine dithiocarbamate	[132]
water	Cr(III) and Cr(VI)	On-line preconcentration system based on a llama fiber-packed column with detection in FAAS	32	0.3	**	[133]
Stream water, seawater, tannery waste-water, tobacco, anodic slime, CRM TWDW-500, CRM Sandy Soil C	Cr(III)	Carrier element-free coprecipitation (CEFC), was used a new synthesized organic as coprecipitant (5-chloro-3-[4-(trifluoromethoxy) phenylimino]indolin-2-one)(CFMEPI)	40	0.7	**	[134]

* Not reported; ** Not employed.

sorbitan monooleate (Tween 80) was used simultaneously as complexing agent and surfactant to determine Bi, Cd, Cr, Cu, Ni, and Pb in water, sediment, and food samples.

Cloud point extraction has been used to improve FAAS capabilities for the determination of several elements. Enrichment factors (i.e., the ratio between calibration curve slopes with and without CPE) up to 200 have contributed to lower LODs and allowed applications in difficult matrices such as food, clinical, and environmental samples [146, 147, 158, 159]. For further improvement of sensitivity, CPE has been used in flame furnace methods such as TS-FF-AAS and double-slotted quartz tube atom trap-FAAS (STAT-FAAS). In this case, LODs comparable with more sensitive methods such as GF AAS and ICP-MS and as low as 2.1, 0.082 and $0.04 \,\mu g/L$ for Co, Cr, and Cd, for example, were obtained in simple procedures using APDC and Triton X-114 [155–157]. Another strategy is to apply flow injection procedures in CPE-FAAS methods to improve sample throughput. Online reactions and entrapment of metal complexes in columns packed with cotton or other synthetic material have been used to determine Cd, Co, Cu, Mn, Ni, Pb, and Zn in food, water, and plant samples, with LODs in the $\mu g/L$ range [146, 159, 160].

Although still restricted to few elements, the sensitivity improvements provided by CPE has allowed FAAS applications in more complex analytical problems, for example, chemical speciation. Chromium and Sn species were determined in water, juice, metal alloys, and soil in procedures using acetylacetone [149], α-polyoxymetalate [161], 1-(2-pyridilazo)-2-naphtol (PAN) [162], or APDC [157] as complexing agents. An interesting application of CPE in FAAS determinations was described by Silva et al. [144]. A CPE sample pretreatment was used to extract organic compounds containing P and eventually reduce spectral interferences related to structured background from PO molecules formed in the flame. The surfactant-poor phase from the first CPE procedure was then submitted to a second extraction to separate Ni as 1,2-thiazolylazo-2-naphtol (TAN) complexes. This double CPE method was successfully applied to plant reference samples with a LOD of $5 \,\mu g/L$. Another interesting application took advantage of the different stability constants of metal diethyldithiocarbamate (DDTC) complexes to determine Ag and Cu using Ni-DDTC in a method referred as one-step displacement CPE [163]. Since Ag and Cu form DDTC complexes with larger stability constants when compared to Ni-DDTC, they can replace Ni to form Ag- or Cu-DDTC, which are then extracted into the Triton X-114 surfactant-rich phase. This strategy is especially advantageous because it reduces interferences due to DDTC side reactions with concomitant ions during CPE. The only ions capable of replacing Ni in Ni-DDTC are Hg(II), Pd(II), Ag(I), Cu(II), and Tl(III). Thus, the number of interfering concomitant ions is significantly reduced in Ag and Cu determinations.

Simplicity, easy implementation, low cost, environment friendliness, robustness, and sensitivity are some characteristics that have made CPE-FAAS an almost perfect combination for trace metal determinations. It has been applied to a myriad of samples in methods with performances comparable to more complex, expensive techniques such as ICP-MS [164].

5.3. Ionic Liquids. Ionic liquids (ILs) are liquids entirely composed by ions and, among their properties, ILs present negligible low vapor pressure under ambient pressures, thermal stability, and high ionic conductivity. The combination of bulky cation and/or anion and conformational flexibility of the ions favor low melt point, at or below 100°C [165, 166]. Due to physical and chemical characteristics, ILs have been widely used in several analytical applications such as extractions, gas and liquid chromatography, capillary electrophoresis, mass spectrometry, electrochemistry, sensors, and spectroscopy as alternatives to conventional toxic and volatile organic solvents as reported in a review recently published [167].

