Simultaneous determination of lead, nickel, tin and copper in aluminium-base alloys using slurry sampling by electrical discharge and multielement ETAAS

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Abstract

The simultaneous multielement determination of Pb, Sn, Ni and Cu in aluminium alloys by electrothermal atomic absorption spectrometry (ETAAS) was performed by a quick method using slurry sampling. The metallic colloidal slurries were obtained by an electrical discharge operated in liquid medium. In this work, the effects of aluminium were evaluated and the results show that it causes a strong retention of Pb, Ni and Cu at low pyrolysis temperatures which is overcome by employing high pyrolysis temperatures. Aluminium also significantly improves the thermal stabilisation of Pb and Sn, it being possible to reach pyrolysis temperatures of 1100 and 1300 °C, respectively. Such stabilisation indicates that the performance of aluminium as a matrix modifier for Pb is better than that obtained using phosphate and magnesium nitrate without substantial changes of the figures of merit. The effects of aluminium on the atomisation characteristics of the elements and those coming from the simultaneous multielement determination on the figures of merit of the elements are also discussed. In this work, a calibration procedure involving a matrix matching method with aqueous aluminium standards is proposed as a simple and efficient way to solve the inconveniences originated by the aluminium matrix. The proposed method was applied to the simultaneous multielement determination of several aluminium-base alloy standards giving results well within the recommended values.
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1. Introduction

Trace element determination plays a significant role in the preparation of alloys since many elements can be added as microcomponents to bring particular characteristics to the alloys. For instance, lead and bismuth added to aluminium

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alloys improve their machineability. However, lead is also one of the elements that affects significantly the machinery properties of high temperature alloys [1]. Electrothermal atomic absorption spectrometry (ETAAS) is an appropriate technique to determine such microcomponents in alloys due to its low detection limits despite the time used to dissolve the sample and chloride interference found in the determination of some elements [2–4]. The latter is unfortunate because many metals and alloys are readily dissolved by hydrochloric acid. Analytical methods based on solid sampling techniques (SS) make it possible to leave out the dissolving step and decrease some problems associated with the dissolution procedures, such as incomplete dissolution, loss of some analytes during the heating and contamination of the samples and blanks [5]. However, those methods involving the direct introduction of solid materials in the atomiser by cups, boats or platforms require a set of well-characterised alloy standards for the calibration [6], and those are rarely available. Slurry sampling, combining advantages of SS and liquid solution, presents a better analytical performance in ETAAS [7,8]. Slurry sampling ETAAS has been extensively used for the analysis of a wide type of materials, such as biological samples [9–15], environmental samples [15–20] and inorganic samples [21–27]. Difficulties arising from the lack of homogeneity of the analyte distribution into the sample can be overcome by taking a greater amount of material for the slurry preparation. Up to now, different mills and size reduction methods have been applied to achieve efficient and reproducible volumetric sampling of slurries. However, slurry sampling of samples, as metallic samples are particularly difficult since mechanical methods typically employed to grind them are unable to produce a powder fine enough to be slurred. As Watters et al. mention [28], spark discharge has been employed since 1907 to generate sprays from conductive materials, and more recently, spark ablation has been recognised as a powerful technique to generate sprays from compact and electrically conductive materials. Human et al. [29] employed this technique for the direct analysis of metallic samples by flame atomic absorption spectrometry (FAAS) and fluorescence spectrometry (FAFS) as well as by inductively coupled plasma atomic optical emission spectroscopy (ICP-OES). Particles of different aluminium-alloys, brass and iron samples prepared by spark ablation characterised by Raeymaekers et al. [30], were mostly spherical in shape with a mean particle diameter between 1 and 2 μm. The composition of these particles matched well with the bulk composition. Ghiglione and Eljuri [31] were the first to report an electrical method to prepare dispersions of metals and alloys by electrical discharge operated in liquid medium. Using this novel method, the authors obtained, in 5 min, slurries that were very stables with a small particle size reaching almost the colloidal state. Their slurry preparing method produced excellent results when applied to Cr determination in steels by FAAS using calibration standards with a similar matrix. An improved design of such a grinding system [32] showed a better control of the distance between electrodes during the spark process. They found a reproducibility of 1% in the determination of Zn, Sn and Pb in bronze and brass, and Cu, Mg and Mn in aluminium alloys by FAAS. Latterly, the same authors determine Cr, Ni, Cu, and Mn in steel slurries, reporting an improvement of the stability of such slurries by adjusting the aqueous medium to pH 2 before the electro-sparking [33]. Eljuri et al. [34] applied this method for direct determination of Mo, Cr, and Mn in steels by ICP-OES by calibration with aqueous standards without internal standard obtaining good results. Pchelkin et al. [35] employing a similar method to prepare steel slurries with particle size less than 1 μm. They employed isopropanol instead of water to improve slurry stability. Differences between slopes of calibration curves obtained from aqueous standards and standards slurries by FAAS by these authors were suppressed employing ETAAS. In addition, they found no significant differences between results obtained for Si, Ni, Cr, Mn, Mo, V and W determination from digested and slurry samples of steel. L'Vov and Novichikhin [36] applied this procedure to determine Sn and Ni impurities in Ti by ETAAS with platform atomisation. Bendicho [37] studied the colloidal solution obtained by

electrical discharge using scanning electron microscopy, showing a particle size of 1 μm, and latterly employed this sampling method to determine Mn, Cr and Cu in electrolytic iron [38].

