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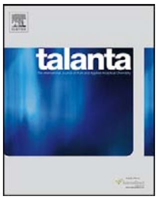

Review

Thermospray generation directly into a flame furnace—An alternative to improve the detection power in atomic absorption spectrometry

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ABSTRACT

Recent developments and applications in the production of thermosprays directly into flame furnaces to improve the analytical sensitivity in atomic absorption spectrometry are reviewed in this manuscript. Principles, characteristics, instrumentation, and applications of this analytical technique for trace elements determination in several matrices are discussed. The use of preconcentration procedures to allow low detection limits for ultra-trace levels using TS-FF-AAS is presented and current perspectives and future trends of this technique are also discussed.

Contents

1. Introduction

Flame atomic absorption spectrometry (FAAS) is largely used for determination of metals and semi-metals in food as well as on biological, environmental, geological, and other matrices. The simplicity and robustness of this method, as well as its low set up and operational costs, few and well-known spectral interferences, and reliable element-selective methods accessible for the majority of laboratories, are some of its favorable characteristics. Although

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FAAS is a common technique, there is a large demand to improve its sensitivity due to some drawbacks in nebulization efficiency since only 5–10% of the primary aerosol reaches the flame [1–3].

The analytical sensitivity of FAAS can be significantly improved by increasing the efficiency of the aerosol production, its transport to the flame, and the atomization efficiency. Therefore, there is interest in the total sample introduction into the flame (*e.g.* total consumption nebulizer/burner, boat in flame technique, etc.) and other methods to trap analytes in the optical pathway (*e.g.* atom trap techniques, tubes for hydride generation, etc.) [4–6].

A successful alternative to improve the detection power of FAAS was proposed by Berndt et al. [7] and is based on the thermospray generation directly into a flame furnace. This method is termed thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). In this technique, a liquid sample is completely transported to the flame furnace through a capillary that is heated by the sample vaporization flame. This technique improves the detection limit, mainly for volatile elements, due to complete sample introduction in the atomizer and atom trapping in the flame furnace, which also improves the sensitivity.

TS-FF-AAS is an excellent alternative to overcome some sensitivity limitations of the flame atomic absorption technique without the need to employ expensive instrumentation. The importance of this technique in the AAS context can be reinforced by the number of contributions recently published that focus on: (a) procedures for volatile element determination in several kinds of samples; (b) application of new methodologies to improve its performance, such as preconcentration procedures, direct analysis of complex matrixes and slurry sampling, and (c) studies related to thermospray production and atomization.

This review highlights the development and applications of thermospray generation into a flame furnace as a technique for improving the analytical sensitivity in atomic absorption spectrometry. The characteristics and components of this technique are presented whereas recent applications are discussed.

2. Thermospray production

The thermospray production after heating a liquid sample that passes through a capillary was first proposed by Blakley et al. [8] as an interface between liquid chromatography (LC) equipment and a mass spectrometer (MS). The original system was designed with a ceramic capillary that was heated by an electrical resistor to produce a fine aerosol. This method presents numerous advantages over pneumatic nebulization because it can generate an aerosol with small drops and it can increase the amount of sample that is transported to the atomizer, thus improving the sensitivity. In atomic spectrometry, thermospray sample introduction has often been applied to ICP OES or ICP-MS and there are some efforts to use it in FAAS [9]. However, nebulization using this system has not been applied to FAAS for it is expensive and difficult to produce. In contrast with the thermospray electrically generated, in which sophisticated electrical and pumping systems are required to maintain a constant temperature and adequate flow rate for sample vaporization, the liquid sample in TS-FF-AAS is vaporized by heating the capillary in contact with the furnace above the spectrometer flame and through heat transfer based on the direct contact of the capillary with the flame-heated tube atomizer. Because only a short part of the wide capillary is heated in the TS-FF-AAS, the flow resistance caused by the backpressure from rapid vaporization of liquid is relatively low. Therefore, a peristaltic pump is effective for the sample transport in the tubing, in contrast with the classical electrical TS generation in which a capillary with a smaller inner diameter and longer heated portion requires an HPLC pump to overcome the high pressure in the system [10].

To produce a thermospray, both temperature and pumping pressure act to vaporize the liquid to generate droplets that are dispersed in the gaseous phase. However, the temperature conditions for achieving thermospray using an electrothermally heated capillary tube and TS-FF-AAS greatly differ (temperatures over 1000 °C are required for the latter). Thus, the pumping pressure is not a critical factor for achieving fragmentation of the bulk liquid in the TS-FF-AAS, which explains the good analytical characteristics achieved using peristaltic pumps [11].

Based on these facts, Brancalion et al. [12] hypothesized that the nebulization process in TS-FF-AAS at low flow rate could be different than in electrothermal thermospray systems. Authors used a high-speed camera to film the thermospray evolution to extract morphological information about this system and its correlation with the analytical information. According to these authors, when are used higher temperature and low flow rate (conditions currently used in TS-FF-AAS), the liquid is partially vaporized in the capillary tube due to heat transfer from the flame to the ceramic capillary, thereby inducing cavitation of the fluid. Consequently, liquid pulses are formed even at temperatures higher than 1000 °C, being ejected from the capillary tip. The thermospray is then formed by random pulsed jets, which greatly differ from conventional thermosprays. The presence of liquid pulses at high temperature is attributed to the Leidenfrost effect. The Leidenfrost effect is a phenomenon in which a liquid in near contact with a hot surface with temperature higher than the boiling point of the liquid produces an insulating vapor layer which momentarily protects the liquid against vaporization [13–15]. After pulse ejection, the formed spray goes through the metallic tube impacting on the opposite wall. Just after impact, a great number of smaller drops are formed, bouncing from the heated furnace wall due to its high temperature. The Leidenfrost effect again insulates the rest of the liquid against the higher wall temperatures, increases the droplet lifetimes and affects the total vaporization process [11].

