# Spark Ablation as Sampling Device for Inductively Coupled Plasma Mass Spectrometric Analysis of Low-alloyed Steels

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**A method for the direct elemental analysis of low-alloyed steels is described. Spark ablation coupled with excitation in a 1.5 kW argon inductively coupled plasma was applied to the direct determination of Mn, Si, P, Al, B, Co, Nb, V, Zr and Sb in low-alloyed steels by mass spectrometry. For aerosol production, a medium-voltage spark at a high repetition rate (500 V, 400 Hz) was used. A cyclone device was designed to control the aerosol particle size; with this system the total amount of material reaching the plasma is low (about 4 µg min$^{-1}$) and a more uniform particle size distribution is achieved, thereby improving the precision of the measurements and preventing deposition of material in the torch injector and sampling cone. Particles re-collected downstream of the cyclone device were mostly spherical in shape, with a particle diameter of less than 1.0 µm. When using optimized operating parameters, and a low abundance iron isotope ($^{58}$Fe) as an internal standard, relative standard deviations at concentration levels of ten times the detection limit were below 2.5%. Detection limits (3s) for Nb, V, Zr, Mn, Co, Al and Sb ranged from 0.08 to 0.32 µg g$^{-1}$; for Si, B and P, detection limits were 1.5, 2.1 and 2.5 µg g$^{-1}$, respectively. These values are comparable to those obtained for continuous-flow sample aspiration of a 0.05% m/v Fe matrix solution. The technique was applied to the analysis of the Bureau of Analysed Samples certified reference materials SS-456/1 to SS-460/1, carbon steels (residual series).**

**Keywords:** *Spark ablation; inductively coupled plasma mass spectrometry; low-alloyed steels analysis*

A method for the inductively coupled plasma mass spectrometric (ICP-MS) analysis of low-alloyed steels is presented, using spark ablation as the sampling system. ICP-MS is most efficient for the determination of trace and ultratrace levels of elements, although this has not been of particular interest to the steel industry in the past. However, owing to the development of specialized types of steels, the importance of determining trace element concentrations in steels has increased[1] and requirements in quality control and analytical specifications of these low-alloyed steels are becoming increasingly strict, with the aim being to establish reliably the influence of specific minor elements. Only a few reports of element determinations in steels by ICP-MS from dissolved samples have been published in the last few years.[2–5] Based on the extensive studies performed by Kuss and co-workers[6,7] on polyatomic interferences caused by the main matrix elements of steels, ICP-MS procedures have been developed for steels analysis.

The nebulization method of sample introduction usually employed in ICP techniques requires the dissolution of solid samples; this inevitably constitutes a source of problems. The preparation of solutions from analyte samples may result in a reduced detection capacity due to analyte dilution, is time-consuming and introduces risks of contamination. With a view to avoiding these disadvantages, interest has been growing in the last few years in the possibility of developing direct solid sample introduction systems for use with spectroscopic techniques. Arc and spark discharges have been used as sampling devices for ICP and other spectrometric techniques, offering the possibility for simplification of the analytical process by elimination of the dissolution step.

The suitability of a variety of discharge types has been reviewed by Scheeline and Coleman.[8] Jiang and Houk[9] used an arc nebulization technique to analyse solids by ICP-MS. Jakubowski *et al.*[10] reported work carried out on the application of a spark ablation-ICP-MS system and discussed the results with reference to the application of glow discharge mass spectrometry (GDMS); they concluded that spark ablation is a promising alternative to laser ablation for direct introduction of conducting solids in ICP-MS analysis. In a previous paper,[11] the authors described a spark ablation-ICP-atomic emission spectrometric (AES) method for the determination of Al, Ti, Nb and V in low-alloyed steels and compared the results obtained with those provided by spark-optical emission spectrometry(OES).

This paper presents a method for the ICP-MS determination of Mn, Si, P, Al, B, Co, Nb, V, Zr and Sb in low-alloyed steels from bulk samples, using a medium voltage spark as the sampling system.

## EXPERIMENTAL

### Instrumentation

A Jobin–Yvon SAS unit was employed as the spark ablation system. This system was developed especially for application in ICP-AES. The sparking chamber used consists of a ceramic body in which a pointed tungsten rod (diameter 2 mm) is used as the anode and the sample serves as the sealing part of a Teflon spark chamber, switched as the cathode (electrode gap: 3 mm). In the former the chamber has a diameter of 10 mm and in the latter it is 20 mm. The argon transport gas enters parallel to the sample surface. The parameters that characterize the spark ablation cycle are: source operation (spark conditions), time parameters (pre-spark, cleaning, transfer and acquisition), argon flow, *i.e.*, permanent flow (which maintains the argon atmosphere), analytical flow (during the analysis) and valve position (during cleaning and pre-spark functions this is for ejection into the room and during analysis into the ICP-MS instrument).

An ELAN 500 spectrometer with an ELAN 5000 computer system (Perkin-Elmer, SCIEX) was used as the ICP-MS system.

The spark sampling conditions and the ICP-MS operating parameters are shown in Table 1.

A cyclone device was installed between the spark chamber and the ICP torch in order to regulate particle size and aerosol uptake rate. The cyclone, made of glass, was designed to remove particles larger than 1.0 µm (Fig. 1).