Cadmium was determined in plastic food packaging materials by online ionic liquid-based preconcentration system by FAAS [168]. Samples were previously digested, and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) reagent was used for Cd complexation. Then, the complex formed in Triton X-100 and pH 9 medium was extracted with ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$). Rich phase IL was separated in a silica gel microcolumn and eluted with ethanol acidified with diluted HNO_3. Differently, Liang and Peng [169] modified silica with ionic liquid ($[C_4mim][PF_6]$) and packed it in a microcolumn for Cd preconcentration step. Dithizone was used as complexant, and quantitative Cd adsorption was found in pHs ranging from 9 to 12. According to the authors, column could be reused for at least 20 adsorption cycles, followed by a regeneration step.

Functionalized ionic liquids (FILs), a new class of ionic liquids, have been studied for metal extraction due to incorporation of different functional groups that can enhance the versatility of ionic liquids and can improve selectivity in some cases. Thiol-functionalized ionic liquid prepared by appending thiol substituted alkyl groups to imidazole and combining with PF_6^- anion demonstrated high selectivity for Cd(II) extraction [170].

Bai et al. [171] reported a liquid-phase microextraction procedure for the preconcentration of Pb in water samples. Dithizone was used as chelating agent and 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6min][PF_6]$ as extraction solvent. Dithizone, $[C_6min][PF_6]$ and sample were mixed at 80°C and afterwards cooled down for phase separation. Lead complex was enriched in the ionic liquid droplets, and rich phase was dissolved in $150 \,\mu L$ methanol and 1.5 mol/L HNO_3 to 0.8 mL. Mahpishanian and Shemirani [172] developed a procedure based on in situ solvent formation microextraction (ISFME) for the determination of Cd in water samples and food grade salts by FAAS. Sample solution, *O,O*-diethyl dithiophosphate, and $[Hmim][BF_4]$ were transferred to a 5 mL tube and shacked. Sodium PF_6 was added, and a turbid solution was immediately formed. Then, the rich phase was separated by centrifugation, and fine droplets of IL were obtained (about $8 \,\mu L$). Aqueous phase was removed and the IL-phase was dissolved in $50 \,\mu L$ of ethanol.

Table 4 presents additional publications [173–176] for trace element determinations after preconcentration using ionic-liquids.

5.4. Functionalized Materials. Solid-phase preconcentration/separation techniques are based on the partition between a liquid (sample matrix) and a solid phase (sorbent), and they have been performed for trace metal determination using FAAS since they present enrichment of analytes and/or matrix elimination [177]. Solid-phase extraction can be easily associated with FIA [178] and the mechanism involved, such as adsorption, ion exchange, chelation, or ion pair formation, depends on the sorbent and analyte interactions [179]. Advantages related to simplicity, high enrichment factor, fast regeneration of solid phase, low reagent and sample consumption, and high throughput were cited in previous papers [180, 181].

Despite the numerous characteristics used to enable efficient extraction, the choice of the solid sorbent is the most critical step [177]. Various SPE sorbents have been employed for the preconcentration and among solid-phase sorbents; a good alternative to achieve versatile systems that can be applied to a wide range of samples is the use of polymeric solid supports functionalized with complexing reagents [182, 183]. A minicolumn packed with a chloromethylated polystyrene functionalized with N,N-bis(naphthylideneimino)diethylenetriamine (NAPdein) was used for the online enrichment of Cd(II) at pH 7.0 in water samples [184]. Authors included among advantages the procedure its low cost, high stability in extreme pH values, and good figures of merit, such as LOD of 0.25 μg/L, analytical throughput of 20/h, and preconcentration factor of 50.

