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Determination of minor elements in steelmaking flue dusts using laser ablation inductively coupled plasma mass spectrometry

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Abstract

Element determination in solid waste products from the steel industry usually involves the time-consuming step of preparing a solution of the solid. Laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS) has been applied to the analysis of Cr, Ni, Cu, As, Cd and Sn, elements of importance from the point of view of their impact on the environment, in electric arc furnace flue dust (EAFD). A simple method of sample preparation as pressed pellets using a mixture of cellulose and paraffin as binder material was applied. Calibration standards were prepared spiking multielement solution standards to a 1:1 $ZnO + Fe_2O_3$ synthetic matrix. The wet powder was dried and mechanically homogenised. Quantitative analysis were based on external calibration using a set of matrix matched calibration standards with Rh as a internal standard. Results obtained using only one-point for calibration without matrix matched, needing less time for standardization and data processing, are also presented. Data are calculated for flue dust reference materials: CRM 876-1 (EAFD), AG-6203 (EAFD), AG-6201 (cupola dust) and AG-SX3705 (coke ashes), and for two representative electrical arc furnace flue dusts samples from Spanish steelmaking companies: MS-1 and MS-2. For the reference materials, an acceptable agreement with certificate values was achieved, and the results for the MS samples matched with those obtained from conventional nebulization solutions (CN). The analytical precision was found to be better than 7% R.S.D. both within a single pellet and between several pellets of the same sample for all the elements.

Keywords: Laser ablation; Inductively coupled plasma mass spectrometry; Steelmaking flue dusts; Pressed powder

1. Introduction

Trace element analysis of powdered or particulate material is often required in environmental monitoring of many industrial wastes. The European Community Council Directive (91/156/CEE) requires control of harmful and toxic products quantity, caused by industrial residues. One of the greatest environmental concerns among steelmakers all over the world is treatment and disposal of dusts from the electric arc furnace (EAF). During steel making in electric arc furnace, 10–15 kg of dust is generated per ton of steel product. These dusts are considered toxic and hazardous products and the disposal of these materials in landfill sites is regarded as an environmental hazard, since toxic metals may leach into drinking water supplies [1,2]. These products, consisting mainly of a mixture of zinc and iron oxides contain trace elements of importance from the point of view of their impact on the environment, such as Cr, Ni, Cu, As, Cd and Sn. The wide variability of their composition makes a complete analysis rather difficult. When using inductively coupled plasma mass spectrometry (ICP-MS) in combination with conventional nebulization of solutions (CN), the usual procedure for completely dissolving EAF dusts, containing carbides and refractory oxides, consists of dissolving the sample in an acid mixture and then melting the eventual insoluble residue with different alkaline fluxes, thus producing complex sample matrices with a high content of total dissolved solids. Microwave ovens can be used to simplify the process, but these systems not always allows completely dissolve these products [3]. To extend the capabilities of the technique and fully exploit its complete potential alternative sample introduction systems should be applied. Powders can be introduced into the plasma through slurry nebulization if a micrometre particle size can

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be achieved [4] or even through slurry sampling electrothermal vaporization [5]. Indeed, to some extent the advent of micro-nebulizers has displaced ETV as the preferred means of introducing micro-samples [6,7]. Laser ablation (LA) can be used to avoid sample dissolution and it was expected that ICP-MS combined with laser ablation would allow the analysis of environmental materials directly from the solid with acceptable speed, accuracy and precision. Materials in a powdered state cannot be ablated by a laser beam, as the shock wave of the laser pulse scatters the powder particles and large amounts of powder will be sputtered out of the cell. It is therefore necessary to immobilize the material, which is possible by using a binder, by pressing to a pellet or by both [8,9]. Previous work with LA on powdered samples has been conducted in the field of geology and the environment. For environmental monitoring, samples preparation as pressed pellets was used for the analysis by LA-ICP-MS of sediments [10] and carbonates [11] and for the analysis of soils by LA-ICP-AES [12]. Different calibration strategies can be used such as calibration with reference materials or calibration against synthetic powders spiked with analytes occurring in solid or liquid form [13]. The applicability of the isotope dilution (ID) technique for trace element determination in powdered samples has also been demonstrated [14].

