Simultaneous or Sequential Multi-element Graphite Furnace Atomic Absorption Spectrometry Techniques: Advances Within the Last 20 Years

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ABSTRACT: Electrothermal or graphite furnace atomic absorption spectrometry (ETAAS or GFAAS) is one of the most widely used techniques for determining elements in different matrices (*e.g.*, foodstuffs, pharmaceuticals, biological specimens, nanomaterials, polymers, fuels and environmental media). Numerous elements can be simply and quickly determined with high precision and accuracy, low detection limits, and at moderate cost. The technique is also suitable for direct solid and slurry sample analysis. A crucial feature of this technique is that it can perform simultaneous or sequential multi-element analysis. Over the years, many instruments have come on the market for multi-elemental analysis using mostly line source (LS) GFAAS and high-resolution continuum source (HR-CS) GFAAS. This review covers publications from 2000 to 2020 related to the simultaneous or sequential multi-elemental analysis by LS-GFAAS and HR-CS-GFAAS. Mainly the applications, the limits of detection, the use of internal standardization and other aspects regarding the matrix, pyrolysis and atomization temperatures and modifiers are discussed. Finally, a critical comparison is made between the LS-GFAAS and HR-CS-GFAAS techniques.

INTRODUCTION

Atomic absorption spectrometric techniques are widely used in many disciplines for the analysis of foodstuffs, environmental samples, water, nanomaterials, pharmaceuticals and biological specimens.[1-8] The selection of the most appropriate technique for a specific analysis depends on many factors, such as sample type and composition, chemical nature of elements, multi-element and isotopic capability of the instrument, desired limits of detection (LODs), available instrumentation and cost of analysis.[9-12]

Atomic absorption spectrometry (AAS) is one of the most used techniques for elemental analysis and is selected based on three different atomization processes: Flame AAS (FAAS), electrothermal AAS (ETAAS) or graphite furnace AAS (GFAAS), and chemical vapor generation AAS.[10] Among these three techniques, GFAAS is the most popular since low LODs can be obtained at levels similar to those obtained by the advanced technique of inductively coupled plasma mass spectrometry (ICP-MS). However, considering several figures of merit (*e.g.*, dynamic range and multi-element capability), ICP-MS is more powerful.

GFAAS is characterized by high precision, good compatibility with many techniques for elemental separation, and of moderate cost (*e.g.*, low consumption of gases, low maintenance and, therefore, low technical support).[10,13-15] Moreover, it is considered a suitable technique for direct solid and slurry sample analysis. Indeed, most published papers in the scientific literature apply GFAAS for these analyses rather than other techniques, such as ICP, coupled to laser ablation or electrothermal vaporization.[9]

The two main multi-element systems used for simultaneous or sequential analysis were line source atomic absorption spectrometry (LS-AAS) and high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS). In the second half of the 20th century, several multi-element GFAAS instruments were developed using both line and continuous sources. These instruments became commercially available from Hitachi, Ltd., Leeman Labs, PerkinElmer, Inc., and Thermo Jarrell Ash Corporation. The LS-GFAAS technique applied hollow cathode lamps (HCLs) and electrodeless discharge lamps (EDLs) and is mainly used to study elements with similar properties. Furthermore, the multi-element determination is usually limited to two and four elements. Multi-element lamps are not widely used because of the observed reduced sensitivity compared to the same element in a single-element lamp.[16] Initially, LS-AAS was the main approach for multi-element determination by GFAAS, but over the last 15 years the HR-CS-AAS has become the dominant technique.[8] The instruments are equipped with an ultra-high pressure Xenon short-arc lamp as the continuum source, an optical system based on a double monochromator, and a linear charge-coupled device (CCD) array detector.[8,17,18]

This work reviewed studies published from 2000 to 2020 for the simultaneous or sequential multi-element determinations by GFAAS. The LS-GFAAS and HR-CS-GFAAS were investigated, since they are considered the main AAS techniques for this purpose. The present study describes and compares these approaches in terms of applications, sensitivity, different elements, instrument performance, and the use of internal standardization (IS) as a quantification method.

SIMULTANEOUS MULTI-ELEMENT ANALYSIS BY LS-GFAAS

At the end of the 1980s, many companies made instruments for multi-element analysis by LS-GFAAS. Hitachi, Ltd., developed the model Z-9000 using the Zeeman background correction system and different photomultipliers able to perform the simultaneous analysis with four HCLs.[19] Thermo-Jarrell Ash Corporation commercialized instruments (*e.g.*, AA Scan 4 and AA Scan 8) with the ability to run up to eight HCLs in an analysis and provided multiple light sources, a single monochromator, a photomultiplier and a self-reversal background correction system.[19] A similar approach was applied by Leeman Labs, which introduced the Analyte 5 model. This instrument has a self-reversal background correction system, a reverse polychromator to combine the source beams and notch filters to achieve wavelength discrimination.[20] PerkinElmer, Inc., produced the models SIMAA 6000 and 6100, which became the main representatives of this technique and are designed for a fully automatic, simultaneous and multi-element analysis. The spectrometer system has echelle polychromator optics in a tetrahedral configuration and a multi-channel detector. The combination of the optical design with the use of the longitudinal Zeeman background correction system produces an ideal double-beam system able to eliminate interferences caused by background effects. The optical system allows the simultaneous determination of up to four elements or up to six when multi-element lamps are used.[21] These dynamic systems led many researchers to perform simultaneous multi-element analysis in numerous matrices (Table 1).[2,22-70]

The LS-GFAAS technique was applied for the simultaneous multi-element analysis in several matrices, including foods,[2,23,45,46,55,60,68,70] beverages,[25,32,39,48,51,53] biological specimen,[26,28,30,31,38,40,50,52] environmental media,[24,27,29,33,42,43,47,58,66,67] crude oil,[57,65,69] fuel[34,49,61] and medicinal plants.[62] In total, 21 elements were determined in numerous studies and Pb, Cu, Cd, As, Cr and Ni were most frequently investigated (see references in Table 1). In general, the simultaneous determination was limited to two elements. However, by using multi-element lamps, one study determined six elements and a few others five in one run.[32,34,45,58] In addition, two other studies determined five and six elements, but not many details can be given as the papers are not provided in English.[71,72] The low number of elements that can be determined simultaneously is considered one of the main disadvantages of this technique, which was solved in the 1980s with the development of the ELAN^{R} inductively coupled plasma instrument by PerkinElmer SCIEX for a truly simultaneous multi-element analysis.

The main wavelength of each analyte was used in almost all studies to obtain higher sensitivity and better figures of merit. However, some researchers selected a less sensitive secondary wavelength, since alternative lines are usually employed to adjust the required sensitivity to the expected analyte concentration. Thomaidis *et al.*[29] monitored the secondary line of Pb (261.4 nm) for its determination in particulate matter. Lead presented high concentrations compared to Cd, As and Ni, which were simultaneously determined and thus the less sensitive line led to good results, avoiding time-consuming and error-prone dilutions.[29] Another study monitored the 283.3 and 261.4 nm lines, since Pb was present in variable concentrations in the samples.[66] Likewise, Cu was found at higher concentration levels in cachaca samples than As and Pb and, therefore, the measurements were done using its secondary line at 249.2 nm.[53] The less sensitive line of As (197.2 nm) was used, instead of the usual As line (193.7 nm), to overcome background issues in soils and sediments. The selected line showed smaller background levels and the atomic absorption signals had better shape.[33] The choice of wavelength is crucial for an element and it was proven that more than one line could be used to avoid sample dilutions and background interference.