The carrier is another important factor for both thermospray formation and overall sensitivity. Each individual solvent has different properties related to cohesive forces associated with viscosity, surface tension, and sometimes density, which works to maintain the “bulk” liquid integrity. Temperature and pumping pressure are alternatively contributing factors to liquid vaporization, generating a large number of drops dispersed in the gaseous phase. Brancalion et al. [16] have studied the influence of several solutions (water, nitric acid, acetonitrile and Triton X-100) on average drop size and sensitivity for Cd using TS-FF-AAS. High-speed images have shown that the fragmentation of the liquid jet and its incidence pattern affects the Cd signal. The authors have concluded that there is a reasonable correlation between the analytical sensitivity and the Sauter mean diameter (SMD) curves, indicating that mainly the surface tension of the solution, as well as the kinematic viscosity, are inherent to the analytical performance of this technique.

In TS-FF-AAS, atomization steps (nebulization, droplet desolvation, vaporization and dissociation of molecular species in the gas phase) are not expected to be as complete in the analytical viewing zone as in FAAS. This adverse effect is caused by the larger droplet volume and the smaller gas phase observed in the thermospray technique. Schiavo and Nóbrega [17] studied the effects caused by concomitants [Na(I), K(I), Ca(II), and Mg(II)] on the atomization of cobalt and manganese in TS-FF-AAS. In this study, severe interference effects were caused by all contaminants. Data have demonstrated a frequent paradoxical situation in spectrochemical analysis in which efforts to introduce a larger sample amount lead to the manifestation of severe interference processes. These processes either require the application of previous separation steps or special calibration strategies. For example, Miranda et al. [18] have reported the use of background signals and multivariate calibration as procedures to assess the total concentration of

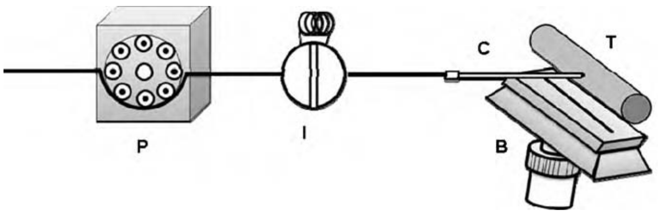

Fig. 1. Schematic diagram of a TS-FF-AAS system. P: peristaltic pump; I: injector; C: capillary; T: tube and B: burner.

four contaminants (Ca, K, Mg and Na) in solutions containing Cd and Pb using TS-FF-AAS. According to the authors, the absorption through molecular bands related to those undissociated species would provoke rise in molecular spectra, hence having a greater extent than FAAS while background signals could be used to predict the total concentration of these contaminants. Thus, partial least squares refinement was used in calibration models using either each wavelength singly, or a combination of both to predict the total concentrations of contaminants.

3. Components of TS-FF-AAS

The components of TS-FF-AAS, in a basic configuration, are simple, cheap and easily adaptable on a flame atomic absorption spectrometer. The required components include a pumping system, injector, capillary and tube. A schematic representation of TS-FF-AAS system is shown in Fig. 1. In this manifold, a carrier is propelled by a pumping system and the injection loop device defines the sample volume. The sample is transported through the capillary where the thermospray is generated into the tube furnace that is positioned above the burner head and longitudinally aligned to the hollow cathode lamp radiation.

3.1. Pumping system

An HPLC pump can be used due to its highly reproducible flow rate, power, and robustness. However, 80% of the TS-FF-AAS applications refer to low-pressure pumps, as peristaltic pumps. Another low cost pumping system that has been satisfactorily used due to the low backpressure generated by non-electrical thermospray is the diaphragm pump. In this way, peristaltic pumps have been largely used in TS-FF-AAS procedures and have resulted in good analytical determination performances [10].

The effect of the solution flow rate inside the thermospray capillary is a factor related to sensitivity. A high flow rate is undesirable for it causes a temperature decrease inside the furnace and it can affect the signal intensity. Similarly, the residence time of the solution in the small heated part of the capillary is too short to complete vaporization; the thermospray is not formed inside the flame furnace. As a consequence, samples enter the tube as a continuous liquid stream and develop large drops that skitter around, and in some cases, jump from the hot inner surface of this atomizer (consequences of increasing the Leidenfrost effect) [12]. On the other hand, low flow rates contribute to thermospray formation due to efficient heat transfer between the liquid and the capillary.

3.2. Injector device

In general, a solenoid valve allows different and precise solution volumes to be inserted into the liquid or gaseous carrier flow to the TS-FF-AAS system to obtain a signal. Furthermore, dispersion of small injected volumes can be avoided by the isolation of the sample solution through air bubbles.

According to Gáspár and Berndt [7], the introduction of sample volumes between 5 and 50 μL leads to sharp transient signals. On the other hand, as it is well-known in FIA techniques, an increase in the injected volumes also causes an increase in the signal width (stead state signal). Thus, the injected sampling volume is a variable that requires adequate optimization.

3.3. Capillary

The capillary is of utmost importance in the TS system because it is responsible for the thermospray generation. It must be introduced into the flame furnace through its central hold, forming a 90° angle with the tube to guarantee heating by direct flame exposure as well as by conduction through the tube.