The goal of this study is to develop a method for the quantitative analysis of the minor and trace elements in EAF dusts by LA-ICP-MS from samples prepared as pressed pellets. External calibration was performed using synthetic powders spiked with multielement standard solutions. In addition, the results of this study are intended to demonstrate the potential of LA-ICP-MS as a quantitative analytical technique for the determination of raw materials and other solid waste products of the steel industry. For this purpose, complementary tests were carried out using CRM 876-1 electric arc furnace flue dust (EAFD) as standard for an one-point calibration, applying LAMTRACE software for data reduction and quantification [15–17], to analyse MS-1, MS-2 (EAFD), AG-SX3705 (coke ashes) and AG-6201 (Cupola dust).

2. Experimental

2.1. Instrumentation

An ELAN 6000 ICP mass spectrometer (Perkin-Elmer, SCIEX, ON, Canada) was used for this work. A LSX-100 laser sampler (CETAC Technologies, Omaha, Nebraska) was used for sampling into the ICP. The ablated material was transferred from the laser sampler to the ELAN 6000, using a tygon tube. Table 1 gives the operating conditions.

Table 1
LA-ICP-MS operating conditions

ICP-MS (ELAN 6000)	LA (XLS-100)
Power: 1100 W	Laser type: Nd-YAG
Ar flow: 14 l/min;	Q-swich pulsed
Carrier Ar flow. 0.65 l/min	Beam profile >95% fit to Gaussian
Analytes: ^{52}Cr, ^{58}Fe, ^{60}Ni, ^{63}Cu, ^{70}Zn, ^{75}As, ^{103}Rh, ^{114}Cd, ^{120}Sn	Wavelength: 266 nm (UV)
Internal standard: ^{103}Rh	Energy output: 5.0 mJ/shot
Dwell time: 10 ms	Repetition rate: 10 Hz
Sweeps/reading: 5 (scan and SP)	Sample movement speed: 60 µm/s
Replicates: 4 (scan)–1 (SP)	Method: line scanning (track wide: 180 µm) and single point (crater diameter: 200 µm
Readings/replicate: 5 (scan)–200 (SP)	Transport from LA chamber to MS:
Sample time: 15.8 s (scan)–2 min (SP)	Tygon tube (40 cm length −5 mm i.d.)

2.2. Samples

The selected samples to carry out the study were: two electrical arc furnace flue dust MS-1 and MS-2, from the steelmaking Spanish industry, that have been analyzed by CN-ICP-MS in four laboratories; two Certified Reference electrical arc furnace flue dust materials, CRM 876-1 (IRSID, Maizières-les-Metz, France) and AG-6203 (Dillinger, Germany); one coke ashes reference material AG-SX3705 and a cupola dust AG-6201 (both also from Dillinger, Germany). The main components of these materials are listed in Table 2.

Pellets were prepared by mixing the powder with a binder in a 4:1 ratio, using the following procedure: a 1 g amount of sample was weighed into a vial, and 1 ml of ethanol and 200 µg of Rh (200 µl of a 1000 $\mu g\,ml^{-1}$ Rh solution) were added. The mixture was homogenised manually and dried at 90 °C for 1 h; 0.25 g of binder were added to the dry powder and the mixture was homogenised for 30 min in a ball-mixer/mill. A layer of 4 g of boric acid was placed in an aluminium capsule 3 cm in width and 8 mm in height, a load of 45 $t\,cm^{-2}$ was exerted for 30 s in a hydraulic press, and then the test mixture was placed on top pressing again for another 30 s period.

The two binders tested were: *N*-butyl-methacrylate (Ervacite, from ICI Acrylics, The Netherlands) and a mixture of cellulose and paraffin (Spectroblend, from Chemplex Industries, USA).