Table 1. Simultaneous Multi-element Analysis by LS-GFAAS – A Literature Review From 2000 to 2020

Analyte	Wavelength (nm)	Matrix	Limit of detection	Characteristic mass (m_0)	$T_{pyr.}/T_{atom.}$ (°C)	Modifier	Instrumentation	Ref.
Cr	357.9	Bismuth tellurite optical crystals	1.14 µg/L – 0.182 µg/g	7.78 pg	1300/2450	triammonium citrate	SIMAA 6000 (Perkin-Elmer)	22
Mo	313.3		4.9 µg/L – 0.777 µg/g	20.9 pg				
V	318.4		6.7 µg/L – 1.07 µg/g	59.8 pg				
Cd	228.8	Spinach, watercress, cauliflower, broccoli, lettuce, apple, tomato, carrot, beet, pea and rice	0.038 µg/L (0.38 pg)	1.46 pg	750/1600	$NH_4H_2PO_4$ + Mg	SIMAA 6000 (Perkin-Elmer)	23
Pb	283.3		0.93 µg/L (9.3 pg)	36.7 pg				
Cu	324.8	Seawater	0.42 µg/L	n.a.	1250/2400	Pd + Mg + 5% H_2	SIMAA 6000 (Perkin-Elmer)	24
Mn	279.5		0.68 µg/L					
Mo	313.3		1.2 µg/L					
Cd	228.8	Wine	0.03 µg/L	0.6 pg	400 & 600/1800	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	25
Pb	283.3		0.8 µg/L	33 pg				
Cu	324.8	Urine	0.08 µg/L	n.a.	1250/2300	Pd + 5% H_2	SIMAA 6000 (Perkin-Elmer)	26
Cr	357.9		0.05 µg/L					
Al	309.3		0.06 µg/L					
Mn	279.5		0.06 µg/L					
Co	242.5	Seawater	1.5×10^{-4} µg/L	n.a.	1200/2300	none	SIMAA 6000 (Perkin-Elmer)	27
Ni	232.0		4.8×10^{-4} µg/L					
Cu	324.8		1.2×10^{-3} µg/L					
Cr	357.9	Urine	0.08 µg/L	7.8 pg	800 & 1300/2500	Mg	SIMAA 6000 (Perkin-Elmer)	28
Mn	279.5		0.16 µg/L	4.6 pg				
Pb	261.4	Atmospheric particulate matter	4.3 µg/L	1.40 ng	650/2300	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	29
Cd	228.5		0.02 µg/L	2.2 pg				
As	193.7		0.26 µg/L	37.3 pg				
Ni	232.0		0.97 µg/L	27.9 pg				
Cu	324.8	Serum	4.0 µg/L	26 pg	700/2300	none	SIMAA 6000 (Perkin-Elmer)	30
Fe	248.3		2.2 µg/L	16 pg				
Zn	213.9		0.4 µg/L	2.7 pg				
Mn	279.5	Serum	0.43 µg/L (6.5 pg)	6 pg	400 & 1200/2300	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	31
Se	196.0		3.3 µg/L (50 pg)	46 pg				
As	193.7	Drinking water	0.7 µg/L	39 pg	1400/2100	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	32
Cu	324.8		0.2 µg/L	17 pg				
Mn	403.1		0.6 µg/L	60 pg				
Sb	217.6		0.3 µg/L	43 pg				
Se	196.0		0.9 µg/L	45 pg				
As	197.2	Soils and sediments	9.5 µg/L	45 pg	-/2200	none	SIMAA 6000 (Perkin-Elmer)	33
Cd	228.8		0.18 µg/L	1.5 pg				
Cr	357.9		6.2 µg/L	5.5 pg				
Pb	283.3		2.5 µg/L	33 pg				
Al	309.3		1.2 µg/L	37 pg				
As	193.7	Fuel ethanol	2.5 µg/L	73 pg	1200/2200	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	34
Cu	324.8		0.22 µg/L	31 pg				
Fe	248.3		1.6 µg/L	16 pg				
Mn	279.5		0.20 µg/L	9 pg				
Ni	232.0		1.1 µg/L	44 pg				
Pb	283.3			43 pg				
Sn	286.3	Aluminium-base alloys	n.a.	256 pg	1100/2400	Al	SIMAA 6000 (Perkin-Elmer)	35
Ni	232.0			26 pg				
Cu	324.8			22 pg				
As	193.7	Standard solutions	n.a.	36.1 pg	1500/2200	Ir	SIMAA 6000 (Perkin-Elmer)	36
Sb	217.6			42.3 pg				
Se	196.0			54.5 pg				
As	193.7	Sodium sulphate matrix	n.a.	n.a.	various	platinum group metals	SIMAA 6000 (Perkin-Elmer)	37
Se	196.0							
In	303.9							
Cd	228.8	Whole blood	0.095 µg/L	1.68 pg	550/1700	$NH_4H_2PO_4$	SIMAA 6000 (Perkin-Elmer)	38
Pb	283.3		0.86 µg/L	30.3 pg				

Cd	228.8		0.02 µg/L	2.2 pg				
Cr	357.9	Mineral water	0.94 µg/L	10 pg	1000/2300	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	39
Ni	232.0		0.45 µg/L	42 pg				
Pb	283.3		0.75 µg/L	66 pg				
As	193.7		0.71 µg/L	44.0 pg				
Mn	279.5	Urine	0.064 µg/L	7.1 pg	1350/2100	Pd + 5% H_2	SIMAA 6000 (Perkin-Elmer)	40
Co	242.5		0.36 µg/L	20.5 pg				
Ni	232.0		0.39 µg/L	30.3 pg				
Al	309.3	Silicon carbide and silicon nitride powders	0.6 µg/g					
Ca	422.7		0.15 µg/g	n.a.	700/2900	none	Z-9000 (Hitachi)	41
Fe	248.3		2.5 µg/g					
As	193.7		3.2 µg/L	35 pg				
Cd	228.8	Non-potable water	0.03 µg/L	1.8 pg	650/2200	W + Rh (permanent)	SIMAA 6000 (Perkin-Elmer)	42
Pb	283.3		0.70 µg/L	43 pg				
Se	196.0		3.0 µg/L	68 pg				
Al	309.3	Aqueous slurry of ambient fine airborne particles	3.80 ng/m^3					
Cu	324.8		1.07 ng/m^3					
Fe	248.3		0.72 ng/m^3	n.a.	1150/2350	Pd + 5% H_2	SIMAA 6000 (Perkin-Elmer)	43
Mn	279.5		0.14 ng/m^3					
Cr	357.9		0.05 ng/m^3					
Se	196.6	Aqueous slurry of ambient fine airborne particles	0.02 ng/m^3					
As	193.7		0.03 ng/m^3					
Pb	283.3		0.31 ng/m^3	n.a.	900/2250	Pd + 5% H_2	SIMAA 6000 (Perkin-Elmer)	43
Ni	232.0		0.18 ng/m^3					
Zn	213.9		7.15 ng/m^3					
Cd	228.8	Aqueous slurry of ambient fine airborne particles	0.04 ng/m^3	n.a.	1800/2400	none	SIMAA 6000 (Perkin-Elmer)	43
As	193.7	Tap water	1.4 µg/L	33 pg	1400/2200	Ru (permanent)	SIMAA 6000 (Perkin-Elmer)	44
Se	196.0		1.9 µg/L	39 pg				
Sb	217.6		1.5 µg/L	35 pg				
Pb	283.3		1.2 µg/L	32 pg				
Bi	223.1		2.6 µg/L	51 pg				
As	193.7	Honey	1 µg/L – 20 ng/g	21 pg	600/2300	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	45
Cd	228.8		0.04 µg/L – 0.8 ng/g	1.3 pg				
Cr	357.9		0.09 µg/L – 1.8 ng/g	4 pg				
Cu	324.8		0.3 µg/L – 5.3 ng/g	12 pg				
Pb	283.3		0.6 µg/L – 12 ng/g	33 pg				
Cd	228.8	Meat	0.13 µg/kg	0.5 pg	900/2000	Pd + Mg + Triton X-100	AAS 5 EA (Analytik Jena)	46
Pb	283.3		1.9 µg/kg	10 pg				
As	193.7	River water	0.14 µg/L		-/2300	none	SIMAA 6000 (Perkin-Elmer)	47
Se	196.0		0.12 µg/L	n.a.				
Sb	223.1		0.10 µg/L					
As	193.7	Wine	5.0 µg/L	24 pg	400 & 700/2200	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	48
Cd	228.8		0.03 µg/L	1.3 pg				
Cu	324.8		1.2 µg/L	13 pg				
Pb	283.3		0.8 µg/L	35 pg				
Ba	553.6	Fuel ethanol	0.6 µg/L	65 pg	1200/2400	none	SIMAA 6000 (Perkin-Elmer)	49
Cr	357.9		0.1 µg/L	3 pg				
Mo	313.3		0.2 µg/L	43 pg				
Cu	324.8	Fuel ethanol	0.6 µg/L	13 pg	1200/2200	W (permanent) + Pd + Mg	SIMAA 6000 (Perkin-Elmer)	49
Fe	248.3		1.8 µg/L	10 pg				
Ni	232		0.4 µg/L	50 pg				
Pb	283.3		0.6 µg/L	35 pg				
Cd	228.8	Whole blood	0.026 µg/L	1.26 pg	200 & 400/1900	W-Rh (permanent) + $NH_4H_2PO_4$	SIMAA 6000 (Perkin-Elmer)	50
Pb	283.3		0.65 µg/L	33 pg				
As	193.7	Cachaca	0.13 µg/L	30 pg	1200/2200	W (permanent) + Pd + Mg	SIMAA 6000 (Perkin-Elmer)	51
Cu	249.2		22 µg/L	274 pg				
Pb	283.3		0.05 µg/L	39 pg				
Cd	228.8	Blood	0.03 µg/L	0.9 pg	500/2100	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	52
Cu	324.8		0.075 µg/L	16 pg				
Se	196.0		0.3 µg/L	39 pg				
As	193.7	Cachaca	1.3 µg/L	32 pg	1200/2100	Ir (permanent) + Pd + Mg	SIMAA 6000 (Perkin-Elmer)	53
Cu	249.2		140 µg/L	95 pg				
Pb	283.3		0.90 µg/L	29 pg				