A large number of online and offline preconcentration procedures have been developed using commercially Amberlite XAD resin series (styrene-divinyl-benzene copolymer) loaded or functionalized with different ligands due to their good physical and chemical properties such as porosity, high surface area, durability, and purity [179, 185–189]. Amberlite XAD-2 resin functionalized with pyrocatechol was used in an online preconcentration system for Cd, Co, and Ni followed by their determination with FAAS [190]. Considering 60 s of preconcentration time, the enrichment factors were 22, 23, and 25, and LODs were 0.95, 1.98, and 2.30 μg/L for Cd, Co and Ni, respectively. Improvements in LODs and sensitivities were observed when the preconcentration time was increased to 180 s. The reusability of the minicolumn packed with the resin was monitored, and it could be used for at least 300 cycles.

Six chelating matrices prepared by functionalizing Amberlite XAD-2 and XAD-16 and silica gel were studied as a sorbent for enrichment of Pd [191]. Amberlite XAD-2 and XAD-16 were anchored with 2,3-dihydroxypyridine (DHP) (I and II), Amberlite XAD-2 and XAD-16 were anchored with 2-{[1-(3,4- dihydroxyphenyl)-methylidene]amino}-benzoic acid (DMABA) (III and IV), and silica gel was anchored with 3,4-dihydroxybenzaldehyde (DHB) and iminodiacetic acid (IDA) (V and VI). According to the authors, all chelating matrices I–VI were suitable for enrichment of Pd; however, IV and VI were the most promising. The pre-concentration factors were in the range 20–150, and optimum conditions for desorption were evaluated for each sorbent considering HCl concentration and flow rate. Moreover, addition of thiourea (*ca.* 3% m/v) to HCl is essential for eluting Pd from the columns packed with chelating matrices, otherwise recovery is not quantitative.

A new trend in SPE for metal determination is ion imprinted polymers (IIP). Ion IPs are nanoporous polymeric materials, and their syntheses are based on polymerization reactions where an ion template complex with an appropriate ligand (a monomer) creates a three-dimensional system. Afterwards, the template is extracted and a selective cavity is formed [192]. The selectivity of a polymeric adsorbent is based on the specificity of the ligand, on the coordination geometry, coordination number of the ions, and also, on their charges and sizes [193]. In 2006, IIPs were reviewed by Rao et al. [194]. Segatelli et al. [195] evaluated Cd II-imprinted poly(ethylene glycol dimethacrylate-co-vinylimidazole) synthesized by bulk method, in which 1-vinylimidazole was used as bifunctional reagent, for online ion-selective extraction/preconcentration of Cd II ions from aqueous solution for following determination by FAAS. The proposed method was applied for Cd determination in urine and water, the enrichment factor was 38.4, and LOD was 0.11 μg/L. Copper(II)-imprinted polymer (Cu-IIP) for Cu preconcentration by SPE online has been proposed by Walas et al. [196]. Copper-IIP was obtained by copolymerization of Salen-Cu(II) complex with styrene and divinylbenzene using suspension polymerization technique. For microcolumn packing particle between 60 and 80 μm in diameter was used and the enrichment factor for 30 s loading time was 16. According to the authors, the only parameter that strongly influenced sorption and selectivity was the pH of the loading solution, and the optimum pH was 7.

Additional publications [197–202] based on preconcentration and functionalized materials are presented in Table 5.

5.5. Flotation Methods. Despite the broad use of FAAS in several applications, some inherent characteristics of this technique related to low nebulization efficiency have restricted it to quantification at mg/L levels. In order to improve its detection power, some researchers have been proposing different strategies for metals preconcentration in various distinct matrices. A method proposed with this concern is the so-called Floating Organic Drop Microextraction (FODME) [203–206]. The idea behind this preconcentration method was developed by Jeannot and Cantwell [207]. These authors proposed a simple and inexpensive approach using a small drop (8 μL) of a hydrophobic solvent immersed in an aqueous solution containing the analyte. After the migration of the analyte from the solution into the drop it was subsequently determined by gas chromatography. Recently, FODME has been used for metals determination by FAAS after they have been properly complexed and extracted from the aqueous solution. This technique was successfully applied for ultratrace levels quantification of Cd [205], Cu [203], Pd [204], and Zn [206] in water samples from natural and synthetic sources. Another outstanding preconcentration method is based on ion-imprinted polymers that hold a

TABLE 4: Selected papers using FAAS and preconcentration strategies with ionic liquids.