The aim of this study was to develop a method for copper, nickel, lead and tin determination in aluminium-base alloy samples by ETAAS, taking advantage of the excellent characteristics of the electrical discharge to produce slurries from metallic samples and the simultaneous multielement detection capability of instruments available nowadays. The performance of aluminium as matrix modifier was evaluated. The effects of some interferences involved with the multielement determination on the figures of merit of the elements were also studied.

2. Experimental

2.1. Apparatus

The electrospark system employed has been described by Eljuri [33]. It consists of a generator ''Varisource'' Jarrel Ash model 70-000 and a dispersor for preparing the metallic suspensions. The conditions employed in the preparation of the aluminium-base alloys slurries were: capacitance 0.0025 μF, inductance 40 μh, resistance 40–50 Ω, R.F, current 3–4 A, distance between electrodes 0.2 mm and time of discharge of 3 min.

The home-made disperser equipment employed to prepare the slurries by electrical discharge under water has been described elsewhere [33]. Particle size distribution of the slurries was determined using a Malvern, model Master Sizer and their stability was followed by a Shimadzu UV–Visible spectrophotometer.

Atomic absorption measurements were performed using a Perkin–Elmer SIMAA 6000 ETAAS system equipped with a background correction system based on the longitudinal Zeeman effect and a AS-72 Autosampler. The spectrometer was employed throughout in four-elements mode using hollow cathode lamps: single element Intensitron® for Ni (232.0 nm), multielement Lumina® for Sn (286.3 nm) and multielement Lumina® for Cu (324.8 nm), and electrodeless discharge lamp EDL

System 2 for Pb (283.3 nm). Standard Transversally Heated Graphite (THGA) tubes were employed.

2.2. Reagents and samples

Deionised water (18 MΩ) was used throughout. Nitric acid, Fisher Ultra Trace Analysis, was used to acidify the slurred samples and aqueous standards. Standard solutions of 1000 μg ml^{-1} of Al, Cu, Pb, Ni and Sn (BDH) were used to study the effects of aluminium and to matrix matching of the aqueous standards. Certified aluminium-base alloys (BSS 501, BSS 502, BSS 503 and BSS 506) from the British Bureau of Analysed Samples Standard were employed to verify the proposed method.

2.3. Procedures

Metallic slurries of the aluminium-base alloys were prepared by dispersion of the alloy samples using electrical discharge operated in water by a method described elsewhere [33]. The metallic slurries were acidified to 0.1% (v/v) HNO$_3$ to ensure their stabilisation. The slurries were manually stirred before to measure their stability and particle size distribution. The stability of the slurries was determined by monitoring the change in transmittance of the light through the slurries for 2 h. The particle size distributions were measured by light diffraction technique.

All the aqueous standard solutions were prepared under similar acid concentration to slurries. Volumes of the samples, standards and blank solutions were sequentially pipette by the auto sampler and mixed into the atomiser as needed. The total volume in the atomiser was always 20 μl.

3. Results and discussion

3.1. Characteristics of the slurries of aluminium-base alloys

Particle size of the slurries prepared by electrical discharge was measured by the light diffraction

technique. Laser diffraction technique is an exceptionally flexible sizing technique able to in principle to measure the size of any one material phase in another. It is an absolute technique. It does not required calibration or detailed knowledge of the physical properties of materials to be measured. It is precise, giving a high resolution size discrimination, up to 32 size bands displayed covering the range of 100:1 in size of any single range and highly repeatable as there are not fine dimensions or apertures clog. Beside that, over the particle size of 1 μm, the measurements are independent of the medium of suspension. The fundamental instrument measurement is one of volume and other all other outputs are numerical transformations assuming spherical particles.

The results, obtained by this technique for six replicates from different slurred alloys, showed that 50 and 90% of the particles had mean diameters smaller than 8.55 ± 1.22 and 37.72 ± 7.17 μm, respectively. The standard deviations (S.D.) of these results come basically from differences amongst samples to be slurred and the precision of the technique employed for the preparation of the slurries. Bendicho [38] reported a maximum size of approximately 1 μm for the particles of electrolytic iron slurries prepared by a similar method but applying an electrosparking time between 30 and 60 min. He carried out the measurement of particle size by scanning electron microscopy.

