Direct Analysis of Slags by Inductively Coupled Plasma Atomic Emission Spectrometry Using Slurry Sample Introduction Techniques

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A practical method is described for the direct determination of Si, Ca, Mg, Al, Fe, Mn, Ti, Na and K in slag samples by the introduction of sample suspensions into the inductively coupled plasma atomic emission spectrometer. The effect of the particle size distribution on the atomization efficiency of these elements when slurries of the slag samples were aspirated into the plasma has been studied. The slurry samples were prepared by dispersing 0.1 g of ground slag in 100 ml of 0.35% ammonia solution; calibration was achieved by the use of a reference slag prepared in the same manner. The results obtained for the direct analysis of slag slurries using such a procedure were in good agreement with those obtained by classical dissolution of the sample. The reproducibility of the results with slurry nebulization (concentration range 1.7–5.5%) were poorer than those observed with aqueous solutions (concentration range 0.5–4.8%) but were acceptable for slag industrial control.

Keywords: *Elemental slag analysis; slurry atomization; inductively coupled plasma atomic emission spectrometry*

An important limitation of the otherwise popular inductively coupled plasma (ICP) as a source for atomic emission spectrometry (AES) is that a conventional ICP technique requires the sample to be in solution. Because of this, the sample preparation time in many solid sample analyses often exceeds the analysis time by unacceptable lengths. This means that the potential analytical speed of ICP-AES cannot be fully realized unless alternatives to the classical, time-consuming and sometimes hazardous dissolution methodologies can be developed. Hence, the considerable interest in recent years in investigations into the possibilities of direct analysis of solid samples.

Perhaps one of the most interesting approaches to solid sampling in atomic spectrometry is slurry injection,[1] that is, the introduction of aqueous (or organic) suspensions of fine powders or finely ground materials, using a high solids nebulizer.

When suspensions are nebulized into the ICP, the atomization efficiency is mainly dependent on the sample transport efficiency, which in turn is a function of the particle size and sample matrix. The application of slurries, as a sample introduction technique to the ICP, has been successfully reported by several workers for the determination of a variety of elements in coals,[2–6] soils,[7,8] geological materials,[9,10] clay,[11] kaolin[12,13] and refractory ore.[14] Watson and Moore[15] used an ion-exchange resin to concentrate noble metals from a dissolved sample and the loaded resin was then mixed with water to form a slurry that was introduced into the ICP. Sugimae and Mizoguchi[16] introduced suspensions in an organic medium into the ICP.

The use of reference materials, in slurry form, as a calibration procedure for slurry atomization has also been reported.[9,17] Watson[17] used an internal standard of $Li_4B_4O_7$ plus 1% Sc_2O_3, and used reference ores and slags in order to obtain calibration functions. Halicz and Brenner[9] employed a similar technique using Sc as the internal standard and calibration was performed by using the ratios of the analyte to scandium internal standard reference signals as a function of the concentration of the reference material slurry.

The application of a flow injection manifold for the introduction of slurries into an ICP has also been reported recently.[18]

Blast furnace slag is a by-product obtained in the manufacture of iron. The bulk of the slag consists principally of silica, alumina and lime, with minor amounts of magnesium oxide, iron oxide and alkali oxides. This by-product is used in road building and fertilizers but the cement industry is by far the largest user of the blast furnace slag. The slag can be used in the production of cement in two basic ways: (*i*) as a raw material for cement manufacture; or (*ii*) as a cementitius material combined with portland cement. The activity of the slag, used in cement or concrete, is determined by its composition and by the rate at which the molten material is cooled when it comes from the furnace. The slag can be added to the cement in order to reduce the cost or to modify the performance (*i.e.*, to produce concrete that is relatively resistant to certain types of chemical attack, such as those from sulphate or seawater).

In this paper, a method is described using compromise conditions for the routine multi-element determination of Si, Ca, Mg, Al, Fe, Mn, Ti, Na and K in slag samples by slurry atomization ICP-AES. The optimum operating parameters in the ICP and the influence of particle size on the analytical signal were investigated. The effect of different dispersants on the stability of the slag suspension and the influence of the solids content on the analytical signal were also studied.