Sample (s)	Analyte	Remarks	Preconcentration factor	LOD	Complexing agent	Ref.
Kidney, liver, tea and water	Cd (II)	TSIL-MBT could be recycled at least 5 cycles.	—	0.19 µg/L	1-Butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆] that contained hydrophobic task specific ionic liquid (TSIL) functionalized 2-mercaptobenzothiazole (MBT)	[173]
Black tea, rice flour, and water.	Ni	PAN complex was back-extracted into acidified aqueous phase	40.2	12.5 µg/L	[C₄mim][PF₆], containing PAN as complexing agent.	[174]
Water, table salt andfood grade NaNO₃	Pb and Cd	Home-made microsample introduction valve combined with atom concentrator tube (ACT) improved sensibility	273 (Pb) and 311 (Cd)	0.6 (Pb) and 0.03 (Cd) µg/L	Analytes were complexed with DDTC and extracted by using NaPF₆ and ethanol containing of [Hmim][PF6].	[175]
Water and milk	Zn	Optimum pH 9.5	71	0.22 µg/L	Zinc was complexed with 8-hydroxyquinoline and extracted with 1-hexylpyridinium hexafluorophosphate [HPy] [PF₆] ionic liquid	[176]

TABLE 5: Selected papers using FAAS and preconcentration strategies using functionalized materials.

Sample (s)	Analyte	Remarks	Preconcentration factor	LOD	Complexing agent	Ref.
Water	Cd (II)	—	120	0.11 μg/L	Polymer based on cadmium(II) 2,2-{ethane-1,2-diylbis[nitrilo(E)methylylidene]} diphenolate-4-vinylpyridine complex	[197]
Soil, effluent, and water	Pb	—	48	1.3 μg/L	Dithiocarbamate functionalized Merrifield Chloromethylated Resin beads	[198]
Soil, effluent, and water	Cd(II) and Cu(II)	—	27	3.0 μg/L	Diethyl ammonium dithiocarbamate surface sorbed Merrifield Chloromethylated Resin beads	[198]
Water	Cu(II)	—	20	18 μg/L	Polystyrene-divinylbenzene resin (PS-DVB) functionalized with a benzothiazole group. PS-DVB treated with BA (ethyl 2-benzothiazolylacetate) (BA-PS-DVB)	[199]
Water	Cd(II) and Cu(II)	—	50 (Cd(II)) and 50 (Cu(II))	9.0 (Cd(II)) and 18 (Cu(II))	Polystyrene-divinylbenzene resin (PS-DVB) functionalized with a benzothiazole group. Amino-PS-DVB was diazotized and coupled with BA (azo-BA-PS-DVB)	[199]
Wine	Cd	—	39	37 ng L^{-1}	5-Br-PADAP functionalized onto the wool	[200]
Urine	Cu, Fe, Mn and Ni	Urine samples were online ultrasound assisted digested by the stopped-flow mode	42.6 (Cu), 21.7 (Fe), 21.3 (Mn), and 44.1 (Ni)	0.5 (Cu), 1.1 (Fe), 0.8 (Mn), and 0.8 (Ni) μg/L	Iminodiacetic functional group resin, Chelite Che	[201]
River and seaside water	Cu	Sorbent was shown to be promising for solid-phase extraction discussed by FT-IR	—	0.5 μg/L	Cu(II)-imprinted interpenetrating polymer network (IPN) gel of epoxy-diethylenetriamine and methacrylic acid-acrylamide-N,N0-methylene-bis-(acrylamide)	[202]

complexing group serving as a solid-phase extractor of ions from liquid solutions. This idea was originally developed by Uezu et al. [208] which proposed a novel molecular imprinting technique named "surface template polymerization." With this new technique, attractive features were attained as rigid polymer matrices, acid resistance as well as high selectivity. Polymers beads formed by Cu(II) and Cd(II) have been used for Cu and Cd determination, respectively, using FIA-FAAS systems [196, 197, 209] exhibiting long-term stability and high enrichment factors. Flotation [210] is another commonly used separation-preconcentration method which is based on coprecipitation of the analyte(s) from a high volume solution (usually hundreds of milliliters). The further step is the precipitate flotation to the solution surface promoted by a stream of N_2 bubbles from the recipient bottom. Finally, the precipitate is collected and dissolved in a small volume and further determined. This method was applied by Ghaedi et al. [211] for preconcentration of several elements (Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn) in digestates of plant materials with LODs in the range of 1.3 to 2.4 ng/mL.