Cr	357.9	Cement	1.1 µg/g	124 pg	1400/2400	none	ZEEnit 60 (Analytik Jena)	54
Mn	279.5		1.9 µg/g	28 pg				
Cu	324.8	Nuts, seeds of cupuassu and coconut pulp	0.72 ng/g	n.a.	1200/2300	none	SIMAA 6000 (Perkin-Elmer)	55
Fe	248.3		1.40 ng/g					
Mn	279.5	Nuts, seeds of cupuassu and coconut pulp	0.66 ng/g	n.a.	1200/2300	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	55
Se	196.0		3.70 ng/g					
Cr	357.9	Alumina	0.11 µg/L - 66 ng/g	10 pg	1000 & 1300/2400	Nb (permanent) + NaF	SIMAA 6000 (Perkin-Elmer)	56
Mn	279.5		0.17 µg/L - 102 ng/g	13 pg				
Cr	357.9	Crude oil	0.07 µg/g	19 pg	1400/2500	Mg	SIMAA 6000 (Perkin-Elmer)	57
Fe	248.3		2.15 µg/g	31 pg				
Ni	232.0		1.25 µg/g	44 pg				
V	318.4		1.15 µg/g	149 pg				
As			0.11 µg/g	36.5 pg				
Cr		Sediments	0.022 µg/g	6.5 pg	300/2100	none	SIMAA 6000 (Perkin-Elmer)	58
Cu	n.a.		0.04 µg/g	28 pg				
Ni			0.2 µg/g	34 pg				
Pb			0.03 µg/g	46.5 pg				
Cd	n.a.	Sediments	0.001 µg/g	1.8 pg	300/1700	none	SIMAA 6000 (Perkin-Elmer)	58
Tl			0.003 µg/g	48 pg				
Bi	223.1	Aqueous solutions	0.82 µg/L	80 pg	1100/1900	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	59
Sb	217.6		0.57 µg/L	41.9 pg				
Se	196.0		0.86 µg/L	62.9 pg				
Bi	223.1	Aqueous solutions	1.50 µg/L	73.3 pg	1200/2000	Ir (permanent)	SIMAA 6000 (Perkin-Elmer)	59
Sb	217.6		1.13 µg/L	55 pg				
Se	196.0		0.75 µg/L	44 pg				
Ni	n.a.	Carrots, onions and potatoes	n.a.	n.a.	n.a.	none	SIMAA 6000 (Perkin-Elmer)	60
Cr								
Cu	n.a	Carrots, onions and potatoes	n.a	n.a	n.a	Pd	SIMAA 6000 (Perkin-Elmer)	60
As								
Cd	n.a.	Carrots, onions and potatoes	n.a.	n.a.	n.a.	Pd	SIMAA 6000 (Perkin-Elmer)	60
Pb								
Cu	249.2	Fuel ethanol	0.086 µg/L	18 pg	1200/2100	W (permanent) + Ir	SIMAA 6000 (Perkin-Elmer)	61
Pb	283.3		2.47 µg/L	36 pg				
Cr	357.9	Medicinal plants	0.04 µg/g	5.8 pg	1600/2300	none	SIMAA 6000 (Perkin-Elmer)	62
Ni	232.0		0.3 µg/g	31 pg				
Cu	324.8	Aqueous solutions	0.28 µg/L	20.5 pg	1100/2000	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	63
Mn	279.5		0.087 µg/L	5.1 pg				
Bi	223.1		1.4 µg/L	80 pg				
Sb	217.6		0.90 µg/L	44 pg				
Bi	223.1	Aqueous solutions	0.82 µg/L	80 pg	700/1900	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	64
Sb	217.6		0.75 µg/L	44 pg				
Cd	228.8		0.0085 µg/L	2.5 pg				
Bi	223.1	Aqueous solutions	1.0 µg/L	73.3 pg	700/2100	Ir (permanent)	SIMAA 6000 (Perkin-Elmer)	64
Sb	217.6		1.06 µg/L	51.8 pg				
Cd	228.8		0.0067 µg/L	1.96 pg				
Co	242.5	Crude oil, gasoline and diesel	0.32 µg/L – 0.02 µg/g	18 pg	200 & 1300/2250	Pd	SIMAA 6000 (Perkin-Elmer)	65
Cu	324.8		0.48 µg/L – 0.03 µg/g	15 pg				
Pb	283.3		0.64 µg/L – 0.04 µg/g	48 pg				
Se	196.0		1.76 µg/L – 0.11 µg/g	47 pg				
Pb	261.4	Atmospheric particulate matter (PM_{10})	5.4 µg/L – 5.5 ng/m^3	1500 pg	550/2100	Zr-Ir (permanent)	SIMAA 6000 (Perkin-Elmer)	66
Pb	283.3		0.69 µg/L – 0.29 ng/m^3	40 pg				
Cd	228.5		0.023 µg/L – 0.019 ng/m^3	1.2 pg				