The stability of the metallic suspension depends on various factors, such as chemical composition, concentration of the solid suspended and dispersion medium. The range of concentration of the suspended solids in the slurries prepared by electrical discharge in this work was 20–165 μg ml^{-1}. The transmittance signal measured for the slurries by UV–Visible spectrometry showed a decrease of 2% after 1 h. This time is enough to perform the complete determination of the elements by simultaneous ETAAS. Slurries obtained by Bendicho [38] were more stable, probably because the particles he obtained were smaller and the solid suspended concentration in their slurries was no larger than 50 μg ml^{-1}.

3.2. Effects of the aluminium mass on the atomic signal and heating programme of Pb, Sn, Cu and Ni

Preliminary experiences carried out in our laboratory showed that the atomisation characteristics of lead in slurries of aluminium-base alloys differ from those in aqueous standards. Therefore, a study of the effects of the aluminium matrix on the atomic signal of lead was considered first. To achieve that, increasing amounts of aluminium were added to aqueous standards of Pb and atomised under different pyrolysis and atomisation temperatures. Likewise, a similar study was simultaneously performed for Sn, Ni and Cu. Pyrolysis and atomisation curves obtained for the elements are shown in Fig. 1a–d and Fig. 2a–d, respectively. The particular effects observed for each element are discussed next.

3.2.1. Lead

Fig. 1a shows how Pb is strongly retained by aluminium at low pyrolysis temperature (700 °C) and the integrated absorbance signal is lower than that observed when aluminium is not present. Such retention increases with the amount of aluminium added. However, employing higher pyrolysis temperature (1100 °C), the integrated absorbance signal is completely recovered regardless of the aluminium mass present. Additionally aluminium significantly improves the thermal stabilisation of lead, it being possible to reach pyrolysis temperatures of up to 1100 °C. In Fig. 2a as in the pyrolysis step, the aluminium added is observed to improve the atomic signal of lead regardless of the mass of aluminium added and the atomisation temperature, compared with that obtained for lead without aluminium. However, such improvement of the atomic signal decreases with the aluminium mass added (see Fig. 1a, Fig. 2a and Fig. 3). The atomisation profiles obtained for lead using 0, 2 and 4 μg of aluminium are shown in Fig. 3 and the integrated absorbance values obtained in each case were 0.0819, 0.0915 and 0.0866 s, respectively. The increase of the integrated absorbance using 2 μg respond to the improvement of the thermal stabilisation by low mass of aluminium. A remarkable delay in the appearance time, a broadening of the absorbance
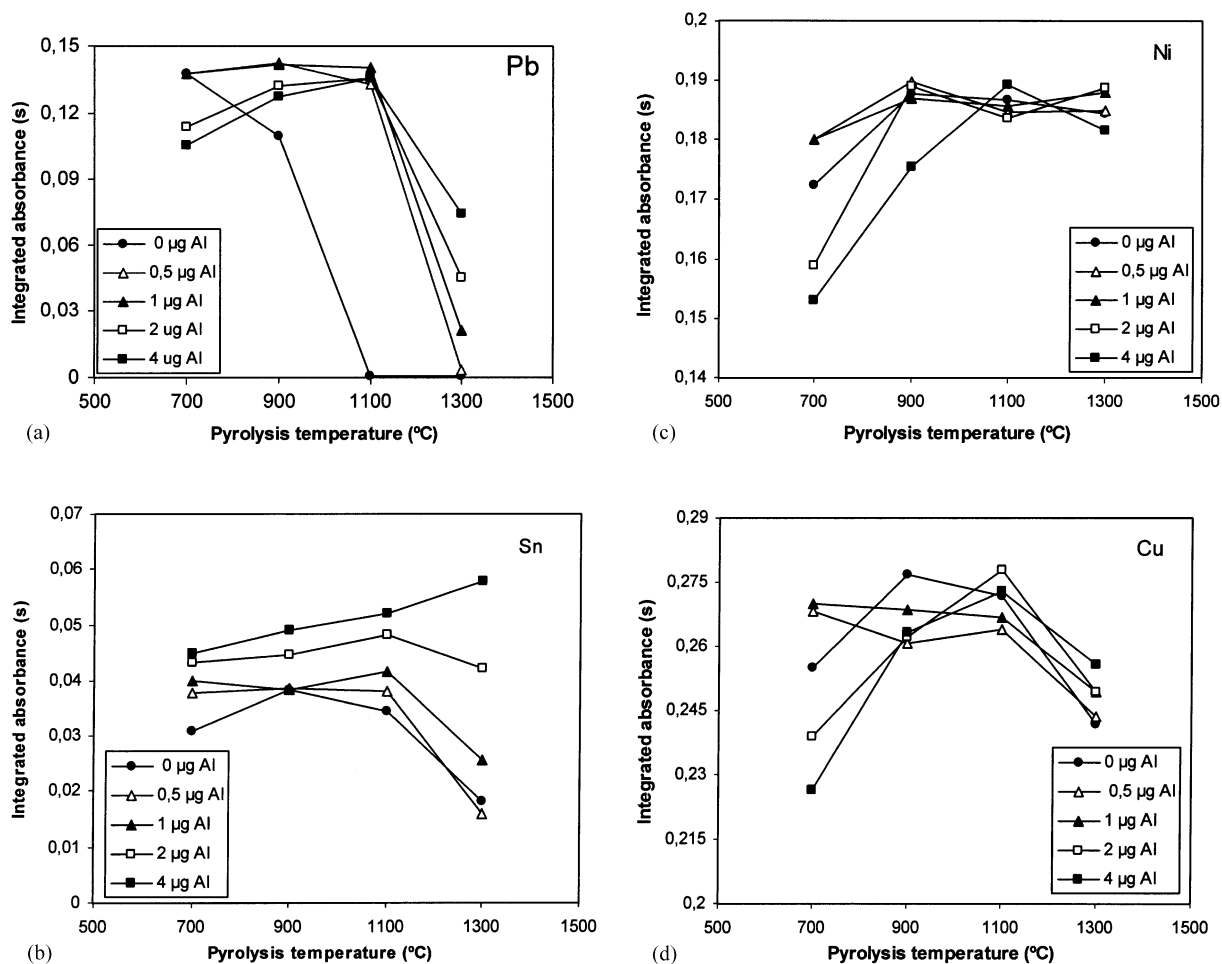
Fig. 1. Effect of aluminum mass on the pyrolysis of 1 ng of Pb, 2 ng of Sn, 1 ng of Ni and 1 ng of Cu. (T_{atom}: 2200 °C).