Experimental

Apparatus

A Perkin-Elmer Model 5000 ICP spectrometer was used. The source and spectrometer characteristics are described in Table 1. A high-solids polytetrafluoroethylene Babington-type nebulizer[19] with a double-pass spray chamber was used for sample introduction. The slurry sample was delivered to the ICP nebulizer through a 0.8 mm i.d. plastic tube, using a peristaltic pump. The ICP operating parameters selected for the slag analysis are also listed in Table 1. Particle size analysis was carried out using a photosedimentometer (Lumosed, Retsch).

Sample Dissolution Procedure

Slag samples, previously hand-ground and dried, were dissolved by weighing 0.1 g of the sample into a Teflon

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Table 1   Instrumentation and plasma operating conditions

Spectrometer—
　Sequential scanning <0.03 nm bandpass
　Holographic ultraviolet grating

ICP source—
　Fassel-fused silica torch 2 kW, 27.12 MHz
　High-solids Babington-type nebulizer

Plasma operating conditions—

Coolant flow rate	16 l min⁻¹
Auxiliary flow rate	0.8 l min⁻¹
Injector flow rate	0.6 l min⁻¹
Nebulizer pressure	193 kPa
Observation height	16 mm
Plasma power	1.25 kW

bomb and adding 5 ml of water, 1 ml of HF and 3 ml of *aqua regia* (3+1, $HCl+HNO_3$). The bomb was heated in an oven at 140 °C for 45 min and then left to cool. Ten ml of a saturated solution of boric acid were added and the bomb was re-sealed and heated to 120 °C for another 20 min. After cooling, the solution was transferred into a 250 ml calibrated flask and diluted to volume with distilled, de-ionized water.

Slurry Sample Preparation

The original slag samples were dry-ground in a ball-mill (Pulverisette Model 6, Fritsch) to a size that allowed them to pass through a 37 μm sieve. The particle size of the sieved sample was further reduced down to <10 μm by wet-grinding[8] as follows: 0.1 g of the sample was added to 30 ml polyethylene bottles containing 1 g of 3 mm zirconium oxide beads and 0.5 ml of water, and ground by shaking for 3 h in a laboratory flask shaker. The resultant slurry was transferred into a 100 ml calibrated flask and diluted to the mark with 0.35% v/v ammonia solution. The slurry was then placed in an ultrasonic bath for 15 min. A magnetic stirrer was used to agitate the sample while it was pumped into the ICP in order to maintain a uniform slurry of the slag.

Results and Discussion

Plasma Operating Conditions for Slag Slurries

The analytical emission lines selected (see Table 2) for the determination of Si, Ca, Al, Mg, Fe, Mn, Ti, Na and K in slags by ICP-AES were selected from the literature[20] and from previous preliminary work with slag slurries.[21,22]

The influence of the more critical operating parameters of the ICP on each analytical line, when using slurry samples prepared as above, were studied by investigating the signal-to-background (S/B) ratio observed as a function of: the viewing height above the load coil; the plasma power
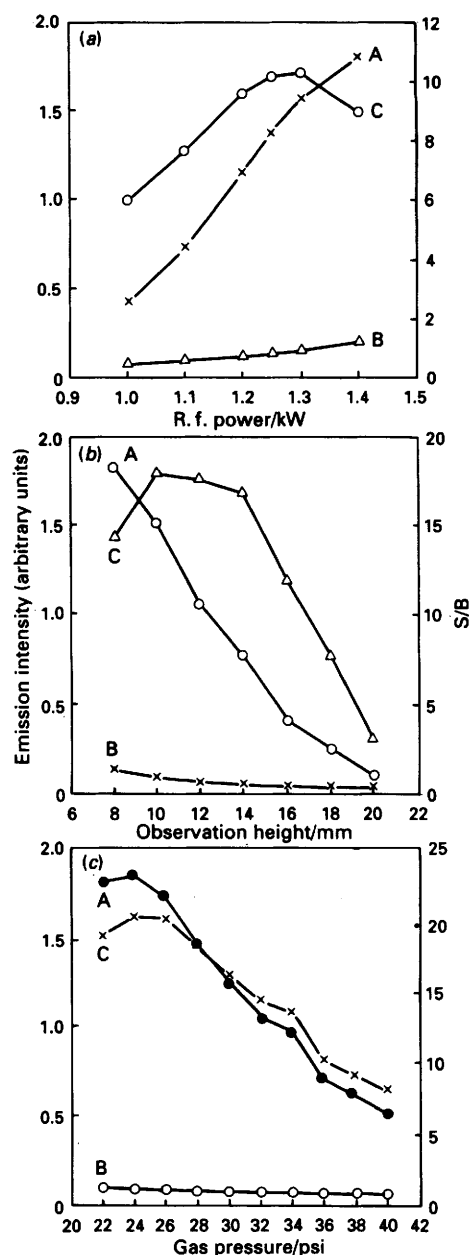
Table 2   Optimum experimental conditions for each element of interest