Davies and Berndt investigated the performance of capillaries manufactured from several materials with various inner and outer diameters. According to these authors, capillaries manufactured from Al_2O_3 ceramic showed the best results (high sensitivity and low noise) being available in a wide range of sizes, inner and outer diameters, and are inexpensive. Stainless steel, Pt/Ir and titanium capillaries can also be used. Yet, capillaries made from these materials showed some limitations. For example, the titanium capillary was seriously damaged after few hours of use due to high temperature and use of acid sample solutions. The capillary was relatively expensive and it similarly maintained high blank responses [10].

These authors also studied the inner diameter of ceramic capillaries. The highest sensitivity was obtained for the smallest inner diameter (0.3 mm). However, this capillary was not robust in routine use. Ceramic capillaries with inner diameters of ca. 0.6 mm have produced aerosols with high percentage of large diameter water droplets, which are not completely vaporized in the furnace tube. Capillaries with an inner diameter greater than 0.7 mm have low efficiency in the nebulization process and the heat transfer between the walls; besides that, the liquid flow seems to be inadequate because the glowing capillary is not long enough to transform the liquid into vapor. This fact demonstrates that the signal's stability is hardly dependent on the inner diameter and the nature of the capillary. Therefore, capillaries with an inner diameter of 0.5 mm are mechanically stable and do not provoke significant losses in sensitivity, then being highly recommended.

3.4. Flame furnace

The metallic tube in the TS-FF-AAS is responsible for the increase in sensitivity when compared to conventional FAAS, due to the atomic cloud confinement on the optical pathway. The capillary is partially inserted into the tube through a hole positioned in the center of the tube. To reach a higher temperature inside the tube, other (4–6) holes are generally drilled into the bottom of the tube forming a 90° angle with the capillary hole. These holes allow partial flame penetration to the furnace and increase the inner temperature, thereby allowing better atomization conditions for some elements. Thus, the increase in the temperature inside the tube plays a deciding role in the number of elements that can be determined by the TS-FF-AAS technique and in its sensitivity [10]. These holes also can influence the atomization environment inside the flame furnace. Brancalion et al. [16] have related the Cd sensitivity to total hole area of the atomizer. Results have shown that using water as a carrier in the absence of flame gases (tube without holes) promotes an increase in Cd sensitivity. Yet, this behavior is not observed when the carrier is different than water, proving that low oxygen content and the presence of carbon from organic substances burning in the flame improves the sensitivity by increasing the Cd from the CdO released in the CO formation.

The materials suitable for the tube are: nickel, super alloys, titanium, quartz and non-porous ceramic. Nickel atomizers are used

Table 1
Comparison of detection limits ($\mu g\,L^{-1}$) for some elements measured by TS-FF-AAS and conventional FAAS on the same instrument (adapted from Ref. [10]).

Element	TS-FF-AAS[a]	Conventional FAAS[b]
Ag	0.6	9
As	260	940
Bi	16	250
Cd	0.3	34
Cu	4.2	14
Hg	68	1500
In	53	144
Pb	2.4	220
Rb	9	300
Sb	40	1600
Se	310	930
Te	18	290
Tl	3.8	120
Zn	0.2	9

[a] $N = 25$, sample volume 200 μL.
[b] $N = 15$, sample volume 200 μL.

more often than other materials due to their cost, efficiency, easy availability, long lifetime and mechanical resistance [19].

The material of which the tube is confectioned can influence on the determination performance. For example, Lobo et al. [21] have evaluated two tubes as atomization cells for tin determination: a metallic tube (Ni-Cr, principal components composition: 73.95% Ni and 16.05% Cr) and a ceramic tube (99.8% Al_2O_3,). The sensitivity for 50 mL of analytical solution with TS-FF-AAS was two and five times higher (to metallic and ceramic tube, respectively) than when using an acetylene-nitrous oxide flame with pneumatic aspiration.

A strategy based on the combination of Ni and Ti tubes (Ni/Ti) was proposed by Gomes and Pereira-Filho [22] to increase the Ti atomizer lifetime in the copper determination. The TS-FF-AAS system was equipped with Ti tubes inserted inside Ni tubes (called Ni/Ti), and also different configurations of Ti tube atomizers placed on an oxidizing air/acetylene flame. This new arrangement combining both tubes allowed an increased sensitivity (approximately four times) when compared to single Ni or Ti tubes. Such high sensitivity is due to the formation of TiO_2 inside the Ti tubes, improving the Cu atomization through the corresponding oxide. The estimated gaseous phase temperatures for the tubes (Ni, Ti and Ni/Ti) had the same magnitude (varied from 1400 to 1800 °C). Tests with concomitants (Na, K, Ca and Mg) showed similar behavior of Ni and Ni/Ti tubes. The differences between Ni and Ni/Ti tube atomizers for Cu sensitivity were not related to differences between the internal volumes of tube atomizers. A 2 $\mu g\,L^{-1}$ Cu detection limit was obtained using a Ni/Ti tube atomizer. The use of a Ti tube inside a Ni tube increased the Ti tube lifetime.

4. Applications of TS-FF-AAS

The applications of TS-FF-AAS in the literature focus on biological, environmental, food, and drug samples. The breadth of these applications can be attributed mainly to the better sensitivity of TS-FF-AAS when compared with FAAS and similarities with GF AAS. Davies and Berndt [10] have reported the detection limits (measured through peak height) for seventeen elements using this technique. For all elements studied, a considerable increase in detection power was obtained when compared to conventional FAAS (Table 1). The greatest improvement in the detection limit was obtained for volatile elements such as Cd, Pb and Tl.