profile and important changes in the shape of the atomisation profile, all increasing with the aluminium mass added, were also observed for lead.

Electrothermal atomisation of lead in matrix with high contents of aluminium has been studied for some authors [21,36,39]. L'Vov and Novichikhin [36] determine Pb in aluminium slurries prepared by spark discharge in water, but they do not report any interference from aluminium. Karwoswska and Jackson [21] examined the atomisation characteristics of lead in slurred alumina matrices employing longitudinally heated tubes and a continuum background correction system. They found that a high temperature alumina matrix has no serious effect on the

atomisation of lead and the quantitative determination of the element is possible if a $PO_4 +$ $Mg(NO_3)_2$ matrix modifier is used. These authors also observed that lead is strongly retained by low-temperature alumina where, consequently, the atomisation appearance time is delayed. Hinds and Jackson [39] showed that Pb adsorption on slurred clays had a similar effect to the adsorption of the element on alumina in retarding analyte vaporisation. It is important to mention that AlO molecular band has been reported to produce spectral interferences and over correction over Pb in the 217.0 nm line but not in the 283.3 nm [40].

The thermal stabilisation of lead by aluminium ($T_{pyr} = 1100$ °C, $T_{at} = 2400$ °C) found in this work
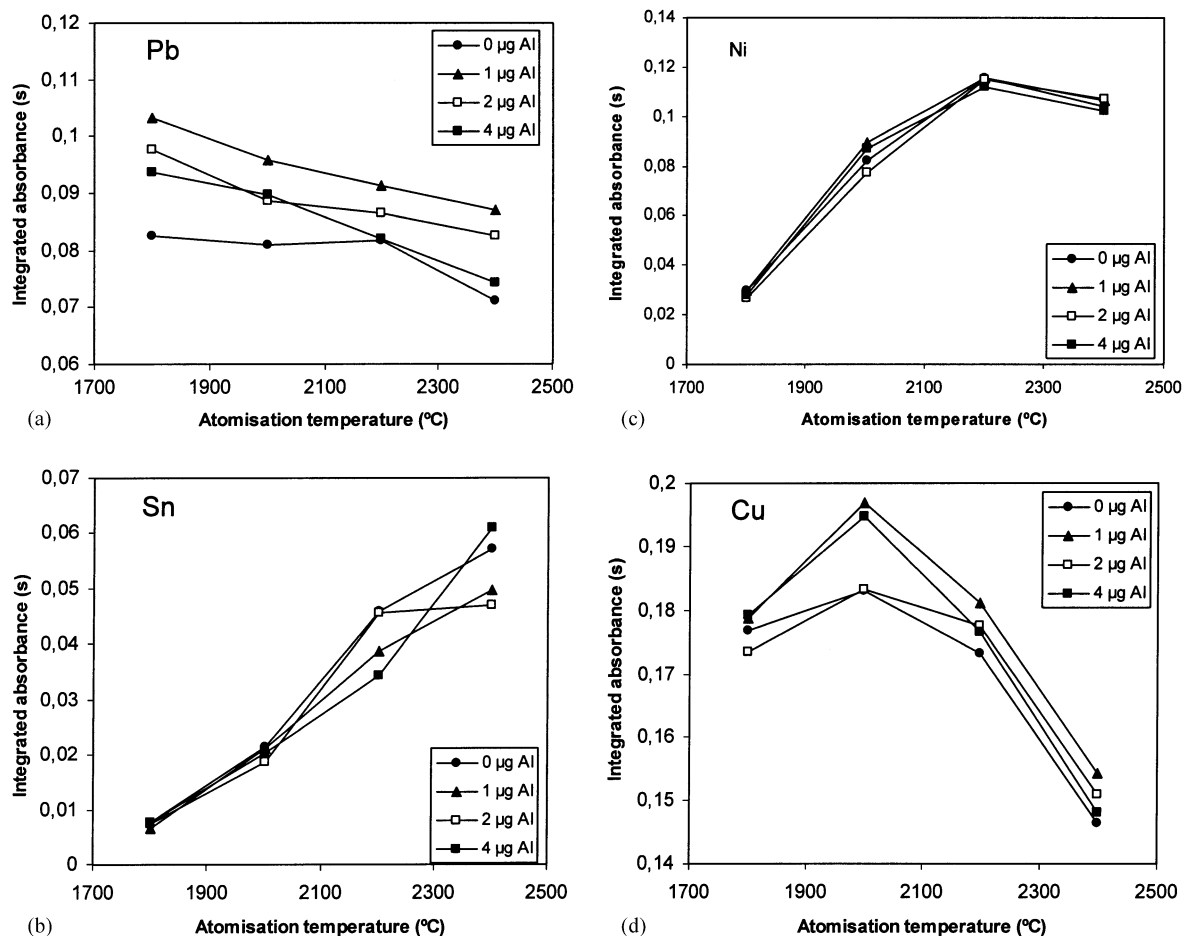
Fig. 2. Effects of aluminum mass on the atomisation of 1 ng of Pb, 2 ng of Sn, 1 ng of Ni and 1 ng of Cu. (T_{pyr}: 1100 °C).
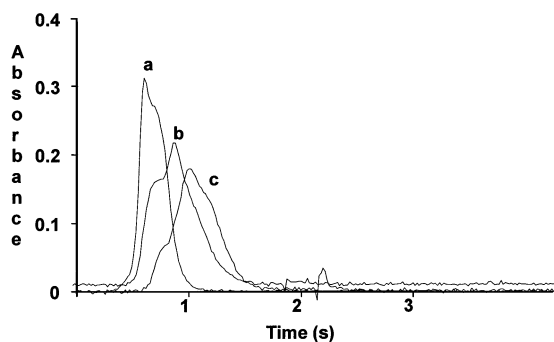

Fig. 3. Effect of aluminum mass on the absorbance profile of Pb: (a) 0 μg of Al, (b) 2 μg of Al and (c) 4 μg of Al (T_{pyr}: 900 °C and T_{atom}: 2200 °C).

