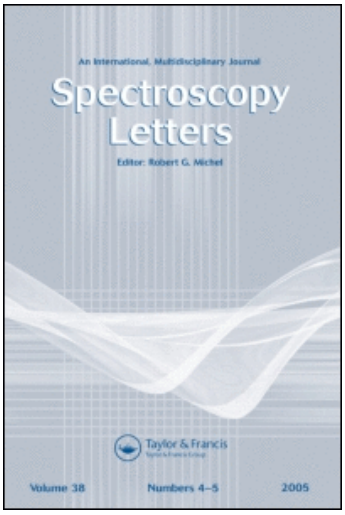

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Interferences in Thermospray Flame Furnace AAS: Co and Mn Behavior

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ABSTRACT The effects caused by concomitants [Na(I), K(I), Ca(II), and Mg(II)] on the atomization of cobalt and manganese by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) were here studied. The main concomitants were chosen according to typical major elements found in foods and beverages. Severe interference effects were caused by all concomitants. The interferences varied from −101.0% to +360.0% and −117.5% to +175.5% for Co and Mn, respectively. These data demonstrated a frequently paradoxical situation in spectrochemical analysis, that is, efforts are directed toward the introduction of a higher amount of sample, however, when this condition is attained, there is the manifestation of severe processes of interferences. These interference processes require the application of either previous separation steps or special strategies of calibration.

KEYWORDS atomic absorption spectrometry, cobalt, manganese, flame furnace, interferences, thermospray

INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is an instrumental technique frequently used for routine analysis due to its robustness, low cost, simplicity, and selectivity. However, the sensitivity of FAAS is low, being limited by several factors. When a liquid sample is nebulized for introduction in a flame, the generated atoms remain a short time in the observation zone (ca. 3–5 ms) and the atomization efficiency can be low depending on the flame composition and thermochemical behavior of the analyte. Another factor that affects the sensitivity is the inefficiency of the nebulization process; typically the aerosol that reaches the flame only contains about 5–10% of the original volume of the solution.[1,2] Therefore, FAAS generally is applied for determinations in mg L^{-1} range.

The efficiency of the sample introduction process was studied and improved. Robinson[3] was the precursor of the application of an atomization cell to increase both the residence time for generation of the atomic cloud and its concentration in the optical path. The atomization cell was made using a quartz "T" tube positioned above the burner head. Afterwards, Delves[4] proposed a method to improve the efficiency of introduction of the

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sample. This strategy was based on nickel cups with 10 mm o.d. and 5 mm of height and a nickel tube with 100 mm length and 12.5 mm o.d. with an opening in the inferior section. The sample was placed in the cup and vaporized in the flame below the metallic tube. The vapors reached the inside of the heated tube and the atomic cloud was formed. As an additional benefit, the sample can be prepared directly in the nickel cup, avoiding contamination problems.

Recently, two new methods involving a metal tube positioned in a flame were proposed to improve the process of sample introduction. In the one termed beam injection flame furnace atomic absorption spectrometry (BIFF-AAS),[5] the introduction of the sample is made by a liquid jet under high pressure. The jet is directed to a hole in a ceramic or nickel tube positioned on the flame. A pump is used (peristaltic or piston type) for the propulsion of the sample and a nozzle to produce the liquid jet that collides with the internal wall of the tube. Taking advantage of the experience with BIFF-AAS, other method was also proposed, the so called thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS).[6] In this case, the sample is introduced through a ceramic capillary connected to the nickel tube positioned on the burner of an atomic absorption spectrometer. One advantage of the TS-FF-AAS approach is that no external heat source is needed to heat the capillary, because it is conductively heated by the flame through its physical contact with the nickel tube positioned into the flame. This simple approach allowed the total introduction of the sample. The sensitivity is also increased owing to the long residence time of the atoms in the optical path.

There are many developed analytical procedures based on BIFF-AAS[7] and TS-FF-AAS.[8,9] However, in spite of their successful applications, it can be seen that most of them are related to volatile elements. This niche of applications is easily understood taking into account the temperature inside the nickel tube of approximately 1200°C measured with thermocouples[5,8] is not enough for atomization of less volatile elements.