5.6. Carbon Nanotubes. As previously stated, FAAS presents, as one of its main limitations, low sensitivity for metals determinations at μg/L levels and may be strongly affected by matrix effects [212]. Among the various approaches to overcome these drawbacks, it has been proposed preconcentration/separation procedures [213]. The application of natural and synthetic adsorbents is one of the most efficient approaches for this purpose.

The relatively low cost, the efficient removal of metals, and high availability are the major advantages of the application of the adsorbents for preconcentration/separation associated with FAAS.

The use of different types of adsorbents has been given special attention, such as the use of bioadsorbent *Geobacillus thermoleovorans* subsp. *stromboliensis* immobilized on Amberlite XAD-4 resin was used in the biosorption of Cd(II) and Ni(II) ions in water and food samples [214]. The authors demonstrated that the use of this type of adsorbent is feasible, since they exhibit higher recoveries, economical advantages, simplicity, and environmental safety. Due to the high superficial area and special chemical and physical structures, they are not influenced by toxic substances or extreme parameters (such as low pH).

Synthetic adsorbents are also gaining prominence in procedures for preconcentration/separation as the use of 5(p-dimethylaminobenzylidene) rhodanine (PDR) complex on silica gel-polyethylene glycol (Silica-PEG) as a new synthesized adsorbent, for the selective SPE of Pd(II) in water, dust, and ore samples spiked [215]. The adsorbed complex was eluted using HCl/acetone mixture, and the concentration of Pd(II) was determined using FAAS.

We can also use adsorbents chemically modified as presented by Pérez-Quintanilla et al. [216]. This study applied the mesoporous silica chemically modified with 5-mercapto-1-methyltetrazole. These authors showed that the matrix effects were reasonably tolerable. In addition, the modified mesoporous silica had high thermal stability and

good resistance to hydrolysis and leaching by acids and buffer solutions with repeated use.

Other alternative to combine preconcentration with FAAS is the use of carbon nanotubes, made of carbon atoms which form a hexagonal structure with a thickness of a graphite sheet and cylindrical [217]. The high surface area and the hexagonal arrays of carbon nanotubes provide a strong interaction with other atoms, thus making it a potential adsorbent [218].

The use of multiwalled carbon nanotubes (MWCNTs) as adsorbent for preconcentration of metal ions has been the subject of several studies [219]. Barbosa et al. [178] proposed the application of MWCNTs as a solid sorbent for Pb preconcentration using a flow system for different types of samples. Moreover, it could be shown that the method is characterized by simplicity, precision, and mainly by absence of chelating agents.

Another interesting study has demonstrated the performance of nanocomposites Al_2O_3/MWCNT as adsorbent for preconcentration of Ni(II) in water samples [220]. The authors have shown that the minicolumn packed with the nanocomposite did not show the swelling effect and the nanocomposite did not present leakages even when working at high flow rates.

Table 6 presents other preconcentration studies [2, 221–255] using biosorbents and carbon nanotubes.

5.7. Other Strategies. The direct elemental determination by FAAS is considered a difficult task when dealing with extremely low concentrations because of insufficient sensitivity, selectivity, or matrix interference. Besides, high levels of concomitant species are often present in the samples to be analysed. To solve these difficulties, a separation step may be required. The separation-preconcentration procedures as CPE, SPE, ion exchange, membrane filtration, solvent extraction, coprecipitation, and liquid-liquid extraction are commonly used prior to detection [256, 257]. Schrijver et al. [258] determined Ag in polymers by solid sampling techniques as laser ablation ICP-MS (LA-ICP-MS), solid sampling electrothermal atomic absorption spectrometry (SS-ETAAS), and wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS), and the accuracy was checked by acid digestion and determination by pneumatic nebulization using ICP-MS or FAAS [258].