2.3. Pellets for calibration

Synthetic powders of different compositions were used to prepare samples with controlled compositions. To compensate for major matrix effects, a 1:1 mixture of the two

Table 2
Main composition of the studied waste dust materials

Sample	SiO_2	Fe_2O_3	ZnO	PbO	Mn_3O_4
MS-1 (EAFD)	3.8	38.0	26.4	3.0	4.7
MS-2 (EAFD)	4.2	55.9	13.8	3.2	7.5
CRM-876 (EAFD)	3.6	35.5	28.9	8.4	3.9
AG-6203 (EAFD)	15.6	36.8	12.3	1.0	5.0
AG-6201(cupola dust)	26.4	–	30.7	–	–
SX3705 (coke ashes)	47.5	8.2	–	–	–

main components ZnO and Fe_2O_3 (both of 99.999%, from Sigma–Aldrich) was spiked with a multielement standard solutions of: Cr, Ni, Cu, As, Cd and Sn at different concentrations to prepare dual phase matrices with different bulk composition of the minor elements.

Multielement standard solution containing 1000 $\mu g\,ml^{-1}$ of each analyte was prepared by mixing in a 500 ml volumetric flask the following solutions: 1.414 g of $K_2Cr_2O_7$ dissolved in 20 ml of water; 2.082 g of $Na_2AsO_4 + 7H_2O$ dissolved in 20 ml of water; 0.5 g of pure Cd dissolved in 20 ml of HNO_3 (1 + 1); 0.5 g of pure Ni dissolved in 20 ml of HNO_3 (1 + 1); 0.5 g of pure Cu dissolved in 20 ml of HNO_3 (1 + 1); 0.5 g of pure Sn dissolved in 20 ml of HCl (1 + 1); The mixture was made up to 500 ml in HCl 10% (v/v).

A series of a blank and six samples with element concentrations between 0.001 and 0.4% was prepared as follows. Firstly, a synthetic matrix was prepared by mixing 2 g of pure ZnO with 2 g of pure Fe_2O_3 and homogenizing for 30 min in a ball-mixer/mill. To 0.5 g portions of the matrix were added: 1 ml of ethanol, 200 μg of Rh to be used as internal standard (200 μl of a 1000 $\mu g\,ml^{-1}$ solution) and 0 (blank), 5, 25, 100, 500, 1000 and 2000 μl of the multielement standard solution 1000 $\mu g\,ml^{-1}$each of Cr, Ni, Cu, As, Cd and Sn. The mixtures were homogenised manually and dried at 90 °C for 1 h and pellets were prepared in the same way as for the samples.

3. Optimization of analytical parameters

For bulk analysis of trace elements in powdered materials prepared as pressed pellets, grain size certainly plays a significant role. The distribution of trace elements within the matrix is likely to be dependent on grain size. Electrical arc furnace dusts have as their primary advantage their extremely fine particle size. The 95% have a particle size of less than 0.5 μm, which makes these products suitable for direct compaction without any previous treatment. The samples appear homogeneous within the sampling volume probed by the laser beam being representative of the distribution of trace elements. The addition of a binder improves the mechanical properties of the pellets, enables a better ablation to be carried out and increases the reproducibility of the eroded material. Both Elvacite and Spectroblend were tested as binders.

A dilution study was performed to determine the optimum proportion of sample and binder in the pellets. This study was carried out by monitoring the ion signal for ^{70}Zn and ^{58}Fe isotopes. The same behaviour discussed by Denoyer [10] for the semiquantitative analysis of environmental materials was observed. When the sample to binder proportion was increased from 20 to 90% (m/m), the ion signals also increased. This increase was very slow for proportions higher that 80% and the stability of the signals was worse. Similar behaviour was observed for all the analytes in both binder materials. Maximum signal response together with a good precision was observed for pellets with sample concentrations from 70 to 80%. Therefore, for the following studies pellets were prepared by mixing four parts of sample with one part of binder. Spectroblend was selected as binder because it was easier to handle.