Element	Wavelength/ nm	Observation height/mm	Nebulizer gas flow/ ml min⁻¹	Plasma power/kW
Si	288.15	10	0.64	1.30
Ca	317.93	12	0.51	1.40
Mg	279.55	9	0.47	1.40
Al	396.15	12	0.64	1.10
Fe	259.94	14	0.64	1.00
Mn	257.61	10	0.51	1.30
Ti	334.94	14	0.69	1.10
Na	589.59	26	0.64	0.90
K	766.49	26	0.60	1.00

Fig. 1   Effect on A, the emission intensity of Mn, B, the background emission intensity and C, the signal to background ratio of a ground, slag slurry as a function of: (*a*) r.f. power; (*b*) observation height; and (*c*) nebulizer gas pressure

applied; and the nebulizer gas flow. This last parameter should be the most critical as the injector gas flow not only affects the efficiency of the nebulization but also determines the sample residence time in the plasma channel.

The results obtained showed that generally the signal and the background increased with increasing power, and decreased with increased viewing height and nebulizer gas flow. As an example, the results for Mn are illustrated in Fig. 1(*a*)–(*c*), which also show the effects of these parameters on the S/B ratios.

The best S/B ratios for Si, Ca, Mg and Mn were observed at low observation heights, low gas flows (longer residence time in the plasma) and high radiofrequency (r.f.) power. In contrast, the best S/B ratios for Na and K were observed for high observation heights and low power, whereas the optimum results for Al, Fe and Ti were obtained using an intermediate observation height and r.f. power, and high gas flows. The optimum operating parameters observed for

the excitation of a slurry of a sample in an ICP are given in Table 2 for each element studied. A simplex technique was used to determine the optimum conditions for each element.[23,24] For multi-elemental analysis a set of compromise conditions were chosen and the values finally used are given under plasma operating conditions in Table 1.

Particle Size

The most critical parameter in slurry atomization is probably the particle size distribution of the sample.[5,7,9,12] In the particle size investigations, 15 g of sample were ground in the ball-mill, for increasing periods of time, and different size fractions were isolated using a series of sieves (by manual agitation of the sieves). It was observed, as expected, that suspensions prepared from different particle size ranges (180–63, 63–37 and <37 μm) produced dramatically different emission intensities for all of the elements studied. This effect for three important elements, *viz.*, Si, Ca and Al is shown in Fig. 2. Only when the particle size of the slag was reduced to <37 μm could analytically useful signals be observed in the system. It was verified that 2.5–3 h of grinding in the ball-mill ensured that all the sample passed through a 37 μm sieve.

Williams *et al.*[8] described an effective method for the rapid reduction of the particle size by shaking the coarse slurry samples with ZrO_2 beads in polyethylene bottles. The use of such a technique was tested by shaking the sieved slag sample for 0.5 and 3 h with a laboratory flask shaker. The measured particle size distribution of these two fractions is shown in Fig. 3. The figure shows how effective the use of ZrO_2 beads during grinding can be in reducing the mean particle size of the slag samples. In fact, the mean particle size diameters were 4 and 2 μm after 0.5 and 3 h of grinding with ZrO_2 beads, respectively. Particle size distribution analysis showed that more than 90% of the particles were below 22 μm after 0.5 h and below 5 μm after 3 h of grinding with ZrO_2 beads.