Consequently, despite the improved sensitivity, it can be supposed that severe interference processes may occur in TS-FF-AAS due to the long residence time of atoms and concomitants in a cloud at relatively low temperature. From a kinetic point of view, it means that there will be time enough for occurrence of recombination processes. On the other hand, from the thermodynamic point of view, it can be supposed that the atomizer temperature will not be enough for fully promoting physical and chemical processes involved with the formation of the atoms cloud. The goal of the developed work was to evaluate this hypothesis for cobalt and manganese. These elements were chosen based on their different thermochemical behavior. Measurements were also made using a conventional FAAS for comparison purposes.

MATERIALS AND METHODS

Equipment and Accessories

All experiments were made using a flame atomic absorption spectrometer (model AA 640; Varian, Mulgrave, Australia) equipped with deuterium lamp background corrector, and hollow cathode lamps (HCL) as source of radiation for Co and Mn (Varian). The instrumental parameters are presented in Table 1 (FAAS) and Table 2 (TS-FF-AAS).

Arrangement of the TS-FF-AAS System

The TS-FF-AAS system consists of a lab-made stainless steel support with four ceramic pins on the flame burner for positioning of the nickel metallic tube.

The tube employed contains 99.7% Ni and has the following specifications: 10 cm length, 1 cm i.d. and 1.2 cm o.d., with six holes in the inferior part each with 2 mm diameter to allow entrance of the flame gases and a central hole with 2 mm diameter. This central hole is perpendicular to the inferior holes, and it is used for introduction of the ceramic capillary tube.

TABLE 1 Instrumental Parameters for Determination of Co and Mn by FAAS

Parameters	Co	Mn
Wavelength (nm)	240.7	279.5
Spectral resolution (nm)	0.2	0.2
Lamp current (mA)	9.0	5.0
Air flow rate (L min^{-1})	13.5	13.5
Acetylene flow rate (L min^{-1})	2.0	2.0
Data acquisition	Peak height	Peak height

TABLE 2 **Instrumental Parameters for Determination of Co and Mn by TS-FF-AAS**

Parameters	Co	Mn
Flow rate (mL min^{-1})	0.4	0.4
Sample volume (μL)	300	300
Air flow rate (L min^{-1})	13.5	13.5
Acetylene flow rate (L min^{-1})	2.0	2.0
Delay time (s)	30	30
Measurement time (s)	30	60
Spectral resolution (nm)	0.2	0.2
Lamp current (mA)	9.0	5.0
Wavelength (nm)	240.7	279.5
Height of the tube (cm)	1.5	1.5
Carrier	Air	Air
Data acquisition	Peak area	Peak area

The nickel tube acts as an atomization cell and is located above the burner head for partial penetration of the flame gases. The radiation beam from the hollow cathode lamp travels through the nickel tube for measurement of the atom cloud. After adjustment of the beam, the tube was removed before the ignition of the flame for preventing the acetylene accumulation inside of it and the occurrence of small explosions[6]. The tube was carefully placed in the support after flame ignition with the aid of a tongs. One extremity of the ceramic capillary tube (Friatec, Mannheim, Germany, with the relation i.d./o.d. of 0.5/2.0 mm) is connected to the flow system and the other extremity is introduced about 2 mm inside the Ni tube furnace producing the thermospray. The schematic representation of the TS-FF-AAS system with tubular oven in the flame is presented in Fig. 1.

A peristaltic pump with eight channels (Ismatec, Labortechnick Analytik, Glattbrugg-Zurich, Switzerland) was employed to fill up the sampling loop and to propel the carrier solution toward the ceramic capillary. For the propulsion and transport of fluids, tubes of Tygon with different diameters and PTFE tube with 0.8 mm i.d. were employed. A commutator injector made in acrylic was employed to insert the sample in the carrier solution.[10]

Reagents

All reagents were of analytical grade. The following solutions were employed: 1% (v/v) nitric acid obtained by dilution of 14 mol L^{-1} HNO_3 (Merck, Darmsdadt, Germany), and reference solutions were prepared by dilution of 1000 mg L^{-1} stock solutions of Mn(II) and Co(II) (Tec-Lab, Hexis, São Paulo, Brazil). The water employed was distilled-deionized in a Milli-Q Plus system (Millipore, Bedford, MA).