The liquid-liquid microextraction system using an automatic sequential injection incorporating a dual-conical microgravitational phase separator was proposed for preconcentration and separation of Pb in water samples with online determination using FAAS. The APDC was employed as complexing agent and isobutyl methyl ketone (IBMK) used as extraction solvent. The organic phase was collected in the upper cavity of the phase separator. The LOD obtained was 1.4 μg/L, and an enhancement factor of 120 was reached for determination of Pb(II) in water sample [259].

The determination of labile Al species was made using two methods. The first method applied SPE using chelating resins Iontosorb Oxin and Iontosorb Salicyl, and the second method applied 1% m/v 8-hydroxyquinoline in 2% v/v acetic acid and 0.2% m/v salicylic acid by a single extraction, and

TABLE 6: Selected papers using FAAS and preconcentration strategies using biosorbents and carbon nanotubes.

Sample (s)	Analyte	Remarks	Pre concentration factor	LOD	Complexing agent	Ref.
Natural waters and human hair	Cu	Column with TDMBAC-treated analcime pyrocatechol immobilized	200	0.05 ng/mL	Pyrocatechol violet	[221]
Natural waters	Mn	—	20	5 ng/mL	1-(2-piridilazo)-2-naftol (PAN)	[222]
Natural water	Cu and Pb	—	250	0.07 μg/L Cu(II) and 2. μg/L Pb(II)	Diethyl dithiophosphate (DDPA)	[223]
Natural water	Cd(II)	—	120	1.3 μg/L	Ammonium O,O-diethyl dithiophosphate (DDTP)	[224]
Water samples and reference materials: sewage sludge (CRM 144R), and sea water (CASS 4)	Cd(II)	Minicolumn	200	0.3 ng/mL	Xylenol orange loaded on activated carbon	[225]
Water	Be	—	300	0.8 μg/L	Octadecyl silica gel modified with aurin tricarboxylic acid (aluminon)	[226]
Industrial wastewater and natural water	Cu	—	100	*	Carboxyl cotton chelator (CCC)	[227]
River and ground water	Cu (II)	—	16	3 μg/L	Peat	[228]
Natural water and commercial tea bag	Mn	Column	200	0.245 μg/L	Amberlyst 36	[229]
Urine	Co (II)	Modified with Cyanex302	133	1.5 μg dm^{-3}	Octadecyl bonded silica membrane disk	[239]
Spinach, black tea and rice flour	Cd, Co, Cu, and Ni	—	39 (Cd), 69 (Co), 36 (Cu), and 41 (Ni)	(Cd) 0.31, (Co) 0.32, (Cu) 0.39 and (Ni) 1.64 μg L^{-1}	Amberlite XAD-2-PC resin	[231]
Environmental and biological	Cd and Cu	—	24 (Cd) and 25 (Cu)	0.30 μg/L (Cd) and 0.11 μg/L (Cu)	Multiwalled carbon nanotubes (MWNTs)	[232]
Tap water, river water	Cd, Co and Cu	—	100	(Cd) 0.062, (Co) 0.084, and (Cu) 0.057 μg/L	Amberlite XAD-2 resin	[233]
Tap water, ground water and river water	Cd, Co, Cu, and Zn	—	42 (Cd), 33 (Co), 28 (Cu), and 31 (Zn)	(Cd) 0.1, (Co) 0.5, (Cu) 0.3 e (Zn) 0.2 μg/L	Amberlite XAD-4 resin	[234]

TABLE 6: Continued.