The work presented by Pereira et al. [24], showed suitability and limits of a simultaneous sample digestion of biological matrices and metal determination in slurries of biological material by applying the TS-FF-AAS. Some powdered biological materials (such as pig kidney, bovine liver, spinach, orchard leaves, citrus leaves, tomato leaves and tomato puree), which were mainly certified samples, were used for Cd, Cu and Pb determinations. Several parameters were investigated, such as the best inner diameter of the thermospray capillary, nitric acid and hydrogen peroxide concentrations, the use of surfactant agents, as well as some calibration possibilities. Finally, the results obtained with TS-FF-AAS were compared with those obtained by ET AAS. No differences between the results obtained and the certified values were observed at a 95% confidence level.

In another example [25], the determination of Cd, Pb and Zn in fresh water, seawater, and marine sediment samples was performed using TS-FF-AAS. The detection limits were lower than those obtained using AAS (30, 4 and 10 times to Cd, Pb and Zn, respectively). The methodology by TS-FF-AAS was validated by determination of the same metals in certified reference materials of water, seawater and marine sediments. No significant statistical differences at the 95% confidence level were established in fresh water and seawater, whereas differences were observed in marine sediment. In this work, Cd, Pb and Zn were determined at the $\mu g\,L^{-1}$ level (fresh water and seawater) and at the $\mu g\,g^{-1}$ level (marine sediment).

Petrucelli et al. [26] also described the use of TS-FF-AAS in Cd and Pb determinations in seven sewage sludge slurry samples (two of them were certified samples). The slurried samples were easily prepared by adding HNO_3 or HCl (from 0.01 to 1 $mol\,L^{-1}$). A Triton X-100 solution was also added to a final concentration of 0.5% (m/v) for slurry stabilization. Authors evaluated two multivariate calibration models based on partial least squares (PLS) refinement, which were compared with a linear calibration using aqueous standard solutions and the standard addition method. In the multivariate calibration procedure, the models were built using the whole peak profile and the concentration obtained by mineralization procedure. Detection limits and quantifications for both metals were found to be three times lower than those limits found when linear calibration with aqueous standard solutions was used. The higher sensitivity can be attributed to the PLS design in which simultaneous parameters are considered for optimization.

The behavior of selenium in the TS-FF-AAS was evaluated by Rosini et al. [27] and the developed procedure was applied for its determination in biological materials. Using a factorial design experiment, authors optimized some of the operating parameters. Results demonstrated that the presence of Na, K, Ca and Mg in the sample significantly affected the selenium analytical signals. The applicability of the TS-FF-AAS procedure was also evaluated for selenium determination in pig kidney and shellfish samples after microwave-assisted sample digestion.

Brancalion and Arruda [28] evaluated medicinal plant decomposition parameters by applying the single vessel concept and using polypropylene minivials heated by microwave radiation. In these experiments, Cd concentrations were determined by TS-FF-AAS in three different medicinal plants (*Equisetum arvense* L., *Maytenus ilicifolia* Reisser and *Phyllanthus niruri* L.) after optimizing the sample preparation conditions. The accuracy of the proposed methods was also assessed using certified reference materials (rye grass and bovine liver). The method increased the capacity of microwave ovens by up to four-fold and reduced the contamination risks when the single vessel concept was used. Finally, the detection limit calculated for Cd determination by TS-FF-AAS was 0.9 $\mu g\,g^{-1}$.

Nascentes et al. [29] determined Cu and Zn concentrations in bovine milk and fruit juice samples by TS-FF-AAS without the requirement of sample pretreatment. Sample preparation was carried out by simple dilution of the sample in water or in water-soluble tertiary amines. TS-FF-AAS system was optimized and a sample volume of 300 μL was injected into the carrier stream. The detection limits obtained for Cu and Zn in aqueous solution were 2.2 and 0.91 $\mu g\,L^{-1}$, respectively, and 3.2 $\mu g\,L^{-1}$ for Cu in a medium containing water-soluble tertiary amines. Accuracy was checked using reference materials (whole milk powder, non-fat milk powder and infant formula).

Nascentes et al. [30] also employed TS-FF-AAS for Cu, Mn, Pb, and Zn determinations in beer without any sample digestion. In that case, beer samples were degassed in an ultrasonic bath and were then diluted using 0.14 mol L^{-1} HNO_3. The dilution factors were chosen depending on the analyte and sample characteristics. The system was optimized (carrier composition and Ni tube height were evaluated in terms of sensitivity) and calibration was based on the analyte addition technique. Results obtained in different beer samples using TS-FF-AAS were compared with those obtained by graphite furnace atomic absorption spectrometry. No statistical differences at the 95% confidence level were observed according to a paired *t*-test.

In a recent work, Schiavo et al. [31] used TS-FF-AAS for direct determination of Cu, Cd and Pb in wine and grape juices without acid digestion of samples. The optimal conditions (influence of solution medium, sample flow rate, sample volume and measurement time) were evaluated. Due to the efficiency on the sample introduction and atomization processes, the LOD obtained using TS-FF-AAS was better than those usually established in FAAS.