In the experiments for evaluating the effects of the concomitants on the atomization of Co and Mn, the following reagents were employed: NaCl (Merck), KCl (Merck), $FeCl_3$ (Labsynth, Diadema, Brazil), $AlCl_3$ (Labsynth), $ZnCl_2$ (Labsynth), $CaCl_2$ (Merck) and $MgCl_2$ (Labsynth). All solutions were prepared dissolving the appropriate amounts of the reagents in 1% (v/v) HNO_3.

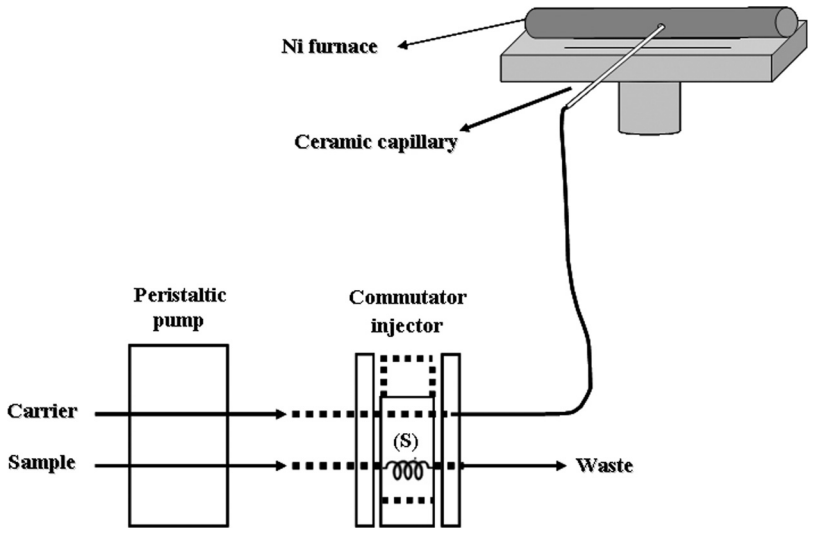

FIGURE 1 **Schematic representation of the TS-FF-AAS system. The side parts of the commutator are fixed. The central part may be slid to the position shown with dashed lines for sample introduction. (S), sampling loop.**

Study of Interference Effects on the Analytical Signals of Co and Mn by FAAS and TS-FF-AAS

The first experiments dealt with the effects caused by major elements, such as Na(I), K(I), Ca(II), and Mg(II), on the analytical signals of Co and Mn. These elements are frequently the major inorganic constituents in foods and beverages. The concentrations tested were 10, 100, 1000 and 10,000 mg L^{-1}. The effect of the solutions containing 10,000 mg L^{-1} of these analytes were preliminarily tested, however they caused obstruction of the ceramic capillary.

In the second series of experiments, the effects caused for minor elements, such as Fe(III), Al(III), and Zn(II), were also evaluated. Thus, solutions were prepared simulating the typical concentrations of them in animal and plant tissues to evaluate the effects of these concomitants in the atomization of Co and Mn. The concentrations investigated were 0.1, 1.0, 5.0, and 10 mg L^{-1}.

All experiments were carried out with the gradual increase of the concentrations of the concomitants and the evaluation of their effects on the analytical signals of Co and Mn obtained by TS-FF-AAS and FAAS.

RESULTS AND DISCUSSION

Preliminary experiments were focused on the establishment of Co and Mn concentrations to generate analytical absorbance signals around 0.4 by TS-FF-AAS and FAAS. This magnitude of absorbance signals led to better repeatability and reliability. The concentrations found for both analytes were 2.0 mg L^{-1} by TS-FF-AAS and for FAAS were 12 and 6 mg L^{-1} for Co and Mn, respectively.