To achieve accurate analysis from laser sampling, it is necessary to optimize the conditions under which the laser is operated. The optimization of the laser operating parameters was performed using the “blank” of the standard prepared for calibration. Time resolved laser ablation signal of the lower abundance isotopes of Zn (^{70}Zn, 0.62%) and Fe (^{58}Fe, 0.33%) and of ^{103}Rh (used as IS) were monitored with the aim of improving analytical performance and verifying the adequacy of the sample preparation procedure. Varying signal responses were generated under different laser power output (from 0.25 to 5 mJ/shot) and pulse repetition conditions (from 1 to 20 Hz). Tests were performed in scanning mode by controlling line pattern.

The laser was fired for 125 s and during firing the sample was moved horizontally at a speed of 40 $\mu m\,s^{-1}$ keeping the focus on sample surface (scanning line: 5000 μm length). Fig. 1 shows the laser energy influence at a pulse repetition rate of 5 Hz in raw and normalized signals ($n = 4$) and Fig. 2 shows the pulse repetition rate influence at an energy output of 3 mJ/shot in raw and normalized signals ($n = 4$).

The scanning speed influence was also investigated at an energy output of 3 mJ/shot and a pulse repetition rate of 5 Hz. Fig. 3 shows the observed trend ($n = 4$).

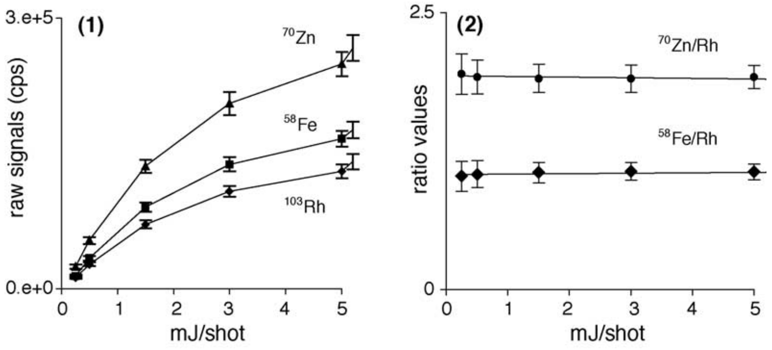

Fig. 1. Analyte intensities as a function of pulse energy output, at a repetition rate of 5 Hz: (1) Zn, Fe and Rh raw signals; (2) Zn and Fe signals rationed to Rh signal.

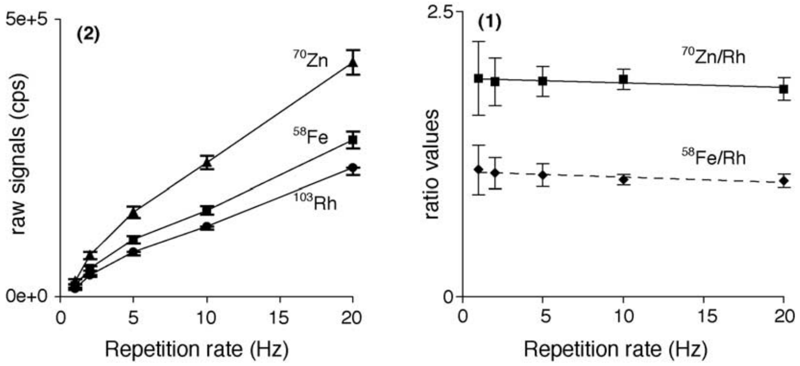

Fig. 2. Analyte intensities as a function of pulse repetition rate, with a energy output of 3 mJ/shot: (1) Zn, Fe and Rh raw signals; (2) Zn and Fe signals rationed to Rh signal.

According to the results of the three above tests the following operating parameters were selected: laser energy output of 5 mJ/shot at a laser shot frequency of 10 Hz and a speed of 60 μm/s. With these parameters the sensitivity of the technique was suitable for the determination of the considered analytes over the required concentration range and with the best precision values (4–5%).

Complementary tests were conducted in single point mode from multiple laser pulses fired at a fixed location (without lateral movement of the sample).

Fig. 4a and b shows the signals for scanning (scanning speed: 60 μm s^{-1}) and single point modes for a measurement period of 2 min with a laser power of 5 mJ/shot and 10 Hz of pulse repetition rate (1200 shots in SP and 7200 μm line in scanning).