As	193.7		0.12 µg/L – 0.14 ng/m^3	14.2 pg				
Ni	232.0		0.22 µg/L – 0.22 ng/m^3	15.9 pg				
Cd	228.8	Soil and sediment	0.14 µg/L – 1.4 pg	1.2 pg	600/2000	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	67
Pb	283.3		1.2 µg/L – 12 pg	25 pg				
Pb	247.6		1 µg/L	80.0 pg				
Cd	228.8	Seafood and fish feed	0.08 µg/L	2.8 pg	400/1900	Pd	SIMAA 6000 (Perkin-Elmer)	2
Cu	324.8		1.27 µg/L	19.6 pg				
As	193.7		6.5 µg/L	44.0 pg				
Pb	247.6	Seafood and fish feed	0.44 µg/L	35.2 pg	500/1500	Pd	SIMAA 6000 (Perkin-Elmer)	2
Cd	228.8		0.013 µg/L	1.9 pg				
Cu	324.8	Seafood and fish feed	1.4 µg/L	24.4 pg	1100/2000	Pd	SIMAA 6000 (Perkin-Elmer)	2
As	193.7		0.27 µg/L	41.9 pg				
Cd	n.a.	Canned tomato paste	0.05 µg/L – 2.0 ng/g	n.a.	500/1500	Pd	SIMAA 6000 (Perkin-Elmer)	68
Pb			0.48 µg/L – 19.2 ng/g					
As	n.a.	Canned tomato paste	0.84 µg/L – 33.6 ng/g	n.a.	800/2000	Pd	SIMAA 6000 (Perkin-Elmer)	68
Cu			1.5 µg/L – 60.0 ng/g					
Cr	n.a.	Canned tomato paste	0.51 µg/L – 20.4 ng/g	n.a.	1100/2300	none	SIMAA 6000 (Perkin-Elmer)	68
Ni			0.79 µg/L – 31.6 ng/g					
Fe	n.a.	Canned tomato paste	1.6 µg/L – 64.0 ng/g	n.a.	800/1900	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	68
Mn			0.43 µg/L – 17.2 ng/g					
Fe	248.3	Crude oil	0.54 µg/g	n.a.	200 & 1400/2500	Pd + Mg	SIMAA 6000 (Perkin-Elmer)	69
Ni	232.0		0.31 µg/g					
V	318.4		0.29 µg/g					
Pb	n.a.	Rice, wheat and tea	0.033 µg/L	n.a.	500/1700	none	n.a.	70
Cd			0.008 µg/L					

Characteristic masses ranged from 0.5 pg (Cd, meat)[46] to 1500 pg (Pb, atmospheric particulate matter)[66] and LODs from 0.15 ng/L (Co, seawater)[27] to 9.5 µg/L (As, soils and sediments).[33] As is mentioned in many of the reviewed studies (Table 1), the LODs were lower than the permissible limits proposed for foodstuffs and other matrices by the different official authorities, such as the European Commission and national legislations.

The selection of optimum instrumental conditions, such as pyrolysis and atomization temperatures, can be a hard task in a simultaneous multi-element analysis, since the final conditions should give good results for all analytes. Indeed, Psoma *et al.*[2] developed different methodologies for the determination of Pb, Cd, Cu and As in seafood and fish feed. The best conditions for the determination of all elements in one run were 400 °C and 1900 °C for pyrolysis and atomization, respectively. These values varied significantly when two elements were monitored in one run: 500/1500 for Pb and Cd and 1100/2000 for Cu and As. The temperature selection was depicted on LODs and, generally, lower values were obtained when two elements were monitored simultaneously.[2] Several studies applied a two-step pyrolysis to improve an analysis when elements with various thermal behaviors were investigated.[25,28,31,48,50,56,65,69] For instance, Luz *et al.* used an additional pyrolysis step for crude oil,[65] gasoline and diesel analysis to eliminate the micro-explosions into the graphite tube. This action resulted in more precise and accurate results. Furthermore, Ajtony *et al.* applied a two-step pyrolysis procedure to remove the dry,[48] residual constituents of the sample, which was necessary for the analysis of wine with a high sugar content. Another study used two pyrolysis temperatures for Cd and Pb determination in wine,[25] due to the produced amount of fume during the pyrolysis step and the accumulation of carbonaceous residue in the tube after several firings that all affected method performance.[25] Multiple pyrolysis and/or atomization steps can be used in an analysis to improve the figures of merit, remove matrix components and aid analytical performance, especially when elements with different thermal behaviors are determined simultaneously.

The universal chemical modifier of Pd + Mg was applied in

most studies, followed by Pd itself. In many cases, a permanent modifier was used because it also enhances the lifetime of the graphite tube (Table 1). The type and quantity of a modifier is usually tested in relation to pyrolysis and atomization temperatures; for the simultaneous multi-element analysis compromised conditions are adopted. For instance, the Pd + Mg modifier assisted with the determination of Se in serum, forming non-volatile solid solutions among Se and Pd and improving the interactions among Se and Pd by adding Mg, which resulted in the formation of smaller droplets and, hence, the production of sharper peaks.[31] A few studies used Pd with a special gas (5% H_2 in Ar) as the modifier for the determination of Al, As, Co, Cr, Cu, Fe, Mn, Mo and Ni.[26,40,43] This modifier minimized chloride interference, permitted the use of calibration curves with matrix-free aqueous standards and uniformly and efficiently facilitated the atomization of some elements.[26,40,43] The use of chemical modifiers is a common strategy, mainly for the thermal stabilization of the elements and, finally, for the improvement of the analytical characteristics of the method. However, the simultaneous determination of multiple elements is limited by the choice of chemical modifiers and the thermochemical behavior of different elements. Thus, the universal modifier was used in most of these studies (Table 1).

SIMULTANEOUS OR SEQUENTIAL MULTI-ELEMENT ANALYSIS BY HR-CS-GFAAS

Analytik Jena developed an instrument based on the work of Becker-Ross *et al.* equipped with a high-pressure Xenon short-arc lamp,[73,74] an optical system based on an echelle monochromator dispersing radiation in two steps and a linear CCD array as a detector.[16] A very important feature of this instrument is that it can perform simultaneous or sequential multi-element analysis (Tables 2 and 3).[75-125]

The HR-CS-GFAAS technique was mainly applied for the simultaneous or sequential multi-element analysis of foodstuffs,[82,87,109,123,125,92,93,99,102-104,106,108] environmental media,[79,82,111,112,117,122,85,86,90,94,96,100,108,110] crude oil[75-77] and biological specimens.[80,107] Twenty-eight elements were determined by this technique and Fe, Ni, Cd and Co were the most frequently examined. Simultaneous or sequential multi-element analysis was mainly based on the determination of two elements, with a few exceptions where three or four elements were studied (Tables 2 and 3). However, this technique does not use HCLs or EDLs (in comparison to LS-GFAAS) and, although there are no restrictions on the adjustment of the lamps, multi-element analysis was only performed for a few elements.

The simultaneous determination of two or more elements can be performed when the absorption lines of the analytes are within the spectral interval of the CCD. When the main lines are not found within the spectral window, alternative spectral lines can be used. However, this reduces the sensitivity and thus, higher LODs should be expected.[126] Many different spectral lines were used for Fe depending mainly on the co-determined elements. For instance, Fe was monitored at 283.245 nm when determined simultaneously with Co (283.443 nm), Ni (283.455 nm) and Pb (283.306 nm),[81] whereas at the 228.725 nm line when co-determined with Cd (228.802 nm) and Zn (228.668 nm).[87] In some cases, more than one wavelength was monitored for an element. Cobalt was determined by summing three different absorption lines (237.185 + 237.283 + 237.386 nm), which were found in the same spectral window. This action increased the method sensitivity and resulted in lower LODs.[88] Vanadium was monitored at both the 304.355 nm and the 304.494 nm line, which helped to extend the linear dynamic range and to estimate the concentration in high-content samples without the need to reprocess them after dilution or modification of the instrumental conditions.[90]

Sequential determination of many elements is performed from one sample injection, applying different temperatures and modifying the wavelength among the temperature cycles (if needed).[16] As an example, Cd and Fe were determined in cereal flakes using the lines presented in the same spectral window but with different atomization temperatures, since both elements differ significantly in their volatility and thus, the furnace program must reflect their thermal behavior.[123] However, in most of the reviewed studies, the spectral lines were not at the same spectral window and the main line of each element was used in order to achieve optimum results. Therefore, the temperature program varied, using different atomization temperatures and/or multiple pyrolysis steps (Tables 2 and 3).