Da-Col et al. [32] employed TS-FF-AAS for Cd and Pb determination in food supplements (minced chicken liver, milk, milk cream, salt, chopped onion, and garlic). A simple procedure for sample preparation in which the sample (100 mg) was mixed with 0.1 mol/L HCl. For Cd, the LOD and LOQ obtained were 0.6 and 2.0 μg L^{-1}, respectively, and for Pb determination the LOD and LOQ were 10 times above that found for Cd. No metal ions were therefore found in the evaluated food samples.

Lobo et al. [33] developed an analytical procedure for on-line determination of tin from analytical solutions obtaining a detection limit and analytical frequency of 1.7 mg L^{-1} and 120 h^{-1} respectively. In another work [34], tin was determinate from canned foods by TS-FF-AAS using a ceramic tube as an atomizer and an air-acetylene flame. The detection limit, relative standard deviation ($n = 12$, 1 mg L^{-1} Sn) and analytical frequency procedure was 0.8 mg L^{-1} Sn, $\leq 8.5\%$ and 90 h^{-1} respectively. Accuracy was checked by performing spike tests. Recoveries ranged from 95.0% to 104% for nine samples of canned foods. All results were statistically compared (*t*-test) to the values obtained by FAAS using acetylene-nitrous oxide flame and the results matched at the 95% confidence level.

Berndt and Pulvermacher [35] proposed compressed air for sample transport to thermospray/flame furnace system in the detection of four toxic elements (Cd, Hg, Pb and Tl) in spices. The detection limits were 0.2–0.4 μg L^{-1} (Cd), 40–100 μg L^{-1} (Hg), 5–9 μg L^{-1} (Pb) and 4–14 μg L^{-1} (Tl), depending on the method, flow rate, and sample volume used.

An on-line derivatization strategy was developed by Matos and Arruda [36] for improving cobalt sensitivity using TS-FF-AAS as analytical technique. This strategy involves the generation of a volatile cobalt compound, providing better sample vaporization efficiency. The effect of sodium diethyldithiocarbamate as a complexing agent on the integrated absorbance signal was evaluated. Parameters including the pH of complex formation, complex concentration and volume, sample volume, flame, gas composition, and tube atomization configuration were optimized. The improvement in the detection power was 17-fold when compared to FAAS, which provides 7 μg L^{-1} as the limit of detection when considering TS-FF-AAS technique. The procedure accuracy was evaluated through certified reference materials (Lake sediment, and Antarctic marine sediment).

Due to high sensitivity, TS-FF-AAS was also used to validate results for zinc determination obtained by application of an alternative analytical methodology for food analyses combining X-ray spectroscopy (XRS) with partial least squares (PLS) data treatment [20]. Aiming to investigate the sediment quality in regards to its influence on the water quality and bioavailable, total Cd and Pb were determined from a wastewater treatment plant by De Paula e Souza et al. [23] using TS-FF-AAS. The wastewater sludge showed concentrations of 4.01 and 171 μg g^{-1}, for the same metals.

Capillary electrophoresis was directly interfaced to TS-FF-AAS for trace element speciation [37]. According to the authors, this system integrated the superiorities of stable capillary electrophoresis separation, complete sample introduction, and continuous vaporization for AAS detection without the need of extra external heat sources or any post-column derivation steps. To demonstrate the usefulness of the developed hybrid technique for speciation analysis, three environmentally significant and toxic forms of methylmercury (MeHg), phenylmercury (PhHg), and inorganic mercury (Hg(II)) were considered as model analytes. The detection limit of three mercury species was 3.0 pg (as Hg), corresponding to 50.8 μg L^{-1} (as Hg) for 60 nL sample injection, which was almost independent on specific mercury species. The developed hybrid technique was successfully applied to the speciation analysis of mercury in a certified reference material (DORM-2, dogfish muscle).

5. Coupling preconcentration procedures

The design and nature of TS-FF-AAS allow its coupling with preconcentration techniques for improving performance. This combination has resulted in powerful procedures that enable determination of many metals in several matrices at low concentrations. Wen et al. [38] carried out the determination of trace cadmium in rice and water by using flow injection on-line precipitation-dissolution in a knotted reactor as a preconcentration scheme for thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). Under optimal chemical and instrumental conditions, a detection limit of 0.04 μg L^{-1} and a sensitivity enrichment factor of 34 for cadmium were obtained with a total initial sample volume of 4 mL.

Solid-phase extraction (SPE) and cloud point extraction (CPE) are the preconcentration techniques most commonly coupled to TS-FF-AAS [39,40]. Both strategies will be discussed in this review.

5.1. On-line solid-phase extraction

The eluent from a minicolumn inserted in an on-line solid-phase extraction system can be easily transported to the tube furnace of TS-FF-AAS. This detail has contributed to the development of interesting preconcentration systems using solid sorbents from several materials, such as polyurethane foam [41], fullerene [39] polymeric resins [42], and others.

An increase in sensitivity related to TS-FF-AAS was observed when a minicolumn packed with polyurethane foam was used in an on-line preconcentration system for cadmium determination [41]. The system was based on the retention of Cd-DDTP (diethyldihiophosphate) complexes on polyurethane foam surfaces. Elution is performed with 80% (v/v) ethanol. The sensitivity enhancement was five times higher than the values obtained with TS-FF-AAS without preconcentration system, and the obtained detection limit was 0.12 μg L^{-1}. This method was applied to cadmium determination in spiked water, pig kidney and rye brass. The combination of polyurethane foam and DDTP was used again in an on-line preconcentration system for copper determination by TS-FF-AAS [43]. In an on-line preconcentration system, Pb(II) ions complexed with ammonium O,O-diethyldithiophosphate (DDTP) were preconcentrated onto polyurethane foam (PUF) packed into a minicolumn

Table 2
Characteristics of on-line solid-phase procedures for metal determination by TS-FF-AAS.