is higher than that reported when using $PO_4 + Mg(NO_3)_2$ as a matrix modifier. Pyrolysis and atomisation temperatures recommended when $PO_4 + Mg(NO_3)_2$ are employed as matrix modifier (850 and 1600 °C, respectively) [41] could be insufficient to assure the complete release of lead from those matrixes where the element is strongly retained such as those with high aluminium contents. Likewise, it has been reported that the use of phosphate as a matrix modifier produces the over correction of the atomic signal of lead due to the presence of the molecular band of PO [42] when background correction systems based on Zeeman effect are applied. Pyrolysis temperatures

of 1000–1200 °C can be also achieved using Pd [43,44], but this matrix modifier causes a decrease of the integrated absorbance signal, which could be recovered increasing the atomisation temperature [45] but for elements as Cd and Pb lead to decrease their sensitivity [46,47].

Results shown in this work strongly indicate that aluminium added as aqueous standard causes important changes in the atomisation characteristics of lead similar to those previously observed for the element in the slurred samples of aluminium-base alloys, alumina [21] and clays [39]. Kinetics studies have indicated that these changes are caused by adsorption of Pb on the alumina particles [21]. Aluminium from aqueous solutions, as well as in the particles of the slurries of aluminium-base alloys, should be oxidised into the furnace to $Al_2O_{3(s)}$. We think that this oxide, stable up to 2100 K, covering the particles of the slurry and/or on the graphite surface of the atomiser, could work as the support where lead can be absorbed similarly as Karwowska and Jackson [21] reported with alumina and clay particles.