The first studies for the simultaneous or sequential multi-element analysis by HR-CS-GFAAS were published in 2009 Dittert *et al.* simultaneously determined Cr and Fe in crude oil using direct analysis and in two other works,[75,108,109] Cd and Fe were sequentially determined using two different atomization temperatures within the same graphite furnace temperature program. Furthermore, a few studies combined both approaches.[86,95,105,116,127] For instance, Boschetti *et al.* determined Cd, Cr, Fe and Al (*via* AlH; molecular absorption spectrometry) in soil samples.[86] Cadmium was determined first at 228.802 nm, using 800 °C and 1700 °C as the pyrolysis and atomization temperatures, respectively. Then, Cr (425.433 nm), Fe (425.076 nm) and Al (425.315 nm) were determined simultaneously from the same aliquot using 2600 °C as the atomization (Cr and Fe) or vaporization (AlH) temperature.

The characteristic masses varied from 0.086 pg (Ni, solar-grade and electronic-grade silicon)[91] to 400 ng (Co, carbon nanotubes)[81] and the LODs from 0.5 ng/L (Cd and Zn, water samples) to 3.8 mg/L (Ba, nuts).[106,112,117] The obtained figures of merit correlate strongly to whether or not chemical modifiers are used. Many

Table 2. Simultaneous Multi-element Analysis by HR-CS-GFAAS – A Literature Review from the Beginning to 2020

Analyte	Wavelength (nm)	Matrix	Limit of detection	Characteristic mass (m_0)	$T_{pyr.}/T_{atom.}$ (°C)	Modifier	Instrumentation (Analytik Jena)	Ref.
Cr	358.120	Crude oil	1 µg/kg	3.6 pg	1400/2500	none	AAS 6 Vario	[75]
Fe	357.868		0.6 mg/kg	0.5 ng				
Co	240.725	Crude oil	8 µg/kg	7.2 pg	1300/2650	Pd + Triton X-100	AAS 6 Vario	[76]
V	240.674		1.2 mg/kg	2.1 ng				
Ni	305.432	Crude oil	1 mg/kg	320 pg	1000/2650	Pd	AAS 6 Vario	[77]
V	305.633		0.3 mg/kg	85 pg				
Co	352.685	NIST SRM 1566a oyster tissue	n.a.	n.a.	1000/2500	Pd	ContrAA 700	[78]
Fe	352.604/352.617							
Ni	352.454							
Cd	228.802	BCR CRM 679 white cabbage	n.a.	n.a.	800/2300	Pd	ContrAA 700	[78]
Ni	228.998							
Ni	232.003	Plants and lichens	25 µg/kg	16 pg	1200/2600	none	ContrAA 700	[79]
Fe	232.036		0.40 mg/kg	0.18 ng				
Mo	319.397	Dried urine spot	1.5 µg/L	1.6 pg	350 & 1400/2650	Pt	ContrAA 700	[80]
Ti	319.200		6.5µg/L	6.6 pg				
Co	283.443	Carbon nanotubes	86 ng	400 ng	800/2500	Pd	ContrAA 700	[81]
Fe	283.245		6 ng	18 ng				
Ni	283.455		65 ng	66 ng				
Pb	283.306		0.023 ng	0.017 ng				
Mo	313.259	Wine	0.05 µg/L	8.3 pg	1200/2650	$NH_4H_2PO_4$	ContrAA 700	[82]
Ni	313.410		0.81 µg/L	189 pg				
Mo	313.259	Soil	0.04 mg/kg	7.0 pg	1200/2650	$NH_4H_2PO_4$	ContrAA 700	[82]
Ni	313.410		0.60 mg/kg	136 pg				
Pt	244.006	Automobile catalyst	8.3 µg/g	0.32 ng	200 & 1800/2600	$NH_4F•HF$	ContrAA 700	[83]
Rh	244.034		9.3 µg/g	0.30 ng				
Pd	360.955	Active pharmaceutical ingredients	0.08 µg/g	0.18 ng	1400/2600	none	ContrAA 700	[83]
Rh	361.247		0.10 µg/g	0.68 ng				
Pt	244.006	Active pharmaceutical ingredients	0.15 µg/g	0.32 ng	1400/2600	none	ContrAA 700	[83]
Rh	244.034		0.10 µg/g	0.30 ng				
Co	231.136	Vitamin B12	1.21 µg/L	n.a.	1100/2500	none	ContrAA 700	[84]
Ni	231.096		0.39 µg/L					
Mo	313.259	Plant materials	0.018 ng	0.12 ng	1600/2600	Mg	ContrAA 700	[85]
Ni	313.410		0.025 ng	0.017 ng				
Cr	425.433	Soil	0.13 ng/mg	27 pg	1700/2600	H_2SO_4	ContrAA 700	[86]
Fe	425.076		0.07 µg/mg	0.09 µg				
Al	425.315		0.42 µg/mg	0.18 µg				
Cd	228.802	Canned foods	0.04 µg/L	1.0 pg	700/2550	Pd + Mg	ContrAA 700	[87]
Fe	228.725		0.04 µg/L	0.9 ng				
Zn	228.668		0.06 µg/L	1.1 ng				
Al	237.312	NCS ZC73013 spinach, NCS	14.0 µg/L	n.a.	800/2100	none	ContrAA 700	[88]
Fe	237.362		16.0 µg/L					

Co	237.185+237.283+237.386	ZC73016 chicken and SRM 1643e, water	12.0 μg/L					
Fe	232.036	Fluoropolymers	221 ng/g	370 pg	800 & 800/2300	5% H_2	ContrAA 700	89
Ni	232.003		9.6 ng/g	7.7 pg				
Co	304.400	Soil	0.044 ng	0.093 ng	1500/2650	NH_4F	ContrAA 700	90
V	304.355/304.494		0.43/0.64 ng	0.43/0.64 ng				
Ni	305.760	Solar-grade and electronic-grade silicon	5.71 mg/kg	0.086 pg	1300/2650	none	ContrAA 700	91
Fe	305.909		1.14 mg/kg	0.54 pg				
Ni	232.003	Bell pepper, tomato, potato, eggplant, physalis and red pepper	0.02 μg/g	95 pg	1400/2500	none	ContrAA 700	92
Fe	232.036		2 μg/g	340 pg				
Cu	217.894	Corn flour, wheat flour and white bean flour	0.03 mg/kg	14 pg	1400/2400	none	ContrAA 700	93
Fe	217.812		0.11 mg/kg	77 pg				
Rh	343.489	River water, road runoff and municipal sewage	1.0 μg/L	12.9 pg	1200/2600	NH_4F•HF	ContrAA 700	94
Ru	343.674		1.9 μg/L	71.7 pg				
Cu	216.509	Ethanol fuels	2.84 μg/kg	n.a.	1100/2400	none	ContrAA 700	95
Fe	216.455		3.06 μg/kg					
In	303.935	Soil and sediment	0.01 mg/L	n.a.	350 & 1200/2600	Pd + Mg	ContrAA 700	96
Ni	303.793		0.26 mg/L					
V	294.2357	Fuel fly ash	24.13 ng	n.a.	1350/2650	Ir (permanent)	ContrAA 700	97
Ni	294.3912		1.20 ng					
Fe	294.2357		9.0 pg					
Ni	352.454	Multimineral and multivitamin supplements	0.517 μg/g	26.64 pg	1000/2700	none	ContrAA 700	98
Fe	352.604		0.011 μg/g	1597 pg				
Fe	232.036	Vegetable oils	0.02 μg/g	n.a.	350 & 1200/2600	none	ContrAA 700	99
Ni	232.195		0.05 μg/g					
Co	344.364	Wastewater	0.015 mg/L	n.a.	1000/2000	none	ContrAA 700	100
Fe	344.388		0.052 mg/L					
Ni	344.626		0081 mg/L					
K	344.641		0.191 mg/L					
Co	352.685	Petroleum asphalt cement	0.001 mg/L	0.096 ng	700/2400	none	ContrAA 700	101
Fe	352.604		0.006mg/L	2.372 ng				
Ni	352.454		0.009 mg/L	0.205 ng				
Fe	352.604	Guarana	1.004 μg/g	1597 pg	1000/2700	none	ContrAA 700	102
Ni	352.454		0.022 μg/g	26.64 pg				
Fe	252.7435	Beer	2.0 μg/L	n.a	1000/2600	Pd + Mg	ContrAA 700	103
Si	252.8508		0.08 mg/L					
Cr	357.869	Powdered milk	8 ng/g	13 pg	350 & 1000/2500	Al	ContrAA 700	104
Fe	358.120		5 μg/g	1.5 ng				
Cu	216.509	Margarine	0.52 ng/g	n.a.	1100/2400	Pd + Mg	ContrAA 700	105
Fe	216.455		224 ng/g					
Ba	352.497	Nuts	3.819 mg/L	20.98 ng	1000/2700	none		106