Metal	Detection limit (ng L^{-1})	Enrichment factor	Reagent	Support	Sample	Ref.
Cd(II)	100	675	APDC	C_{60-70} fullerenes	Water	[39]
Pb(II)	2400	200				
Cd(II)	120	5	DDTP	PUF	Water and vegetable	[41]
Cd(II)	8.0	24	TAM	Amberlite XAD-2	Cabbage and powdered guarana	[42]
Cu(II)	220	65	DDTP	PUF	Water	[43]
Pb(II)	150	6	DDTP	PUF	Water and vegetable	[44]
Cd(II)	7.0	1960	APDC	C-18-bonded silica gel	Standard reference materials	[45]
Pb(II)	170	610				
Cd(II)	28	102	DHB	Amberlite XAD-4	Standard reference materials	[46]
Cu(II)	100	91				
Zn(II)	77	62				
Cd	30	33	–	Grape bagasse	Standard reference materials	[47]
Cd	11.4	51	–	MWCNT	Waters and cigarettes	[48]

APDC: ammonium pyrrolidine dithiocarbamate; DDTP: O,O-diethyldithiophosphate; PUF: polyurethane foam; TAM: 2-(2-thiazolylazo)-5-dimethylaminophenol; DHB: dihydroxybenzoic acid, MWCNT: multiwall carbon nanotubes.

[44]. The complex retained in the sorbent was then released to TS-FF-AAS by using an ethanol solution. The method was applied to Pb(II) determination in water samples and vegetable materials.

A 3 cm HPLC column packed with C18 RP material was used in an elegant system for on-line separation and preconcentration of cadmium and lead coupled with TS-FF-AAS. Compressed air was used to drive the sample through the column and eluent to the TS-FF-AAS. The reagent ammonium pyrrolidine dithiocarbamate was immobilized onto the column. The system was used for the determination of Cd and Pb in biological standard reference materials [45].

The TS-FF-AAS determination of Cd was successfully performed by using a microcolumn packed with the reagent 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM) loaded in Amberlite XAD-2 resin [42]. This method was applied for the determination of Cd in cabbage and powdered guarana samples.

Improvements in the detection limits of TS-FF-AAS were made by applying a hyphenated technique using fullerene for on-line preconcentration of Cd and Pb in tap and mineral waters [39]. The chelation of Cd and Pb with ammonium pyrrolidine dithiocarbamate and posterior adsorption of the chelates on a minicolumn packed with C_{60-70} fullerenes is the basis for the method. Chelates were eluted from the minicolumn using a continuous flow of ethanol.

Cadmium, copper, and zinc were determined using an on-line preconcentration system coupled to the TS-FF-AAS [46]. A minicolumn packed with 3,4-dihydroxybenzoic functionalized in Amberlite XAD-4 (XAD4-DHB) was inserted in the on-line system. The procedure was used for the metal determination in biological standard reference materials. Grape bagasse was used as sorbent in an on-line preconcentration system for Cd determination by FAAS [47]. The procedure was also applied for certified reference materials.

Tarley et al. [48] have used fractional factorial designs and response surface methodology for the development of a method for cadmium determination based on the on-line coupling of a flow preconcentration system using multiwall carbon nanotubes as sorbent with TS-FF-AAS determination. The excellent characteristics of this sorbent, mainly owing to its high surface area, make it possible to obtain a preconcentration factor of 51-fold, thus improving the detection limits in TS-FF-AAS (11.4 ng L^{-1}). In order to demonstrate the accuracy of the system, recovery studies in water (mineral water, tap water and river water) and cigarette samples were carried out. Cadmium was also determined in certified biological materials (Bovine Liver and Rye Grass).

Procedures for determination of metals using TS-FF-AAS and on-line solid-phase extraction are summarized in Table 2.

5.2. *Cloud point extraction*

The cloud point extraction technique has been used for preconcentration of metals prior to their determination by different techniques, including TS-FF-AAS. A cloud point extraction procedure was developed for the determination of Ag in soil, marine sediment, and ore samples by TS-FF-AAS [33]. The method is based on two steps of cloud point extraction. First, copper ions react with diethyldithiocarbamate (DDTC) forming Cu-DDTC. A cloud point extraction procedure is performed and the aqueous phase is discarded. After that, silver ions are added and a second cloud point extraction procedure is conducted. Silver ions can displace Cu^{2+} from the pre-extracted Cu-DDTC, thus achieving the preconcentration and separation of Ag^{+} from sample matrix. Under optimal conditions, the detection limit and sensitivity enhancement factor were respectively 200 and 21 ng L^{-1}.

A method for determination of Cd in water and urine samples by TS-FF-AAS, based on the formation of analyte-entrapped surfactant micelles by mixing the analyte solution with an ammonium pyrrolidinedithiocarbamate (APDC) solution and a Triton X-114 solution, has been developed [49]. A solution containing 10% (v/v) HNO_3 and 20% (v/v) methanol was added to reduce the viscosity of the surfactant-rich phase before TS-FF-AAS determination. A detection limit of 40 ng L^{-1} and a sensitivity enrichment factor of 13 were achieved.