3.2.2. Tin

Tin showed a significant increase of the integrated absorbance signal and thermal stabilisation during the pyrolysis when adding aluminium amounts as those employed here (Fig. 1b). As a consequence, the pyrolysis temperature could be raised from 900 up to 1300 °C, depending on the aluminium mass employed. The aluminium mass added had no significant influence over the atomisation temperature (Fig. 2b), over the appearance time and atomisation profiles of the element.

3.2.3. Copper and nickel

The presence of aluminium seems not to affect the pyrolysis and atomisation temperatures and the integrated absorbance signal of neither of these elements. However, under low pyrolysis temperatures (700 °C), the integrated absorbance signal for both elements showed to be slightly increased by small amounts of aluminium (up to 1 μg) and decreased when adding higher aluminium mass (Fig. 1c and d). This indicates that, under low

pyrolysis temperatures and depending on the added mass, aluminium can improve the thermal stability of Ni and Cu, but it can also partially retain these elements. In both cases, the absorbance signal can be totally recovered employing higher pyrolysis temperatures.

Based on this study, the effects of the aluminium mass on the pyrolysis and atomisation steps of Pb, Sn, Ni and Cu were established and the results indicate that its presence modifies some of the atomisation characteristics of the elements. Pyrolysis and atomisation temperatures chosen for the simultaneous multielement determination of Pb, Sn, Ni and Cu in the presence of aluminium were 1100 and 2400 °C, respectively. These compromised conditions were selected in order to avoid retention and obtain the best thermal stabilisation observed with the aluminium. The complete temperature programme employed is shown in Table 1.

3.3. Standardisation and characteristic mass

Lead, tin, copper and nickel simultaneous multielement determination in the slurred aluminium-base alloys was achieved by a simple calibration procedure involving a matrix matching method of the aqueous standards with aluminium. The ranges of concentration of the calibration curves were 12.5–50.0 μg l^{-1} for Pb, Ni and Cu and 25.0–100.0 μg l^{-1} for Sn. The correlation coefficient (r^2) obtained for the calibration curves were higher than 0.996. The aluminium mass added to aqueous standards was almost the same as that present in 20 μl of the slurred aluminium-base alloys, i.e. 2 μg.

Four certified BSS aluminium-base alloys from the British Bureau of Analysed Samples Standard were analysed under the optimised temperature programme and the results obtained for Pb, Sn, Cu and Ni for three replicates of each sample, shown in Table 2, demonstrate no significant differences ($P = 0.05$) between the concentrations of the elements obtained in this work and the certified values for each sample of the aluminium-base alloys.

The experimental characteristic mass values (m_o) obtained are given in Table 3. m_o results

Table 1
Temperature programme for the simultaneous multielement determination of Pb, Ni, Sn and Cu in aluminium-base alloys by ETAAS

Step	Stage	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar Flow (ml min^{-1})
1	Dry	110	1	20	250
2	Dry	130	15	30	250
3	Pyrolysis	1100	10	20	250
4	Atomisation	2400	0	5	0[a]
5	Clean	2500	1	3	250

[a] Read (integrated peak area).

obtained in this work for the multielement determination of Pb using aluminium as modifier are comparable to the mean value from those reported employing Pd+Mg(NO$_3$)$_2$ [48,53–55], despite employing high pyrolysis temperatures which reaffirms the efficient performance of aluminium as a matrix modifier for Pb. Differences between particular m_o values obtained for Pb compared with some of those from literature mentioned appearing in Table 3 are also a result of differences in temperature programme and elements in the run.

In the case of Sn, high m_o values were obtained. We study the effect of the aluminium on the sensitivity of Sn and the results indicated that Al is not responsible for such decrease of the sensitivity as similar m_o values were obtained for Sn with and without aluminium (256 and 272 ρg, respectively). According to published data [49], tin converted to SnO$_{2(s)}$ during pyrolysis should be stable at pyrolysis temperatures employed in this work, since the atomisation of the SnO$_{2(s)}$ to Sn$_{(g)}$ is supposed to occur at 1400 K. In addition, losses of any volatile specie of Sn during the pyrolysis step should not be expected to be from samples free of chlorides as those employed in this work. Based in this information we should not expect any loss of Sn under the condition employed in our work for the decrease of sensitivity should have other reason. We think that the very narrow absorbance profiles (about a second) obtained for Sn in this work could lead to possible losses of atomic vapour by diffusion being this partially responsible for the low sensitivity observed for Sn. Other possible reason taken into account for the decrease of the sensitivity of Sn is discussed in the next section.