Co	352.685		2.274 µg/L	0.078 ng				
Fe	352.604		0.095 mg/L	2.566 ng			ContrAA 700	
Ni	352.454		2.138 µg/L	0.050 ng				
Fe	307.572	Blood	n.a.	n.a.	1600/2400	W (permanent)	ContrAA 700	[107]
Zn	307.589				900/2400			

Table 3. Sequential Multi-element Analysis by HR-CS-GFAAS – A Literature Review from the Beginning to 2020

Analyte	Wavelength (nm)	Matrix	Limit of detection	Characteristic mass (m_0)	$T_{pyr.}/T_{atom.}$ (°C)	Modifier	Instrumentation (Analytik Jena)	Ref.
Cd	228.802	Beans	2.0 µg/kg	0.7 pg	700/1700	W-Ir (permanent)	AAS 6 Vario	[108]
Fe	228.726		4.5 mg/kg	1.0 ng	700/2600			
Cd	228.802	Soil	14 µg/kg	0.7 pg	700/1700	W-Ir (permanent)	AAS 6 Vario	[108]
Fe	228.726		170 mg/kg	2.0 ng	700/2600			
Cd	228.802	Grain products	0.6 µg/kg	0.9 pg	700/1700	W-Ir (permanent)	AAS 6 Vario	[109]
Fe	228.726		0.5 mg/kg	1.2 ng	700/2600			
Cd	228.802	Sewage sludge	0.03 mg/kg	0.99 pg	-/1300	Pd	AAS 6 Vario	[110]
Fe	228.725		90 mg/kg	1.6 ng	-/2300			
Cd	228.802	BCR CRM 679 white cabbage	n.a.	n.a.	700/1300	Pd	ContrAA 700	[78]
Ni	234.554				1300/2500			
Cd	228.802	Biomass and biomass ashes	1.1 µg/kg	0.4 pg	400/1500	none	ContrAA 700	[111]
Cr	357.869/428.972		21/90 µg/kg	2.5/72 pg	400/2600			
Fe	248.327	Seawater, lake water, mine water and tap water	4 ng/L	n.a.	300 & 1100/2000	Mg	ContrAA 700	[112]
Zn	213.857		0.5 ng/L		300 & 400/1300	Pd + Mg		
Mo	313.259	Certified reference materials	25 pg	7 pg	510 & 1200/2650	none	ContrAA 700	[113]
V	318.398		130 pg	18 pg	510 & 1100/2600			
Cd	228.802	Tannins	0.5 µg/kg	0.3pg	400/1500	none	ContrAA 700	[114]
Cr	357.869		17 µg/kg	2.2 pg	1500/2500			
Mn	279.4817	Vegetable oil and biodiesel	1.34 ng/g	n.a.	350 & 1300/1900	Mg	ContrAA 700	[115]
Cr	357.8687		1.07 ng/g		350 & 1300/2500			
Cd	228.802	Soil	7.3 pg/mg	3.9 pg	800/1700	H_2SO_4	ContrAA 700	[86]
Cr	425.433		0.13 ng/mg	27 pg	1700/2600			
Fe	425.076		0.07 µg/mg	0.09 µg	1700/2600			
Al	425.315		0.42 µg/mg	0.18 µg	1700/2600			
Mn	403.076	Powdered stimulant plants	0.005 µg/g	n.a.	1000/2500	none	ContrAA 700	[116]
Ni	231.096		0.002 µg/g		1000/2600			
Rb	420.018		0.1 µg/g		1000/2500			
Sr	407.771		0.01 µg/g		1000/2600			
Cd	228.8018	Seawater, lake water, river water, stream water, mine water and tap water	0.5 ng/L	n.a.	350 & 600/1700	Pd + Mg	ContrAA 700	[117]
Pb	283.306		10 ng/L		350 & 800/1800			

Cd	228.8018	Seawater, lake water, mine water, tap water	0.001 µg/L	n.a.	350 & 600/1300	Pd + Mg	ContrAA 700	[118]
Pb	283.306		0.03 µg/L		350 & 800/1500			
Li	610.353	Scintillator materials (ox orthosilicate)	20 µg/g	n.a.	350 & 800/2400	none	ContrAA 700	[119]
Na	285.3013		80 µg/g					
Li	323.2657	Scintillator materials (krill)	20 µg/g	n.a.	800/2400	none	ContrAA 700	[119]
Na	268.034		80 µg/g					
Cd	228.802	Organic pharmaceutical formulations	4 ng/g	1.6 pg	800/1400	Pd + Mg	ContrAA 700	[120]
Pb	217.001		49 ng/g	12.4 pg	1400/2000			
Cd	228.802	Yerba mate	2.5 ng/g	0.37 pg	450/1500	none	ContrAA 700	[121]
Cr	357.869		7.2 ng/g	2.4 pg	1500/2500			
Pb	217.0005	Ethanol fuels	0.94 µg/kg	n.a.	850/1400	none	ContrAA 700	[95]
Cu	216.509		3.06 µg/kg		1100/2400			
Fe	216.455		136 µg/kg		1100/2400			
Ga	287.424	Soil, seawater, river water and mine water	0.02 µg/L	n.a.	350 & 1100/2400	Pd + Mg	ContrAA 700	[122]
In	303.935		0.01 µg/L		350 & 1000/2300			
Tl	276.786		0.04 µg/L		350 & 900/2000			
Cd	228.802	Cereal flakes	2 µg/kg	n.a.	350 & 700/1250	Pd + Mg	ContrAA 800 G	[123]
Fe	228.725		1.41.4 mg/kg		350 & 700/2325			
Cd	228.802	Margarines	0.03 ng/g	n.a.	850/1400	Pd + Mg	ContrAA 700	[104]
Cu	216.509		0.52 ng/g		1100/2400			
Fe	216.455		224 ng/g		1100/2400			
Ag	328.068	Nanomaterials	0.1 µg/mL	n.a.	1000/1800	Pd + Mg	ContrAA 600	[124]
Au	242.795		0.2 µg/mL		1600/2200			
In	303.935		0.5 µg/mL		1200/2200			
Zn	213.857		0.03 µg/mL		900/1500			
Cd	228.802	Milk powder and infant formula	0.63 µg/kg	0.49 pg	350 & 900/1400	Pd	ContrAA 700	[125]
Cu	324.754		6.4 µg/kg	3.8 pg	1400/2200			

studies did not use a modifier and some applied the universal Pd + Mg. A simultaneous multi-element analysis is fundamental for establishing good results uniform for all elements, even if they present different characteristics. Therefore, it was probably ideal to use the universal chemical modifier or nothing at all, since a modifier should provide acceptable thermal conditions for all investigated elements.