After the particle size reduction studies, the relation between the particle size distribution in the slurry and the analyte emission intensity observed in the ICP was investigated: slag slurries (0.1% m/v) were prepared from each of the three sieved fractions. They were as before, 180–63, 63–37 and <37 μm, and were subsequently analysed for Ca, Fe, Ti and Na by ICP-AES. The results obtained (as illustrated for Ca, Fe, Ti and Na in Fig. 4) show that the
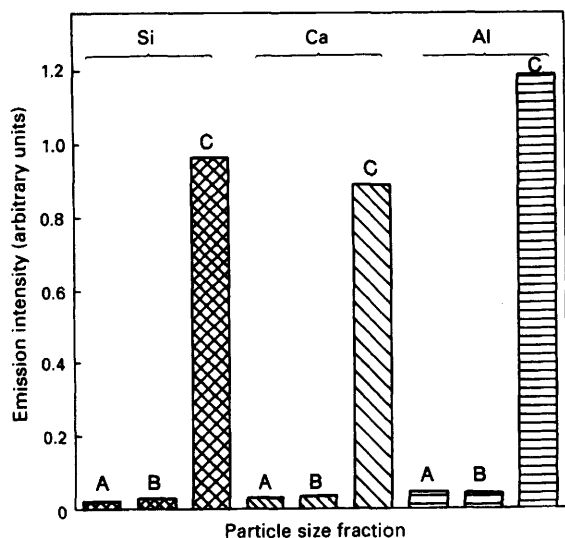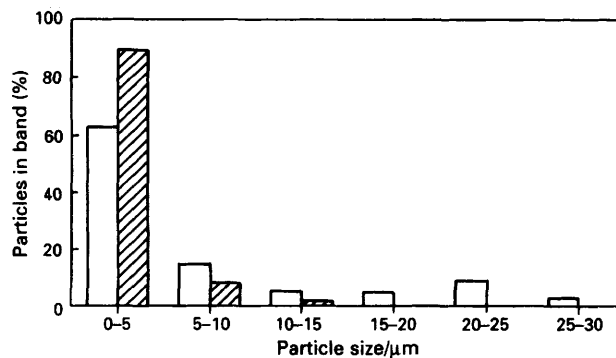

Fig. 3 Effect of grinding time upon the particle size distribution of slag slurries using the wet ZrO_2 bead method: unshaded area, 0.5 h; and shaded area, 3 h
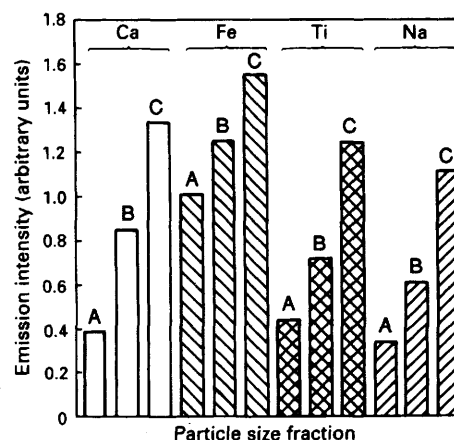

Fig. 4 Effect of slag particle size upon the emission intensity of Ca, Fe, Ti and Na: A, before sieving (180–63 μm); B, after sieving (63–37 μm); C, after sieving and wet grinding with ZrO_2 beads (<37 μm)

simple sieving of the sample can double the signal (*e.g.*, the emissions from fractions A and B for Ca). All of the analyte signals were increased further by grinding with ZrO_2 beads, but the magnitude of the increase was not equal for each of the different elements under study: for instance, the Ti and Na emissions show a higher percentage increase with wet-grinding than the Fe emission signal (compare B and C fractions in the observed signals in Fig. 4).