3.4. Simultaneous multielement determination

The advantages of the simultaneous multielement determination by ETAAS also have certain inconveniences such as the impoverishment of detection limits (DL) due to the decrease of up to 1/4 the normal light intensity has been indicated

Table 2
Simultaneous multielement determination of lead, nickel, tin and copper in BSS certified aluminium-base alloys by ETAAS using the proposed method

BSS alloys	Concentration[a] (% w/w)							
	Lead		Nickel		Tin		Copper	
	Found	Certified	Found	Certified	Found	Certified	Found	Certified
501	0.27±0.01	0.22±0.02	0.21±0.02	0.24±0.02	0.12±0.02	0.11±0.01	0.20±0.05	0.20±0.01
502	0.19±0.02	0.17±0.01	0.06±0.01	0.07±0.01	0.24±0.05	0.21±0.01	0.39±0.15	0.44±0.02
503	0.16±0.02	0.14±0.01	0.27±0.05	0.30±0.02	0.057±0.002	0.07±0.01	0.098±0.01	0.10±0.01
506	0.03±0.02	0.02±0.01	0.13±0.02	0.13±0.01	0.11±0.01	0.13±0.01	0.019±0.002	0.02±0.01

[a] The % w/w found values are the mean ±range ($P = 0.05$) obtained in this work for three replicates for each slurred sample. The % w/w certified values are the mean ±S.D. for the BSS samples from the British Bureau of Analysed Samples Standard.

Table 3

Characteristic mass values obtained in this work for the simultaneous multielement determination of Pb, Ni, Sn and Cu and other values reported in the literature employing THGA

Element	m_o (ρg)		
	Data obtained in this work	Data from literature	
	Multielement determination	Single element determination[a]	Multielement determination
Pb	43	30	60[b], 31[c], 48[d], 34[e]
Ni	26	20	22[d], 16.6[e], 28[f]
Sn	256	90	
Cu	22	17	20[b], 35[c], 22[d], 22[f], 14.7[e]

[a] Modifiers and temperatures of pyrolysis/atomisation in °C employed in each case: Pb: $PO_4 + Mg(NO_3)_2$ and 850/1600; Ni: no modifier and 1100/2300; Sn: $Pd + Mg(NO_3)_2$ and 1400/2200; Cu: $Pd + Mg(NO_3)_2$ and 1200/2000 [41].

[b] $Pd + Mg(NO_3)_2$ was employed as modifier; furnace program no specified [48].

[c] Fast program (no ashing step, no modifier); T_{atom}: 2300 °C [53].

[d] $Pd + Mg(NO_3)_2$ was employed as modifier; T_{pyr}/T_{atom} (°C): 350/2500 [54].

[e] $Pd + Mg(NO_3)_2$ was employed as modifier; T_{pyr}/T_{atom} (°C): 450/2500 [55].

[f] T_{pyr}/T_{atom} (°C): 250/2250 [52].

by the manufacturer of the SIMAA 6000 [48]. In addition to this, when several lamps are operated at the same time, there is a small but not negligible risk of emission line overlap within the spectral band pass of the polychromator [50]. When a spectral line overlap is possibly present, a timing for the modulation of the lamps is automatically set by the SIMAA 6000 software and a decrease of at least 1/8 the normal light intensity could lead to additional changes in the DL and m_o. Reports of these effects on the figures of merit of different elements are scarce since even though the first simultaneous multielement designs appeared a long time ago [51] and many approaches and commercial instrumentation has been developed, their use was not widely spread up to the end of the 1990s. Some of these works [52–55] present m_o and DL data obtained for some of the elements studied in this work using the same equipment (SIMAA 6000) but they do not present additional data on the effects of the additional modulation of the lamps on the figures of merit of the elements when an emission line overlap is present. Recent studies show that DL and m_o values of Pb and Ti from aqueous solutions are impoverished when these elements are simultaneously determined due to the spectral interference observed between them originating from the unusual optical system [56]. In that work, m_o values for the simultaneous

multielement determination of Pb and Ti were reported to decrease 60 and 25%, respectively, in comparison to those obtained separately for each element under the multielement mode.

For the lamps and elements combination in our work some spectral interferences occur at the same time: the Cu detector receives light from the Sn HCL lamp and Sn and Pb detectors receive light from the multielement Lumina® lamp employed for Cu due to Fe included in the multielement lamp. Therefore, timing of these lamps should be split when the determination is simultaneous multielement. The effect of such timing splitting on the DL and m_o of Sn, Pb and Ni was studied in this work in aqueous solutions and the results obtained for their single element determination and simultaneous multielement determination in the presence and absence of the interfering multielement lamp are shown in Table 4. In these experiences an Intensitron® single element HCL of Sn was employed. Cu was not included in this study as the m_o found for it was comparable to those reported. The results indicate that the determination under the simultaneous multielement mode without the interfering lamp leads to a deterioration of the LD of both elements but their sensitivities are not affected. However, the presence of the interfering lamp in the simultaneous multielement determination promotes a 30% im-

Table 4
Figures of merit obtained in this work for Sn, Pb and Ni under single element and simultaneous multielement determination and the effect of the presence of an emission line overlap (T_{pyr} 400 °C and T_{atm} 2400 °C)