Then, Co and Mn were determined sequentially in the same solution to verify the occurrence of mutual interferences between both. Results are shown in Table 3.

According to Welz and Sperling, cobalt and manganese can be determined by FAAS in an air-acetylene flame without any interference effects.[11] Our data confirmed this statement. However, Table 3 also shows that in TS-FF-AAS, an increase of 76% occurred in the analytical signal of Co when the solution contained 2.0 mg L^{-1} Mn; on the other hand, we observed a decrease of 30% on the analytical signal of Mn when the solution contained 2.0 mg L^{-1} Co. Based on these preliminary data, it was concluded that the study of the effects caused by concomitants on the analytical signals of Co and Mn must be made for solutions containing only one of the analytes. Additionally, this is a first indication of the occurrence of severe interference processes in TS-FF-AAS.

The solutions containing Co or Mn and each one of the concomitant or combinations of them were prepared and the analytes were measured by TS-FF-AAS and FAAS. Results for cobalt are shown in Fig. 2. It can be seen that effects observed in FAAS are less severe in TS-FF-AAS. Thus, as expected, cobalt can be determined without interferences in air–acetylene flame by FAAS, but the sensitivity generally is not enough for most biological samples.[11] On the other hand, in TS-FF-AAS the concomitants generally caused negative interferences. The low temperature inside the nickel tube atomizer and the long residence time of the cloud containing a gradually complex chemical environment allows conditions for poor atomization and species recombination, and these processes probably would explain the negative interferences observed. It was demonstrated by Donati et al. that the determination of cobalt in biological samples by TS-FF-AAS is critically dependent on preliminary steps of sample preparation to reach both analyte preconcentration and matrix separation. The thermochemical behavior of cobalt should also be changed by a derivatization reaction before TS-FF-AAS measurements. All these aspects were implemented by cloud point extraction.[12,13]

TABLE 3 Absorbance Signals Obtained for Co and Mn by TS-FF-ASS and FAAS (Mean Values ± Standard Deviations, n = 3)

	TS-FF-AAS		FAAS	
	Co	Mn	Co	Mn
Without concomitant	0.419 ± 0.015	0.443 ± 0.047	0.402 ± 0.001	0.385 ± 0.007
With Co + Mn	0.705 ± 0.0368	0.274 ± 0.005	0.404 ± 0.037	0.390 ± 0.006

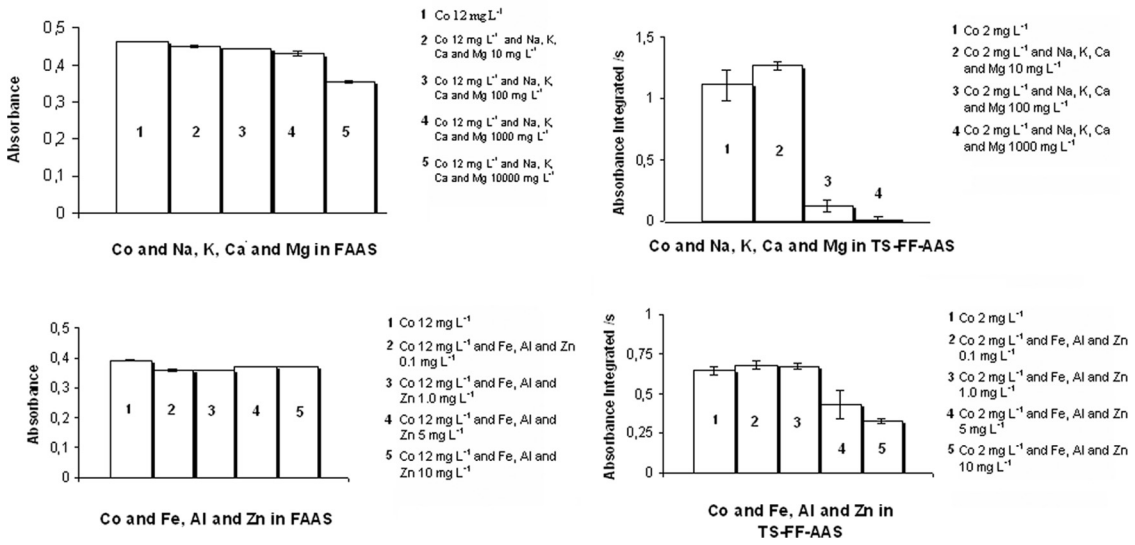

FIGURE 2 **Effect of the concomitants Na(I), K(I), Ca(II), Mg(II), Fe(III), Al(III), and Zn on the analytical signals of Co by FAAS and TS-FF-AAS.**