COMPARISON OF MULTI-ELEMENT LS-GFAAS AND HR-CS-GFAAS TECHNIQUES

Simultaneous multi-element analysis by LS-GFAAS has been performed for over 30 years (first papers published in the 90s[128–133]), while simultaneous or sequential multi-element analysis by HR-CS-GFAAS started in 2009 (Fig. 1). Even though LS-GFAAS is older as a technique, more papers have been published on HR-CS-GFAAS within the last decade. Indeed, use of LS-GFAAS in the field of simultaneous multi-element analysis has reduced significantly in the last few years (Fig. 1). This is probably due to the fact that most studies were based on the SIMAA model which was discontinued, thus leading to some applications using LS-GFAAS.

Both techniques have shown their ability to perform simultaneous multi-element analysis. However, this feature is mainly limited to two elements. The maximum number of

Fig. 1 Number of publications reporting on the use of LS-GFAAS and HR-CS-GFAAS

elements that have been determined simultaneously is six with LS-GFAAS when using multi-element lamps and four elements with HR-CS-GFAAS. Furthermore, various matrices were analyzed with these techniques, such as foodstuffs, pharmaceuticals, biological specimens and environmental media, showing their wide range of application. Many elements were investigated by both techniques, including Al, Ba, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, Ni, Pb, Tl, V and Zn. However, As, Bi, Ca, Sb, Se and Sn were among the analytes proposed for the simultaneous determination with other analytes by LS-GFAAS, with no respective references to HR-CS-GFAAS. On the contrary, Ag, Au, Ga, K, Li, Na, Pd, Pt, Rb, Rh, Ru, Si, Sr ant Ti were only included in simultaneous or sequential determinations by HR-CS-GFAAS. Arsenic and Se are not usually determined by HR-CS-AAS, probably due to their short main wavelength. Indeed, the most sensitive lines for these elements are 193.696 nm and 196.026 nm, respectively. The same issue also appears for Bi, Te, Sb, and Ge with the main wavelengths below 260 nm. In this wavelength area, it is more frequent to find interferences that are spectral overlaps with diatomic molecules such as PO, CS, NO or SiO. Finally, more combinations of analytes are found with LS-GFAAS compared with HR-CS-GFAAS, probably because there is no need to select alternative spectral lines in LS-GFAAS, except for avoiding sample dilutions.

The achieved sensitivity of the LS-GFAAS and HR-CS-GFAAS techniques is subject to various parameters, such as the sample matrix, the selected instrumental conditions (*e.g.*, pyrolysis and atomization temperatures), the determined element in relation to other elements in a simultaneous multi-element analysis, the chosen wavelength, the use or not of a chemical modifier and the selection of the most appropriate modifier. The LS-GFAAS and HR-CS-GFAAS techniques estimated very low characteristic masses equal to 0.5 and 0.3 pg for Cd, 18 and 7.2 pg for Co, 3 and 2.2 pg for Cr, 13 and 3.8 pg for Cu, 21 and 1.6 pg for Mo, 16 and 8 pg for Ni, 10 and 6 pg for Pb and 60 and 18 pg for V, respectively. The lowest characteristic masses among the studied techniques were similar, with lower values obtained by HR-CS-GFAAS and no major differences for most of the analytes were detected.

A direct comparison of the sensitivity among the two techniques cannot be performed, since the published works used different matrices and the same elements were not always monitored. However, a more critical analysis of the results showed that Fe, V, Co, Ni and Cr were determined by both techniques in the same matrix (crude oil).[57,65,69,75-77] The LODs were 0.54-2.15 μg/g and 0.6 μg/g (Fe), 0.29-1.15 μg/g and 0.3-1.2 μg/g (V), 0.02 μg/g and 0.008 μg/g (Co), 1.25 μg/g and 1 μg/g (Ni) and 0.07 μg/g and 0.001 μg/g (Cr) for LC GFAAS and HR CS GFAAS, respectively. Furthermore, Cd and Pb were determined in various water samples[39,42,117,118] with LODs 20-30 ng/L (LS GFAAS) and 0.5-1 ng/L (HR CS GFAAS) for Cd and 700-750 ng/L (LS GFAAS) and 10-30 ng/L (HR CS GFAAS) for Pb. Analysis of soil, sediments and sludge was done for Cd, Cr, and Ni using both approaches.[33,58,67,82,86,108,110] The estimated characteristic masses were 1.2-1.8 pg (Cd), 5.5-6.5 pg (Cr) and 34 pg (Ni) for LS GFAAS and 0.7-3.9 pg (Cd), 27 pg (Cr) and 136 pg (Ni) for HR-CS-GFAAS.

Several studies investigated and compared the performance of LS-GFAAS and HR-CS-GFAAS instruments, carrying out the same analysis for both techniques. Resano *et al.* compared their performance for the direct determination of Hg in polymers,[134] using different reference materials with a wide range of Hg content. The main limitation of LS-GFAAS was that different atomization temperatures had to be used for the various types of plastics. HR-CS-GFAAS significantly improved this problem, since all materials were determined using the same conditions, and satisfactory results were obtained for all matrices applying aqueous standards for calibration. Finally, the latter technique presented a lower LOD, a broader dynamic range, good precision, better sensitivity, and high sample throughput, as well as a reduced risk of analyte loss and contamination.[134]

Vale *et al.* determined Ni directly in crude oil using both techniques.[135] It was found that the superior background correction capabilities of HR-CS-GFAAS and the low pyrolysis temperature (not higher than 400 °C), which cannot be achieved by conventional LS-GFAAS using deuterium background correction, was the only way to determine the total nickel content. Furthermore, HR-CS-GFAAS provides the option to monitor a second Ni line at 232.138 nm simultaneously which helped to determine high Ni concentrations (which would be out of the dynamic range of the main line of 232.003 nm), without performing sample dilution and re-injection. The figures of merit were also improved.[135]

Cobalt was determined in biological samples using both solid sampling and alkaline treatment. The optimum conditions concerning background correction were obtained only by HR-CS-GFAAS and LS-GFAAS, the background absorption was considerable. It was concluded that both instruments are

recommended, since the results obtained for certified reference materials were statistically insignificant. However, it was emphasized that a sample containing a high phosphate matrix and low Co content would suffer from over-correction issues and likely result in incorrect values by LS-GFAAS. Lower LODs and characteristic mass and a higher correlation coefficient were calculated using alkaline treatment with LS-GFAAS. To the contrary, better values were obtained using solid sampling with HR-CS-GFAAS.[136]

Quantification of Se in bean samples was investigated thoroughly using LS-GFAAS and HR-CS-GFAAS.[137] Comparing the LOD using different chemical modifiers, lower values were obtained by LS-GFAAS, but direct determination of Se at low concentrations (< 5 ng/g) in beans using both techniques was characterized by a notable degree of uncertainty. This was due to the presence of interferences at 196.026 nm originating from PO, NO, the Schumann-Runge absorption bands and the iron lines.[137]

Coco *et al.* developed an analytical method for the determination of Pb in incense sticks by solid sampling HR-CS-GFAAS.[138] Analysis of real samples was also performed by LS-GFAAS after acid digestion and both methodologies presented similar results. However, the use of solid sampling HR-CS-GFAAS is superior, since samples are injected directly without requiring conventional pretreatment, thus saving time, in addition to making this procedure environmentally friendly as no hazardous reagents are used.[138] Another study investigated spectral interferences on Pb determination in fertilizer and limestone samples. Interferences at 283.306 nm were completely corrected using least-squares background correction, but the most sensitive line of 217.001 nm presented interferences, which were not eliminated. LS-GFAAS with Zeeman-effect background correction was also employed obtaining similar results. Therefore, the latter technique is also able to correct the spectral interferences to a reasonable extent.[139]

INTERNAL STANDARDIZATION

The introduction of multi-element instrumentation enabled the use of internal standards (IS) for quantification by increasing the analytical potential of the LS-GFAAS and HR-CS-GFAAS systems. This strategy is capable of compensating for both random and systematic errors and for improving the precision and accuracy compared to other quantification methods (*e.g.*, method of addition). Several articles have been published concerning the application of internal standard (IS) for simultaneous multi-element analysis by LS-GFAAS[38,51,140-152] and HR-CS-GFAAS[78,80,85,153,154] (Table 4).