Element	Single element determination		Simultaneous multielement determination (no emission line overlap)		Simultaneous multielement determination (presence of an emission line overlap)[a]	
	m_o (ρg)	DL (ρg)	m_o (ρg)	DL (ρg)	m_o (ρg)	DL (ρg)
Sn	295	75	306	206	396	1152
Pb	36	11	37	40	37[b]	19[b]
Ni	26	15	34	57	36	49

[a] Interfering line from Cu multielemental HCL.
[b] m_o and DL values reported for the simultaneous multielement determination of Pb in presence of the same emission line overlap were; 48 and 17 ρg, respectively; the T_{pyr} and T_{atom} employed were 350 and 2500 °C, respectively [54].

poverishment of the m_o and 5-fold on the LD for Sn. Figures of merit of Pb and Ni are not affected. Feuerstein and Schlemmer [54] reported the m_o and DL for the simultaneous multielement determination of Pb, Cu, Fe, Al and Ni in different samples and the m_o value obtained for lead is similar to that obtained in this work. Unfortunately, these authors did not study the effect of the emission line overlap produced by Fe source on the figures of merit of Pb.

Since the equipment modifies the time set of the lamps when it detects the presence of an interfering lamp an additional factor to be included is the brightness of the lamps involved. In our work, the single element Intensitron® and multielement Lumina® new HCLs of Sn employed in this work were much less bright than the lamps for the other elements. The timing splitting set by the presence of the interfering lamp provoked a deep decrease of their total counts below a 100 counts, which represented a decrease of about 9-fold the original counts of the source. In addition, the Sn HCL was also observed to be strongly affected by the additional modulation as the total counts of the lamp monitored under single element mode of determination during the study were significantly decreasing. The EDL lamp of Pb, brighter than the Sn HCLs, only experienced a change by 1/2 in its total counts by the presence of the interfering lamp, and surprisingly the total counts in that mode were higher than in absence of the interfering lamp. That is possibly the reason why the DL obtained for lead in the multielement mode of

determination in presence of the interfering lamp mode was better than without it.

These observations would indicate that the timing splitting affects the lamps and that some of the lamps suffer more than other by the timing splitting. In consequence, the effect of timing splitting on the figures of merit varies with the element and lamp. That seems to indicate that the magnitude of the effect studied basically depends on the brightness of the lamp to be modulated. That also would indicate that the low light intensity of the lamp of Sn and the deep decrease by the timing splitting are the origin of the low sensitivity obtained for the element Sn rather than possible losses by diffusion. Similar observation was found for Pb when it was simultaneously determined with Tl [56]. In that study counts for the Pb EDL and HCLs were strongly decreased by the time splitting and also the m_o of the element. Brithness of the Pb lamp also decreased in short time. The results obtained in this work and those reported [54,56] indicate that the presence of an emission line overlap in simultaneous multielement determination by ETAAS can affect the figures of merit of the analytes, DL and m_o and also seems to affect the useful time of some lamps. In addition, the magnitude of the effect of the modulation of the lamps to overcome the emission spectral overlap on the figures of merit seems to varies with the brightness of lamps involved and the element combination.

The compromise atomisation in simultaneous multielement determination make difficult to compare m_o and DL values obtained for a given

element, m_o data reported differ by up to 30–40% from its optimum [57]. Since the photon integration time for a given element also depends on the other elements in the simultaneous multielement run [50], greater differences in the figures of merit should be expected for those elements simultaneously determined when an emission line overlap is present. However, despite of inconveniences mentioned in choosing the appropriate element combination, lamps and matrix modifiers, the simultaneous multielement determination by ETAAS offers the possibility of decreasing one of the handicaps of this technique that is the high time consuming of analysis.

4. Conclusions

Results of this study also indicate that aluminium improves the thermal stabilisation of Pb and Sn for it can be employed as a matrix modifier for these elements. Aluminium shows a performance as a matrix modifier better than that reported for $Pd + Mg(NO_3)_2$. In this work, the matrix matching method of aqueous standard with aluminium proved to be an effective and simple procedure for the simultaneous multielement determination of Pb, Sn, Ni and Cu in aluminium-base alloys employing a simple calibration curve. This method in conjuction with the slurry sampling of the aluminium-base alloys samples by electrical discharge in water is shown to be a quick procedure for the simultaneous multielement determination of Pb, Sn, Ni and Cu in aluminium-base alloys by ETAAS. Observations and results obtained in the simultaneous multielement determination made in this study indicates that the presence of an emission line overlap in the simultaneous multielement determination can produce important changes on the figures of merit, m_o and DL, of the elements and on the useful time of the lamps involved. However, despite of inconveniences mentioned, choosing the appropriate element combination, lamps and matrix modifier, the simultaneous multielement determination by ETAAS offers the possibility of diminishing one of the handicaps of this technique that is high time consuming of analysis.

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