Figure 3 shows the effects of concomitants on the absorbance signals of Mn by TS-FF-AAS and FAAS. The results obtained for FAAS are in agreement with those previously described in the literature.[14] As early as 1959, Allan[14] demonstrated that Na(I), K(I), Ca(II), and Mg(II) did not cause interferences in Mn determination by FAAS. More recently, Grossmann and Müller[15] investigated interference effects on the determination of Mn by several constituents of alloys and concluded that Fe, Co, and Mo did not interfere. However, negative interferences were caused by Al, Cu, and Ni. Consequently, Mn can be determined by FAAS without critical interference effects.[11] On the other hand, it can be seen in Fig. 3 that negative interferences occurred in the measurement of Mn by TS-FF-AAS.

The essential differences between TS-FF-AAS and FAAS are related to the residence time and the efficiency of the atomization process. These two factors are greater for TS-FF-AAS, which implies greater concentrations of the analyte and concomitants in the atom cloud and longer time for occurrence of reactions among the chemical

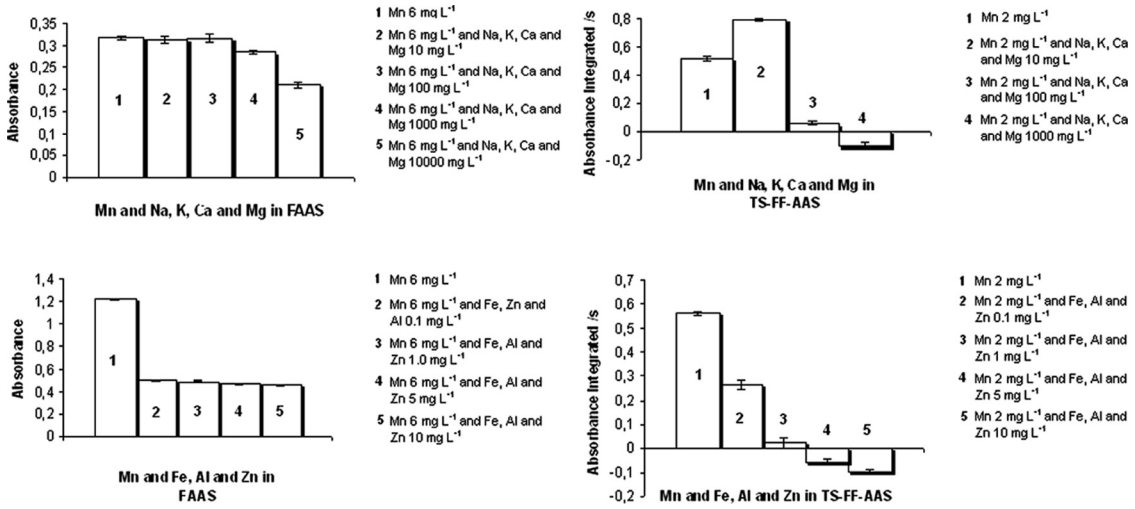

FIGURE 3 **Effects of the concomitants Na(I), K(I), Ca(II), Mg(II), Fe(III), Al(III), and Zn(II) on the analytical signals of Mn by FAAS and TS-FF-AAS.**

species. As mentioned, the elevated concentration of chemical species in the cloud at a relatively low temperature favors the occurrence of interferences in TS-FF-AAS.

All experimental data are shown in Table 4. In FAAS measurements, the percentages of interferences varied from −24.4% to +5.5% and −62.4% to +17.5% for Co and Mn, respectively. For TS-FF-AAS, these ranges were −101.0% to +360.0% and −117.5% to +175.5% for Co and Mn, respectively.