Table 4. Internal Standardization in Selected Studies

Analyte	Internal standard		Matrix	Ref.
	Evaluated	Adopted		
			LS GFAAS	
Cd, Pb	Ag, Bi, Tl	Ag	Whole blood	38
Cu, Pb	Bi	Bi	Beverage (cachaca)	51
As	Sb	Sb	Beverage (cachaca)	51
Pb	Bi	Bi	Wine	145
Cd	In	In	River water	146
Se	As	As	Sparkling drinking water	147
As, Se	Co, Sn	Co	Urine	148
Sb	As	As	Aqueous solution	149
Ni	Co	Co	Soft drinks	150
Se	As	As	Coconut water, coconut milk, soybean milk, cow milk, tomato juice, mango juice, grape juice and drinking water	151
Se	As, Ge	Ge	Milk	152
Pb	Bi	Bi	Vinegar	140
As, Se	Bi, Te	Te	Sediments	141
Pb	Bi	Bi	Household cleaning solutions, colored sugars, hard candies, mouthwash, fruit juices, energy drink, tea drink, soft drinks, beer, vodka, sugar-cane spirit, mineral water, vinegar, ethanol fuels, peanut, polyethylene terephthalate bottle, medicinal plants, liquid fertilizer, solid fertilizer, shampoo and milk	142
As	Se	Se	Particulate matter (PM_{10})	143
B	Ge	Ge	Shrimps	144
			HR CS GFAAS	
Ag	Ni	Ni	Aqueous standard solutions	78
Ni	Co	Co	Aqueous standard solutions, urine and blood	78
Mo, Ti	Co	none	Urine	80
Mo, Ni	Co	Co (only for Ni)	Plant materials	85
Cu	Au, Cr, Fe, Os, Na, Rh	Cr, Fe and/or Rh	Alcoholic beverages	153
Pb	Tl	Tl	Automotive gasoline	154
Ni	Sb	Sb	Automotive gasoline	154

An element is considered an ideal IS when specific requirements are fulfilled such as: The IS does not occur in the matrix at significant concentration levels; it is capable of performing simultaneous measurements with the analyte; it presents physicochemical properties as similar as possible to those of the analyte; and the signals of both the analyte and the IS are found within the dynamic range. A potential IS and the investigated analyte should have similar kinetic properties and analogous thermodynamic and thermochemical behavior. Thus, it is expected that they have similar pyrolysis and atomization temperatures, melting and boiling points, vaporization and dissociation heat for their oxides and chlorides and activation energy for atomization of the element. Furthermore, the atomic line of IS in HR-CS-GFAAS must be located near the selected line of the analyte. Finally, the IS concentration should be chosen appropriately, providing integrated absorbance equal to the integrated absorbance of the analyte in the centroid of the dynamic range.[85,126,141,143,144]

The IS quantification method has been used for different matrices, such as foodstuffs and environmental and biological samples (Table 4). It was proved that As can be used as IS for the quantification of Se and Sb in various samples.[147,149,151] Accordingly, Se was found to be a good IS for the determination of As.[143] However, a study investigated both As and Ge for Se determination in milk samples and concluded that the use of Ge enhanced the analytical performance of the method compared to As, and the results of standard reference materials analysis were in agreement with the certified values.[152] Germanium was also used for the determination of B in shrimp samples, which helped to decrease the matrix effect and obtain better recoveries.[144] Bismuth has been successfully used for the determination of Pb and Cu in several different samples, since it was able to minimize the matrix effects and the absorbance variations due to the changes in the experimental conditions.[51,140,142,145] Moreover, Bi improved the analytical method performance and allowed the correction of random errors during some procedures (*e.g.*, sampling and heating processes). Further, its combination with W, as a chemical modifier, did not require matrix-matched calibration.[51] Even though Bi presents similar thermochemical and physicochemical parameters to Cd and Pb, the use of Ag was finally considered the most appropriate IS for whole blood analysis, since better results were obtained.[38] Another study investigated both Bi and Te as IS for As and Se determination in sediments and concluded that the thermal stability of Bi was adversely affected due to the matrix; it also showed less repeatable aptitude for the different modifiers. Tellurium did not present these limitations and thus was finally selected.[141] Furthermore, Co has been adopted as a suitable IS for the determination of As, Se and Ni.[78,85,148,150] Cobalt was effective as IS to reduce sampling issues associated with the presence of gaseous bubbles in soft drinks which could alter the sample volume in the autosampler pipette, leading to analytical problems.[150] However, the application of Co as IS for the determination of Mo and Ti was rejected, since it gave poor repeatability results, increasing the uncertainty of the measurement. Cobalt is more volatile than Mo and Ti and thus, no good correlation among the sources of noise of Co and the investigated elements was detected.[80]

The studies highlighted that the use of IS helps to improve the analytical figures of merit compared to other quantification methods without IS, since matrix effects are minimized, better linearity is achieved (higher correlation coefficient), reproducibility is improved by decreasing the % relative standard deviation, higher accuracy is reached, LODs are reduced and better results for certified reference materials are obtained.[38,51,148-152,80,140-145,147] Likewise, it has been demonstrated that the lifetime of the graphite tube is increased by the internal standardization method.[141,145,147] It was also proved that the use of IS is beneficial for heterogeneous samples (samples containing gaseous bubbles, organic matter, fat and/or dissolved solids) since it is able to correct sampling errors.[147,150,151]

CONCLUSIONS

Graphite furnace atomic absorption spectrometry is a widely used analytical technique for the determination of elements in various matrices. Two different approaches were investigated for the simultaneous or sequential multi-element analysis by GFAAS, namely LS-GFAAS and HR-CS-GFAAS. Both techniques have shown the potential to determine many elements in samples with different physicochemical properties at low concentration levels with high accuracy and precision. Furthermore, they have shown their extensive field of application, since they have been applied for matrices such as foodstuffs, pharmaceuticals, biological specimens, nanomaterials, polymers, fuels and environmental media (*e.g.*, water and soil). LS-GFAAS was used to determine more elements simultaneously compared to HR-CS-GFAAS and most studies were limited to the determination of two elements. This is the main limitation of both techniques, which has been superseded by the development of the inductively coupled plasma technique for the truly simultaneous determination of many elements. Analytes with short wavelengths (*e.g.*, As and Se) were monitored mainly by LS-GFAAS, due to the presence of many interferences in this spectral area that could be problematic for HR-CS-GFAAS. Furthermore, more combinations of analytes can be determined with LS-GFAAS compared to HR-CS-GFAAS, since there is no need to select alternative spectral lines.

It was demonstrated that HR-CS-GFAAS presented improved analytical performance, as lower LODs and characteristic masses were calculated. Additional advantages include solid and slurry sampling application, one source for all elements, monitoring of many wavelength of an element to extend the dynamic range, ability to perform sequential analysis, recording the complete environment of an analytical line, thus allowing for simultaneous

background correction. Finally, it was proven that the internal standardization method is beneficial for both techniques since it can improve the analytical figures of merit, increase the lifetime of the graphite tube and correct sampling errors that come from heterogeneous samples. Simultaneous or sequential multi-element analysis by GFAAS will continue to be used for various matrices and HR-CS-GFAAS will be the main representative, as can be seen by the number of publications recently published. However, more work needs to be done by companies and researchers to develop a truly simultaneous HR-CS-GFAAS instrument before the analysis of many elements in onerun can become a reality.

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Notes

The authors declare no competing financial interest.

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