A procedure for simultaneous preconcentration of Cd, Cu, and Pb using CPE and multi-elemental sequential determination in mineral water samples by TS-FF-AAS was proposed [50]. The method is based on the metals extraction into micellar media of Triton X-114 after reaction with 1-(2-pyridylazo)-2-naphthol (PAN). The optimization of pH, buffer concentration and NaCl volume used in the extraction procedure was performed with a Box–Behnken design. Enrichment factors were 59, 25, and 21 for Cd, Cu, and Pb, respectively, and the detection limits obtained were 25 (Cd), 380 (Cu) and 430 ng L^{-1} (Pb).

TS-FF-AAS was employed for Co determination in biological materials after cloud point extraction for improvement of sensitivity [51]. Cobalt presents a high atomization temperature and poor sensitivity is consequently obtained without changing its thermochemical behavior. The effect of different complexing agents on sensitivity was evaluated based on the formation of Co volatile compounds. The detection limit obtained for Co was 2.1 μg L^{-1}. Accuracy was checked using two certified reference materials (tomato leaves and bovine liver). Co was quantified in different biological materials (plant and animal tissues) employing the developed procedure.

TS-FF-AAS was employed to determine Cd and Pb in different Brazilian tobacco samples [52]. Sample pretreatment consisted of acid decomposition and cloud point (CP) preconcentration optimized by Doehlert design. To promote phase separation in the cloud point procedure, polyoxyethylene(8) isooctylphenyl ether (Triton X-114) and 2-(bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) were used as a nonionic surfactant and a complexing agent, respectively. The limits of detection and relative standard deviations obtained for Cd and Pb when CP and TS-FF-AAS were associated were 4.0 and 13 $\mu g\,kg^{-1}$, and 3.1 and 0.7%, respectively. Accuracy was checked by addition-recovery experiments, as well as by using two certified reference materials (tea and peach leaves).

6. Future trends

Taking into account some characteristics and advantages previously discussed in this review, it is not surprising the crescent utilization of TS-FF-AAS in recent years. Thus, some drawbacks must be overcome and new studies on the development and improvement of methods are required.

The volatilization and determination of elements forming thermostable compounds is a limitation when the low working temperature is limited by the characteristics of the flame. To overcome this problem, derivatization or chemical vapor generation methods could be a viable alternative.

Because the environment inside the tube atomizer can affect the atomization of some elements, number and size of the atomizer holes need to be optimized. The tube dimensions (diameter and size) similarly play an important role in the signal, due to the influence of these parameters on the homogeneity of the tube's inner temperature.

New methods based on coupling preconcentration procedures (such as solid-phase extraction, cloud point extraction, precipitation in knotted reactor, liquid–liquid extraction) can be developed to decrease the detection limits allowing the determination of elements at lower concentrations in several matrices. Slurry sampling techniques can also be an attractive option for decreasing the number of sample manipulation steps. Besides that, the mechanism of slurry nebulization in TS-FF-AAS should be further studied.

Due to its excellent detection limit, TS-FF-AAS could be coupled as a detector to liquid chromatography and capillary electrophoresis for detection of organometallic compounds and metalloproteins, thus making AAS appropriate for speciation and metallomic studies. Because high sensitivity is often needed in such investigations, the thermospray method may be ideal for the applications.

7. Conclusions

The thermospray flame furnace technique is an efficient, simple, low cost and robust alternative to improve the detection power in atomic absorption spectrometry for volatile or moderately volatile elements that can make this technique as sensitive as graphite furnace AAS. Moreover, detection limits can be lowered by coupling preconcentration procedures, such as solid-phase and cloud point extractions, thereby allowing the conduction of ultra-trace analysis. On-line or batch preconcentration procedure can also be used for increasing the sensitivity of the method. Although the flame furnace does not present a temperature program that allows sample pretreatment and it does not attain temperatures as high as GF AAS, analysis of some samples using an acid dilution without prior decomposition is possible. Applications of TS-FF-AAS for elemental determination from several matrices have increased and the detectability of seventeen elements was improved using TS-FF-AAS. Finally, this accessible technique is promising for the analysis of biological and environmental samples that demand capacity for determination of analytes at low concentrations.