CONCLUSIONS

In the studies carried out to evaluate the effects of interferences on the analytical signals of Co and Mn by FAAS and TS-FF-AAS, it was verified that higher concentration of concomitants can intervene in the physical and chemical processes of the analyte. The interferences were worst in TS-FF-AAS, due to the long residence time of atoms and concomitants in a complex cloud at relatively low temperature. Thus, the atomizer temperature will not be enough for

TABLE 4 Interference Effects on the Analytical Signals of Co and Mn

	Co		Mn	
Interferents	FAAS	TS-FF-AAS	FAAS	TS-FF-AAS
10 mg L^{-1} Na	−0.8	−48.4	+4.4	+3.0
100 mg L^{-1} Na	−0.5	−52.3	+2.0	+4.0
1000 mg L^{-1} Na	−1.4	−58.6	+0.5	−26.0
10,000 mg L^{-1} Na	−3.5	—	−6.5	—
10 mg L^{-1} K	+5.5	−49.8	−1.0	+23
100 mg L^{-1} K	−5.1	−69.6	−1.0	−4.0
1000 mg L^{-1} K	−5.2	−83.5	−2.7	−36
10,000 mg L^{-1} K	−8.0	—	−10.0	—
10 mg L^{-1} Ca	−7.6	+43	−5.5	+175.5
100 mg L^{-1} Ca	−6.3	+48	−9.5	−12
1000 mg L^{-1} Ca	−10.3	+12	−15.0	−98.3
10,000 mg L^{-1} Ca	−12.0	—	−20.0	—
10 mg L^{-1} Mg	−5.3	+123.6	−5.1	+73
100 mg L^{-1} Mg	−9.0	−42.2	−6.4	−79
1000 mg L^{-1} Mg	−10.0	−99.7	−14	−132
10,000 mg L^{-1} Mg	−13.0	—	−23.2	—
10 mg L^{-1} Na, K, Ca and Mg	−2.8	+14.2	−1.6	+52.4
100 mg L^{-1} Na, K, Ca and Mg	−4.2	−89.1	−0.2	−88.7
1000 mg L^{-1} Na, K, Ca and Mg	−7.0	−101	−10.3	−120
10,000 mg L^{-1} Na, K, Ca and Mg	−23.1	—	−33.8	—
0.1 mg L^{-1} Fe	−1.2	−6.0	+14.3	+7.8
1.0 mg L^{-1} Fe	−2.9	−13	+17.5	−22.6
5 mg L^{-1} Fe	−3.7	−42.2	+12.0	−53.7
10 mg L^{-1} Fe	−3.5	−55.4	+2.6	−79.0
0.1 mg L^{-1} Al	−6.4	+360	−55.4	−29.4
1.0 mg L^{-1} Al	−8.8	+324	−55.8	−53.2
5 mg L^{-1} Al	−17	+225	−55.8	−90.0
10 mg L^{-1} Al	−22	+144	−57.2	−93.0
0.1 mg L^{-1} Zn	−24.4	+107.4	−57.8	−34,2
1.0 mg L^{-1} Zn	−15	+104	−57.2	−60.4
5 mg L^{-1} Zn	−12.4	+164	−56.2	−50.0
10 mg L^{-1} Zn	−8.8	+186	−58.0	−49.5
0.1 mg L^{-1} Fe, Al and Zn	−9.0	+105.8	−59.4	−53.0
1.0 mg L^{-1} Fe, Al and Zn	−9.0	+104.4	−60.0	−96.0
5 mg L^{-1} Fe, Al and Zn	−5.7	−33.0	−61.5	−110.0
10 mg L^{-1} Fe, Al and Zn	−5.7	−50	−62.4	−117.0

[a] Values are percent (%).

promoting dissociation, atomization, and volatilization processes. It means that either previous separation steps or special strategies for calibration should be applied for successful analytical applications using TS-FF-AAS despite the superb sensitivity of this simple and attractive approach for volatile analytes.

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