The relationship observed between the ZrO_2 grinding time and the analyte intensities for all of the elements under study is illustrated in Fig. 5. The signal increases with grinding time (as smaller particles are produced with extended grinding, which in turn affects the solid transport
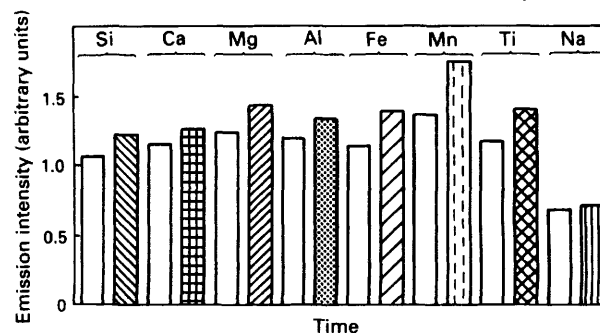

Fig. 2 Effect of different particle size fractions on the emission intensity of Si, Ca and Al: A, 180–63 μm; B, 63–37 μm; and C, <37 μm

Fig. 5 Effect of grinding time using the wet ZrO_2 bead method upon analyte emission intensity from slag slurries: unshaded area, 0.5 h; and shaded area, 3 h

efficiency). However, the emission intensity did not increase to the same extent for the different elements. This indicates that the slag is a multicomponent material and that the different degrees of hardness of each of the components has resulted in different particle size distributions for each mineral.

Selection of Dispersant

The use of a dispersant helps to maintain the small particles of a slurry sample in suspension. In order to achieve a stable suspension of ground slag the dispersants tested were: Triton X-100, sodium pyrophosphate ($Na_4P_2O_7$) and ammonia solution. The effect of the dispersants was investigated using slurries (0.1% m/v, prepared with each of the dispersants) which were aspirated into the ICP. The stability of the observed analyte signals was determined over a period of 6 min. The results showed that in suspensions prepared in 0.02, 0.1, 1 or 2% m/v Triton X-100 a depression of the signal was evident and the stability of the signals was poor. A slurry prepared in 0.1% m/v $Na_4P_2O_7$ showed good stability when monitoring the emission lines of Ca and Mg. The ammonia solution (0.35% v/v), as found by Ebdon and Collier for kaolin slurries,[13] proved to be the most effective dispersant for the fine slag particles as it produced the most stable emission signals for all of the elements under examination.

Effect of Solids Content in the Suspension

In order to evaluate the influence of the percentage of solid present in the suspension on the ICP emission signal intensity, slurry calibration graphs were obtained by varying the concentration of solids in the slag slurry (from 0.05 to 0.5% m/v). The results obtained are shown in Fig. 6. The intensity increases linearly with the amount of slag in the slurry in all instances, except for Mg where the observed response was not linear above 0.2% m/v. This can be attributed to self-absorption phenomena, which were also detected in aqueous solutions of Mg^{2+} with concentrations similar to those of the slag slurry (at 0.2% m/v).

Analytical Application

When the slag slurry was analysed by ICP, using aqueous standards and using the slurry preparation as detailed (*i.e.*, 3 h grinding with ZrO_2 beads), the recoveries (as calculated from the slurry to aqueous solution signal ratio) ranged from 60 to 80%, depending on the analyte. It was thought
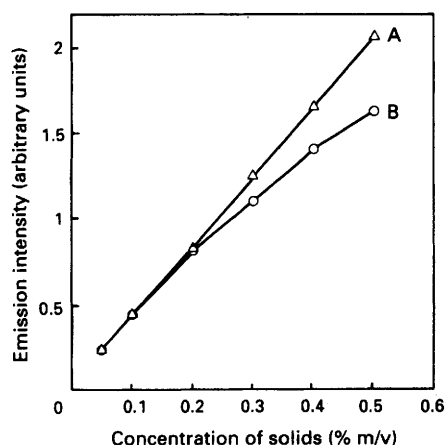
Table 3 Comparison of elemental content of a slag as determined by the slurry technique and by acid digestion. Each value is the mean of 3 determinations with a 1 s integration time