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References

[1] B. Welz, M. Sperling, Atomic Absorption Spectrometry, third ed., Willey–VHC, Weinheim, 1999.
[2] C. Vandecasteele, C.B. Block, Modern Methods for Trace Element Determination, John Wiley & Sons, Chichester, 1993.
[3] A. Gaspar, E. Szeles, H. Berndt, Anal. Bioanal. Chem. 372 (2002) 136.
[4] H. Matusiewicz, Spectrochim. Acta B 52 (1997) 1711.
[5] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, fifth ed., Saunders College, Philadelphia, 1998.
[6] A. Klassen, M.L. Kim, M.B. Tudino, N. Baccan, M.A.Z. Arruda, Spectrochim. Acta B 63 (2008) 850.
[7] A. Gáspár, H. Berndt, Spectrochim. Acta B 55 (2000) 587.
[8] C.R. Blakley, M.J. McAdams, M.L. Vestal, J. Chromatogr. A 158 (1978) 261.
[9] X. Zhang, D. Chen, R. Marquardt, J.A. Koropchak, Microchem. J. 66 (2000) 17.
[10] J. Davies, H. Berndt, Anal. Chim. Acta 479 (2003) 215.
[11] M.A.Z. Arruda, E.C. Figueiredo, Spectrochim. Acta B 64 (2009) 477.
[12] M.L. Brancalion, E. Sabadini, M.A.Z. Arruda, Anal. Chem. 79 (2007) 6527.
[13] B.S. Gottfried, C.J. Lee, K.J. Bell, Int. J. Heat Mass Transfer 9 (1966) 1167.
[14] G. Bleiker, E. Specht, Int. J. Thermal Sci. 46 (2007) 835.
[15] H. Xie, Z. Zhou, Int. J. Heat Mass Transfer 50 (2007) 5328.
[16] M.L. Brancalion, E. Sabadini, M.A.Z. Arruda, Spectrochim. Acta B 64 (2009) 89.
[17] D. Schiavo, J.A. Nobrega, Spectrosc. Lett. 41 (2008) 354.
[18] K. Miranda, M.I.M.S. Bueno, E.R. Pereira-Filho, J. Anal. At. Spectrom. 24 (2009) 304.
[19] G.A. Petrucelli, P.K. Stocco, M.I.M.S. Bueno, E.R. Pereira-Filho, J. Anal. At. Spectrom. 21 (2006) 1298.
[20] F.M.V. Pereira, E.R. Pereira-Filho, M.I.M.S. Bueno, J. Agric. Food Chem. 54 (2006) 5723.
[21] F.A. Lobo, A.C. Villafranca, A.P. de Oliveira, M. de Moraes, Atom. Spectrosc. 28 (2007) 17.
[22] M.S. Gomes, E.R. Pereira-Filho, Microchem. J. 93 (2009) 93.
[23] S.N. de Paula e Souza, P.S. Fadini, E.R. Pereira-Filho, Quim. Nova 32 (2009) 2367.
[24] E.R. Pereira, H. Berndt, M.A.Z. Arruda, J. Anal. Atom. Spectrom. 17 (2002) 1308.
[25] E. Gonzalez, R. Ahumada, V. Medina, J. Neira, U. Gonzalez, Quim. Nova 27 (2004) 873.
[26] G.A. Petrucelli, R.J. Poppi, R.L. Mincato, E.R. Pereira, Talanta 71 (2007) 620.
[27] F. Rosini, C.C. Nascentes, J.Y. Neira, J.A. Nóbrega, Talanta 73 (2007) 845.
[28] M.L. Brancalion, M.A.Z. Arruda, Microchim. Acta 150 (2005) 283.
[29] C.C. Nascentes, M.A.Z. Arruda, A.R.A. Nogueira, J.A. Nóbrega, Talanta 64 (2004) 912.
[30] C.C. Nascentes, M.Y. Kamogawa, K.G. Fernandes, M.A.Z. Arruda, A.R.A. Nogueira, J.A. Nóbrega, Spectrochim. Acta B 60 (2005) 749.
[31] D. Schiavo, J.Y. Neira, J.A. Nóbrega, Talanta 68 (2009) 1113.
[32] J.A. Da-Col, S.M.A. Domene, E.R. Pereira-Filho, Food Anal. Methods 2 (2009) 110.
[33] F.A. Lobo, A.C. Villafranca, A.P. de Oliveira, M. de Moraes, Eclética Química 30 (2005) 61.
[34] F.A. Lobo, A.C. VillaFranca, A.P. Oliveira, M. Moraes, At. Spectrosc. 29 (2008) 186.
[35] H. Berndt, E. Pulvermacher, Anal. Bioanal. Chem. 382 (2005) 1826.
[36] G.D. Matos, M.A.Z. Arruda, Talanta 76 (2008) 475.
[37] Y. Li, Y. Jiang, X.P. Yan, Electrophoresis 26 (2005) 661.
[38] X.D. Wen, P. Wu, K.L. Xu, J. Wang, X. Hou, Microchem. J. 91 (2009) 193.
[39] M.G. Pereira, E.R. Pereira-Filho, H. Berndt, M.A.Z. Arruda, Spectrochim. Acta B 59 (2004) 515.
[40] P. Wu, Y. Gao, G. Cheng, W. Yang, Y. Lv, X. Hou, J. Anal. At. Spectrom. 23 (2008) 752.
[41] C.R.T. Tarley, M.A.Z. Arruda, Anal. Sci. 20 (2004) 961.
[42] F.A.C. Amorim, M.A. Bezerra, Microchim. Acta 159 (2007) 183.
[43] C.R.T. Tarley, G.D. Matos, E.C. Figueiredo, Anal. Sci. 21 (2005) 1337.
[44] C.R.T. Tarley, M.A.Z. Arruda, Anal. Lett. 38 (2005) 1427–1443.
[45] E. Ivanova, H. Berndt, E. Pulvermacher, J. Anal. At. Spectrom. 19 (2004) 1507.
[46] V.A. Lemos, M.A. Bezerra, F.A.C. Amorim, J. Hazard. Mater. 157 (2008) 613.
[47] G.D. Matos, M.A.Z. Arruda, Spectrosc. Lett. 39 (2006) 755.
[48] C.R.T. Tarley, A.F. Barbosa, M.G. Segatelli, E.C. Figueiredo, P.O. Luccas, J. Anal. At. Spectrom. 21 (2006) 1305.
[49] P. Wu, Y. Zhang, Y. Lv, X. Hou, Spectrochim. Acta B 61 (2006) 1310.
[50] L.M. Coelho, M.A. Bezerra, M.A.Z. Arruda, R.E. Bruns, S.L.C. Ferreira, Sep. Sci. Technol. 43 (2008) 815.
[51] G.L. Donati, C.C. Nascentes, A.R.A. Nogueira, M.A.Z. Arruda, J.A. Nóbrega, Microchem. J. 82 (2006) 189.
[52] F.P. Andrade, C.C. Nascentes, L.M. Costa, J. Braz. Chem. Soc. 20 (2009) 1460.