Sample (s)	Analyte	Remarks	Pre concentration factor	LOD	Complexing agent	Ref.
Geological and water	Au	Microcolumn	50	0.21 ng/mL	Nanometer TiO_2 immobilized on silica	[235]
Water	Cd	Ultrasound-assisted emulsification-microextraction (USAEME)	95	0.91 μg/L	Sodium diethyldithiocarbamate trihydrate solution (NaDDTC·3H$_2$O)	[236]
Fruit juices	Zn	—	25	1.7 μg/L	Zincon	[237]
River water, human serum, and urine samples, and standard alloys	Cu	Modified with bis-(3-methoxy salicylaldehyde)-1,6-diaminohexane	100	30.0 ng/L	Octadecyl silica membrane disk	[238]
Water	Fe(III)	Modified by synthesis (Bis-(4-nitro phenyl azo) salisilidine-1,3-diamino propane)	100	20.0 ng/L	Octadecyl silica membrane disk	[239]
Tobacco, black tea, coffee, soil and river sediment	Cd(II) and Pb (II)	Dowex Optipore V-493	50	(Cd) 0.43 μg/L and (Pb) 0.65 μg/L	Sodium dibenzyldithiocarbamate (DBDTC)	[240]
Water	Ag	Dispersive liquid-liquid microextraction (DLLME)	16	1.2 ng/mL	**	[241]
Road dust and water	Pd	Dispersive liquid-liquid microextraction (DLLME)		1.4 ng/mL	**	[242]
Tap water, pond water, and seawater	Cu(II)	Sorbent	20	9.0 μg/L	Modified silica containing amidoamidoxime group	[243]
Black tea, rice flour, sesame seeds, tap water and river water	Co (II) and Ni (II)	—	83.3	0.37 ng/mL Co(II) and 0.71 ng/mL Ni(II)	Silica gel-polyethylene glycol	[244]
Dust and rock	Pd (II)	—	17(AC), 80 (EG), 66.5 (fullerene), 25 (MWCNT) and 10 (SWCN)	1.0 μg/L	Diethyl ammonium dithiocarbamate (DDTC)	[245]
Street/fan blade dust and rock	Pd (II)	—	—	1.0 μg/L	Diethyl ammoniumdithiocarbamate (DDTC)	[246]
Natural water	Cd (II)	—	50	*	Carbon-encapsulated magnetic nanoparticles	[247]
Human hair, Beet, Kadoo Apple juice	Cu and Mn	Sorbent	—	5.2 μg/L (Cu) and 5.4 μg/L (Mn)	Polyethylenimine polymer	[248]

TABLE 6: Continued.

Sample (s)	Analyte	Remarks	Pre concentration factor	LOD	Complexing agent	Ref.
Biological and plan	Cu and Cd	Sorbent	300 for Cd and 400 for Cu	4.5 μg/L (Cu) and 1.54 μg/L (Cd)	Polyacrylic acid/alumina	[249]
Water	Cd and Pb		20	0.021 (Cd) and 0.15 ngmL^{-1} (Pb)	thioureasulfonamide resin	[250]
Water, hair, urine, and saliva.	—	Microcolumn	144	0.2 μg/L	Immobilized Alizarin Red S on alumina	[2]
Tap water and converter	Pd (II)	—	75	1.1 μg/L	Poly [N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene]	[252]
Food	Pb(II) and Cd(II)	—	40	2.3 ng/mL (Pb^{2+}) and 0.2 ng/mL (Cd^{2+})	Modified peanut shell as Microcolumn packing material.	[253]
Environmental	Pb (II)	—	101	0.24 μg/L	1-(2-pyridylazo)-2-naphthol (PAN)	[254]
Water	Ni and Cd	—	66.7	0.25 ng/mL (Cd) 1 ng/mL (Ni)	TiO$_2$ nanotubes	[255]

* Not reported; ** Not employed.

Table 7: Selected papers for miscellaneous applications using FAAS.