Fig. 4a shows that in scanning mode a steady state ablation can be observed after the 20 first seconds of laser ablation, and it remains stable for at least 2 min. Fig. 4b shows that in single point mode after 80 s (800 shots) the Boron of the substrate started to appear, and provided that the sample layer in the pellet is about 650 μm thick, that means that approximately 0.8 μm in depth is ablated per laser shot. Also it can be observed that the plot of Fe/Rh and Zn/Rh versus time presents steady state ablation between 20 and 80 s (200 and 800 pulses), being the R.S.D. of the isotopes ratio about 3% for both. The constant ablation ratios demonstrate that there is no time-dependent fractionation of these elements over the ablated time monitored and the power density applied.

The power density estimated from the laser beam energy and the measured laser track width (180 μm) for the scanning mode and the laser crater diameter (200 μm) for single point mode is at the 10^9 W cm^{-2} order.

Fig. 5 shows an image of the laser track and crater diameter for both tests.

After optimization of the operating parameters affecting measurement precision, the homogeneity of the pellets was verified in surface and in depth. To evaluate surface homogeneity the ^{58}Fe, ^{70}Zh and ^{103}Rh signals of three scanning lines at different positions for each of the calibration pellets were averaged and for depth homogeneity three signals of the same analytes in each pellet were also averaged from 20 to 80 shots fired at a fixed location. R.S.D. values lower than 7% were calculated in both cases and no significant differences were observed between the repeatability of replicate determinations carried out on the same pellet and those on different pellets. No distinction could be made between measurement imprecision and sample heterogeneity, suggesting that representative sampling was achieved. No differences were observed for the R.S.D. values between determinations on the same pellet and on different pellets.

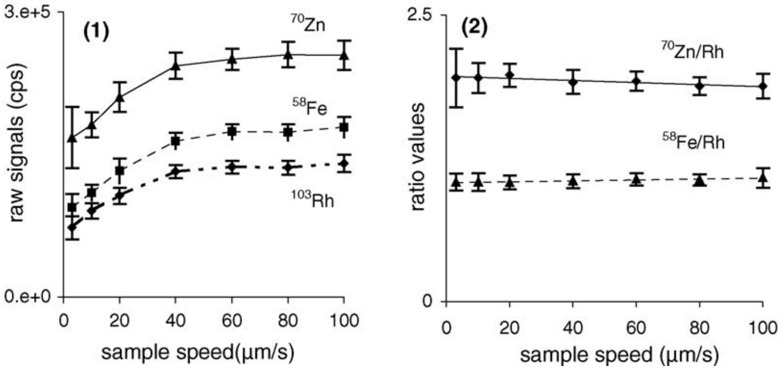

Fig. 3. Analyte intensities as a function of scanning speed: (1) Zn, Fe and Rh raw signals; (2) Zn and Fe signals rationed to Rh signal.