Oxide	Acid digestion		Slurry atomization	
	Content (%)	RSD (%)	Content (%)	RSD (%)
SiO_2	40.99	0.5	41.15	1.7
CaO	8.66	0.6	8.54	2.5
MgO	4.10	0.8	4.40	1.2
Al_2O_3	3.16	0.9	3.14	2.1
Fe_2O_3	0.43	1.3	0.38	5.2
MnO_2	0.91	1.5	1.02	1.8
TiO_2	2.52	1.2	2.54	1.4
Na_2O	0.22	1.3	0.16	3.7
K_2O	0.56	4.8	0.50	5.3

that these low recoveries might be due to transport losses of the slag slurry aerosol in the commercial spray chamber and possibly incomplete atomization and/or excitation in the ICP.[7,12,14]

As shown previously by other workers,[5,7,9,12] poor recoveries are related to particle size. A particle size distribution of <5 μm (see Figs. 3 and 5) should overcome this problem, but at the expense of unacceptably long grinding times. Therefore, a more practical approach was finally selected: the sieved sample was ground for 30 min with ZrO_2 beads (a more reasonable period than 3 h for routine determinations); and the loss in sensitivity was compensated for by using a reference slag (in slurry form) in order to calibrate the ICP. As described above, this method of calibration for slurry samples has been used by several workers, notably, Sugimae and Mizoguchi for airborne particles,[16] and Halicz and Brenner for various geological materials.[9] These workers found that close matching of sample and standard suspensions was vital for correct calibration. Although Sugimae and Mizoguchi concluded that differences in the response to the iron present in air particles, between samples and reference standards, was mainly due to the particle size composition, Halicz and Brenner in addition stressed that the textural, mineralogical and chemical compositions must also be similar. For the present investigation this was achieved by the use of the slag reference material Slagg S_1-S_8 (Institutet für Metallforskning, Germany), which underwent the same treatment as the samples so as to satisfy the conditions mentioned above.

The total concentration of Si, Ca, Al, Mg, Fe, Ti, Mn, Na and K obtained by the direct analysis of slag suspension by ICP are given in Table 3. These results are comparable in terms of accuracy and precision, with those obtained by the acid digestion method described above. Good agreement is also observed between the results obtained by both methods (direct analysis by slurry atomization and the acid digestion of the sample). However, the precision is worse when the slag slurry is introduced into the ICP. For routine analysis, the poorer precisions observed with the slurry technique are more than compensated for by simplicity and speed of operation, which reduces the analysis time, the risks of contamination and loss, and the use of hazardous chemicals, when compared with classical acid dissolution.

Conclusions

Direct solids analysis for the total concentrations of Si, Ca, Mg, Al, Fe, Mn, Ti, Na and K in slags by ICP-AES is possible by nebulizing suspensions of each.

As previously shown[5,7,9,12] the most critical factor affecting the ICP signal has proved to be the particle size of the ground slag, generally, the ICP analytical signals increase with a reduction in the particle size distributions of the

Fig. 6 The effect of solid concentration upon the emission intensity of A; Si, Ca, Al, Fe, Ti, Na and K; and B, Mg in a slag slurry

slurries. The longer the grinding time, the closer the emission signals of slurries come to those of aqueous solutions containing an equivalent concentration of the analyte being studied. By using the proposed procedure the ratios between the two emission signals, as stated earlier, were always below 1.0 (normally between 0.6 and 0.8, depending on the analyte). This variability demonstrates the complexity of the multicomponent nature of the slag material, and points to preferential particle size reduction, depending on the hardness of each mineral component, when the longer wet-grinding times are not used. On the other hand, when the solid content in the slurry was increased from 0.05 to 0.5% m/v, no viscosity effects were observed. Therefore, the reduced recoveries observed are perhaps due to less effective transport of the slag slurry from the nebulizer to the ICP, as compared with aqueous solutions, in addition to the possibility of incomplete volatilization and/or atomization (the extent of which would be mineral or element dependent).[14] As found by other workers[9,16] these phenomena necessitate the use of slag reference materials in the form of slurries instead of aqueous solutions, for the calibration of the instrument.

The results obtained show that the slurry technique holds promise for the direct and accurate analysis of solid slags by ICP-AES and, with the calibration limitation detailed above, offers a straightforward, non-hazardous technique for monitoring both major and minor elements in routine slag analysis.

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