Sample (s)	Analyte	Remarks	Pre concentration factor	LOD(μg/L)	Complexing agent	Ref.
Water and certified reference material	Ag	Novel flow injection (FI) online displacement SPE	110	0.2	Sodium diethyl dithiocarbamate	[262]
Water	Cd	New simple flow injection wetting film extraction was desenvolved and used diisobutyl ketone (DIBK) as extraction solvent	35	0.7	Diethyl dithiocarbamate	[263]
Water	Cu	The microextraction was realized using of ethanol as dispersive solvent and 1,2-DCB as extraction solvent.	*	0.5	**	[264]
Water	Cu (II)	Dispersive liquid-liquid microextraction (DLLME) method using dispersive solvent as methanol	42	3	8-Hydroxy quinoline	[265]
Water	Cu and Pb	Online sequential injection (SI) dispersive liquid-liquid microextraction (DLLME)	560 and 265	0.04 and 0.54	ammonium diethyldithiophosphate	[266]
Water, vegetable, Rice and spices	Cu(II) and Fe(III)	SPE method was developed for the determination of the elements	50.0	0.82 and 1.05	N-benzoyl-N-phenylhydroxylamine	[267]
Water	Mn	On-line preconcentration procedure using flow injection with determination by FAAS	30	12.0 and 16.0	5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin	[268]
Seawater, stream water, well water and vegetable	Cd and Pb	Cu(II)-mercaptobenzothiazole was used as a new coprecipitant	150	0.04 and 1.08	**	[269]
Water	Ag	Dispersive liquid-liquid microextraction method with microsample introduction	575	0.018	Dithizone	[270]
Seawater, urine, mineral water, soil and physiological solution	Pb(II) and Fe(III) Pb(II),	Coprecipitation using the violuric acid-copper(II) system and optimization step using two-level full factorial desig	*	0.16 and 0.18	**	[271]
Synthetic metal mixture solution and river water	Cu(II), Cd(II), and Ni(II)	New chelating was used to preconcentrate the metals	~ 200 and ~ 100 for Cd(II)	0.58, 0.86, 0.65 and 0.92	silica gel modified with gallic acid (GASG)	[272]
River water and Sewage water	Cu	SPE method and copper complex was adsorbed on the naphthalene column	40	2.0	Methylthymol blue	[273]
Environmental	Fe (III), Cu (II), Cr (III), Zn (II), and Pb (II)	New co-precipitation method was developed using an organic coprecipitant, 3-benzyl-4-p-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on (BPNBAT) without any carrier element	150, 150, 100, 100, and 50	0.7, 0.3, 0.4, 0.3, and 2.0	*	[274]
Natural water	Be, Pb, Ni, and Bi	Use of syringe loaded with sorbent for the separation and enrichment of the elements	100	0.30, 0.25, 0.20, and 0.34	2 propylpiperidine -1-carbodithioate	[275]

* Not reported; ** Not employed.

for quantification, FAAS and ICP OES were used. The use of a second method without requiring sample filtration can replace the SPE procedure for determination of Al in soils [260].

A rapid and straightforward sample treatment employing emulsion by ultrasound system with a probe was developed for determinations of As, Cd, Cr, Hg, Mn, Ni, Sr, and Zn at trace levels by ETAAS, ICP OES, FAAS, and CV-AAS in cosmetic samples. The emulsion was stable for more than 3 months after applying 1 min of ultrasonic shaking in a dispersion medium containing 0.5% m/v of sodium dodecyl sulphate plus 3% v/v of HNO_3 or HCl. The accuracy was checked by microwave-assisted digestion and determination by ICP-MS [50].

The SPE procedure was developed for fractionation of Fe in wine. An adsorbing Amberlite XAD-7HP column followed by a cation exchange Dowex 50W-X8-200 column was used, and three different groups were discriminated, hydrophobic species (phenolic fraction), cationic species and labile forms (cationic fraction), anionic, or neutral species (residual fraction). The results obtained were verified using another adsorbing Amberlite XAD-16 column for Fe determination [261]. More studies [262–275] employing different strategies for preconcentration can be seen in Table 7.

6. Conclusions

Flame atomic absorption spectrometry has several nuances, and its capability to solve analytical challenges is virtually endless. Its applications are observed in various scientific and technological fields with interesting results. In this paper it was possible to see that the FAAS field remains strong and more applications will appear in the coming decades. New advances in commercial instruments and lab-made solutions are enlarging the scope of AAS techniques and surely had brought new horizons for this fertile area in instrumental analysis.

Acknowledgments

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