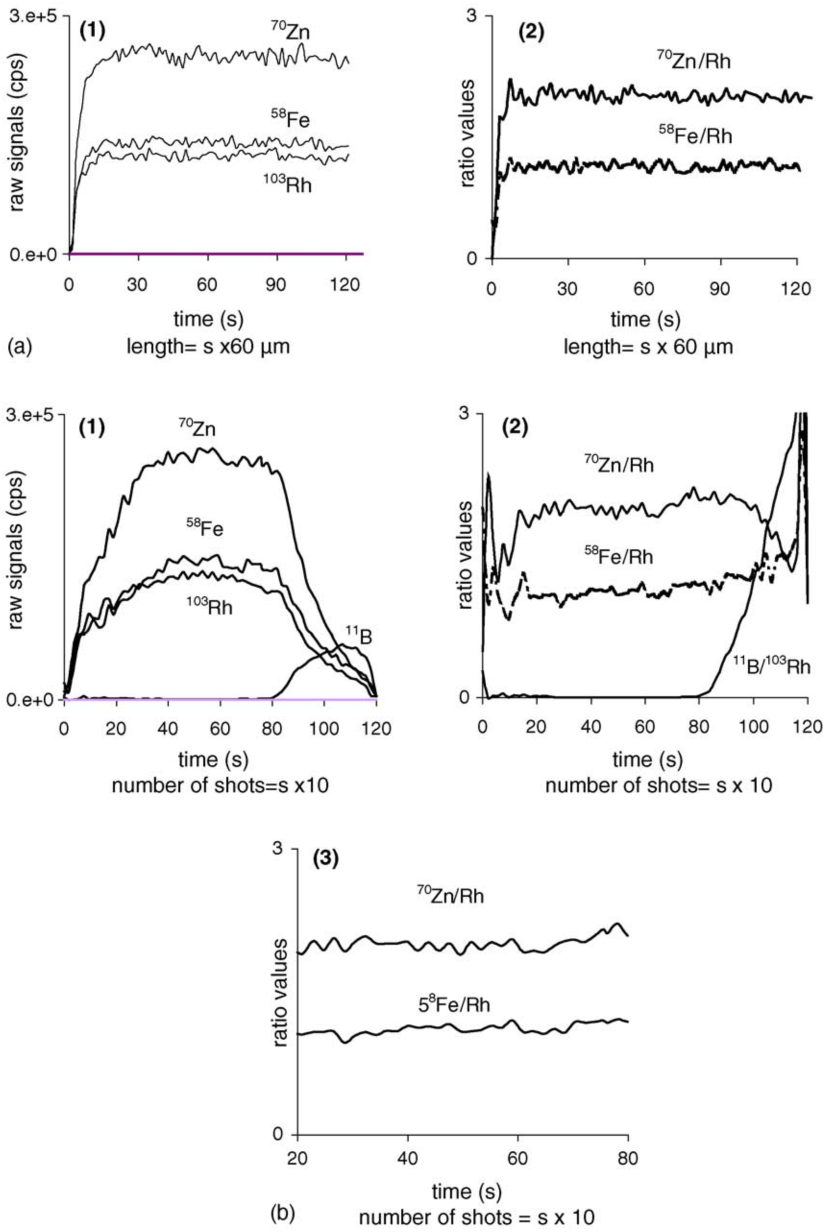

Fig. 4. (a) Time resolved signals for scanning mode (scanning speed: 60 µm s^{-1}, line length: 7200 µm; 5 mJ/shot at 10 Hz of pulse repetition rate): (1) Zn, Fe and Rh raw signals; (2) Zn and Fe signals rationed to Rh signal. (b) Time resolved signals from single point mode (1200 shots, 5 mJ/shot at 10 Hz of pulse repetition rate): (1) Zn, Fe and Rh raw signals (time interval 0–120 s); (2) Zn and Fe signals rationed to Rh signal (time interval 0–120 s); (3) Zn and Fe signals rationed to Rh signal (time interval 20–80 s).

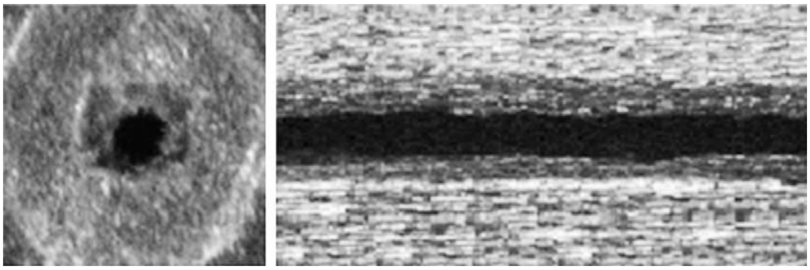

Fig. 5. Microphotographs of laser crater (200 µm diameter) from single point mode (1200 shots), and of laser track (180 µm width) from scanning mode (7200 µm length).

Table 3
Calibration statistics for calibration pellets

Element y = Ax	DL (μr/g)	Net intensities (cps)			Ratio signals (Rh as IS)		
		Slope (cps)	R.S.D. slope (%)	Cor. coefficient (r^2)	Slope (cps)	R.S.D. slope (%)	Cor. coefficient (r^2)
^{52}Cr	3.0	806972	1.21	0.99970	12.50	0.45	0.99996
^{60}Ni	0.42	163188	1.7	0.99941	2.42	0.40	0.99990
^{63}Cu	0.33	387944	0.73	0.99989	5.84	0.62	0.99990
^{75}As	0.15	256843	0.66	0.99985	3.65	0.60	0.99990
^{114}Cd	0.25	556097	0.61	0.99991	7.90	0.48	0.99994
^{120}Sn	1.2	1561930	1.12	0.99973	27.10	0.85	0.99993

Curve type: linear through zero (blank subtracted).

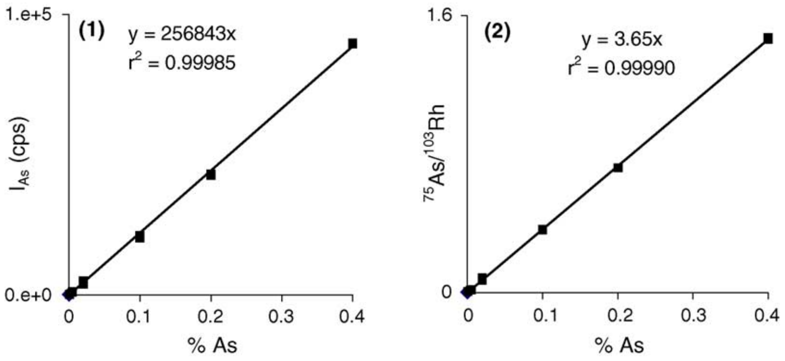

Fig. 6. Correlation between As concentration and the integrated intensity: (1) raw signals (cps); (2) rationed to the integrated ^{103}Rh signal (used as IS).

4. Results

LA sampling was performed in scanning mode. MS measurements were carried out with the following operating parameters: dwell time 10 ms, sweeps/reading 5, readings/replicate 5 and replicates 4. According to these conditions, the ICP-MS measurement period was about 15.8 s. Thus, the duration of an LA-ICP-MS process, including a read delay period of 30 s (time elapsed between starting to fire the laser and the beginning of the data acquisition, allowing the signal intensities to reach a steady state), was about 45 s (scanning line 2700 μm).

Calibration graphs were obtained relating the analyte response of the calibration standards pellets to the respective concentrations. Calibration curves with least-squares regression correlation coefficients of better than 0.999 (when using net intensity signals), and better than 0.9999 (when using Rh as IS), were obtained for all the elements investigated. Calibration statistics of lineal through zero curve type (blank subtracted), both for net intensities and ratio signals are listed in Table 3. As an example and to illustrate the linearity Fig. 6 shows the As calibration graphs.

Table 4 lists comparatively the certified values for CRM-876 and AG-6203, and the mean values obtained by four laboratories for samples MS-1 and MS-2, using continuous nebulization, with the values from pellets using LA.

For the two reference materials, an acceptable agreement with certificate values was achieved, and the results for the CENIM samples reasonably matched those obtained from conventional nebulization solutions.

In order to simplify the calibration procedure and to prove the possibility of analysing samples with different matrices: EAFD (Fe_2O_3 and ZnO), Cupola dust (Si_2O_3 and ZnO) and coke ashes (SiO_2 and Al_2O_3) one-point calibration procedure was applied, using EAFD certified reference material CRM 876-1 as standard. The raw response data were manipulated by applying LAMTRACE data reduction software (15). LAMTRACE is a comprehensible data reduction spreadsheet

Table 4
Certified and found results for four EAF dusts (%, $n = 4$)

Element	AG-6203		MS-1		MS-2		CRM-876	
	Cert	LA	CN	LA	CN	LA	Certified	LA
Cr	0.003	0.0025 (0.0010)	0.397 (0.008)	0.401 (0.016)	0.590 (0.010)	0.581 (0.034)	0.167 (0.012)	0.151 (0.007)
Ni	0.042	0.0500 (0.0007)	0.0310 (0.0020)	0.0353 (0.0033)	0.0280 (0.0024)	0.0285 (0.0036)	0.0344 (0.0027)	0.0325 (0.0010)
Cu	0.25	0.298 (0.011)	0.200 (0.008)	0.203 (0.013)	0.265 (0.015)	0.261 (0.019)	0.419 (0.011)	0.379 (0.013)
As	–	<0.001 (0.0015)	0.0080 (0.0015)	0.0076 (0.0012)	0.0115 (0.0005)	0.0132 (0.0010)	0.0231 (0.0014)	0.0257 (0.0023)
Cd	–	0.0032 (0.0012)	0.0418 (0.0019)	0.0450 (0.0020)	0.132 (0.003)	0.135 (0.007)	0.133 (0.009)	0.150 (0.012)
Sn	0.004	0.0056 (0.0031)	0.0425 (0.0034)	0.0400 (0.0032)	0.0460 (0.0027)	0.0438 (0.0037)	0.0942 (0.0042)	0.0913 (0.0183)

developed for examining time resolved signals allowing judicious selection of integration intervals. Samples were analyzed in SP mode, 600 shots were fired at each spot and recorded as cps. Gas blank was acquired for 30 s and afterwards the sample was ablated for 60 s. To measure 10 isotopes with a dwell time of 10 ms, the estimate time per reading is about 632 ms. The number of readings was set to 200 to get a total analysis time of about 2 min, first 30 s for background, 60 s for laser ablation and 30 s for washout). The integration interval selected was from 50 to 100 s. The detection limits and the results provided by this system are presented in Table 5.

The obtained results show that a single sample can be used for calibration (one-point calibration method) and that exact matrix matching is not always a prerequisite when using laser ablation for ICP-MS analysis.

Table 5
Comparative results for different waste products (%, $n = 4$)

Ele	DL (μg/g)	AG-6201		MS-1		MS-2		AG-SX3705	
		Cert	LA	CN	LA	CN	LA	Cert	LA
Cr	2.3	0.026	0.0278 (0.0020)	0.397 (0.008)	0.408 (0.029)	0.590 (0.010)	0.606 (0.052)	0.036	0.0345 (0.0036)
Ni	0.21	0.0035[a] (0.0006)	0.0032 (0.0003)	0.0310 (0.0020)	0.0363 (0.0065)	0.0280 (0.0024)	0.0332 (0.0051)	0.027	0.0253 (0.0036)
Cu	0.10	0.124	0.117 (0.007)	0.200 (0.008)	0.230 (0.022)	0.265 (0.015)	0.283 (0.024)	0.040	0.373 (0.0047)
As	0.17	0.0105[a] (0.0004)	0.0090 (0.0005)	0.0080 (0.0015)	0.0071 (0.0020)	0.0115 (0.0005)	0.0095 (0.0009)	0.085[a] (0.005)	0.075 (0.012)
Cd	0.32	0.0533[a] (0.0011	0.0353 (0.0025)	0.0418 (0.0019)	0.0487 (0.0032)	0.132 (0.003)	0.143 (0.008)	0.0017	0.0010 (0.0002)
Sn	1.4	0.235[a] (0.010)	0.213 (0.012)	0.0425 (0.0034)	0.0479 (0.0052)	0.0460 (0.0027)	0.0516 (0.0054)	0.0045[a] (0.0006)	0.0030 (0.0007)

[a] Results from CN solutions.

5. Conclusions

The LA-ICP-MS technique is a viable approach for determination of minor and trace elements in powdered waste products without dissolution procedures. It has been shown to be useful for the quantitative analysis of samples prepared as pressed pellets. By using rhodium as the internal standard, a good accuracy and precision were demonstrated for the quantitative analysis of electrical arc furnace flue dust when using matrix-matched standards. The analytical precision was found to be better than 7% both within a single pellet and among several pellets of the same sample. Time response measurements both in surface (scanning lines 7 mm length) and in depth (craters depth 600 μm) showed that the signals achieved a steady state after the first 20 s remaining constant through the sampling period. The acceptable concordance between results when using an one-point calibration standard without matrix-matching, demonstrated the potential of the system as a more than semi-quantitative analytical tool for the determination of minor and trace elements in different solid waste products of the steel industry. The number of analytes can be extended to any present in the standard used for calibration.

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