**Table 1** Spark ablation and ICP-MS operating conditions

| | |
|---|---|
| *Spark ablation:* | |
| Voltage | 500 V |
| Frequency | 400 Hz |
| Resistance | 2.2 $\Omega$ |
| Times | Pre-spark 30 s |
| Gas flow rates | Permanent carrier gas 1.8 l min$^{-1}$ |
| | Analysis carrier gas 1.0 l min$^{-1}$ |
| Carrier gas pressure | 3 bar |
| *ICP-MS conditions:* | |
| Interface cones | Pt sampler and skimmer |
| Rf power | 1500 W |
| Plasma Ar flow rate | 12.0 l min$^{-1}$ |
| Auxiliary Ar flow rate | 1.00 l min$^{-1}$ |
| Dwell time | 100 ms |
| No. of sweeps | 50 |
| Number of replicates | 1 |
| Data acquisition | Multichannel analyses, |
| | one point per mass |
| Resolution | 0.6 u |
| Estimated time | 60 s (per sample) |
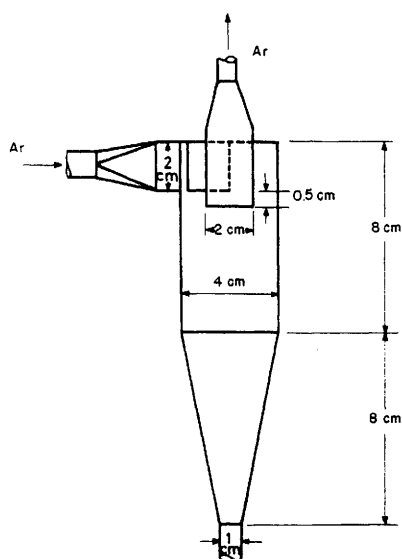


**Fig. 1** Cyclone dimensions. Sample enters the cyclone dragged by the argon flow

## Samples

The Bureau of Analysed Samples (BAS) certified reference materials (CRMs) SS-456/1 to SS-460/1 carbon steels (residual series) and the Bundesanstalt für Materialforschung und -prüfung (BAM) CRM 098-1 pure iron were used. The disc-shaped samples were prepared by wet grinding, rinsing with de-ionized water and acetone and drying with compressed air.

## RESULTS AND DISCUSSION

### Optimization of the Spark Sampling Conditions

The use of a spark discharge to generate sample aerosols directly from metal samples with a view to excitation in the ICP has long been attempted. Since the use of a spark for sample aerosol generation separates the sampling and excitation processes into two distinct events, it is useful to study the sampling process itself by examining the physical and chemical characteristics of the aerosol produced by the spark discharge.

The aim of this study was to optimize and control the operating conditions of spark ablation in order to be able to introduce a representative sample amount, control the particle size and maintain the sample uptake rate constant for the

duration of the spark ablation-ICP-MS measurement. It is important to note that for any given set of operating conditions, the plasma energy is only sufficient to dissociate and ionize a finite amount of material without unacceptable disturbance to the equilibrium; if this load is exceeded or if the solid particles are too large, undissociated material passes through the plasma and deposits on the sample cone orifice, resulting in a loss of sensitivity.[12] The spark condition is defined by three parameters: resistance ($R$), voltage ($V$) and repetition rate (sparks per second) ($f$). This condition, and consequently burn, is stronger with decreasing $R$, and with increasing $V$ or $f$. Particle size increases with increasing applied voltage, but not with increasing repetition rate. Consequently, a high repetition rate is to be preferred to a high voltage, because the finer the particles the better the stability in the plasma. The system was optimized by studying one variable at a time, even though the three variables in the system are inter-related. The objective was to establish the optimum conditions defined as the operating setting for achieving a representative sample input with the best reproducibility.

Some of the earliest work performed on ICP-MS clearly showed that the system was not tolerant to solutions containing significant amounts of dissolved solids. Depending on the specific matrix, it is usual to limit analyte solutions to a total content of dissolved solids of nominally $<2000$ μg ml$^{-1}$. When nebulizing an Fe solution containing this maximum recommended level of dissolved solids (0.2% m/v Fe (NO$_3$)$_3$ $<$ $>$0.05% m/v Fe) with a pneumatic nebulizer (estimated efficiency 1%) and a sample uptake rate of 1 ml min$^{-1}$, approximately 5 μg min$^{-1}$ of Fe would arrive in the plasma. Consequently, in order to obtain high sensitivities from the sparking system and to avoid signal drift and progressive blocking of the sampling aperture, the aerosol rate produced by spark ablation should be comparable to that produced by pneumatic nebulization in analysis with liquids. Spark sampling efficiency was determined by trapping the particles obtained from the spark sampling process. In order to measure the sampling rates directly, the output of the spark chamber was passed through a Teflon filter with a pore diameter of 0.2 μm, with a view to collecting the particles in the stream. The collection efficiency was monitored by passing the filtered argon flow into an ICP-MS instrument to measure Fe, and comparing the intensities obtained with and without the filter; a collection efficiency of better than 98% was found. Particles were collected on the filter for 3 min and, after sampling, the filters were dissolved in a solution containing 1.5 ml of *aqua regia* diluted to 25 ml with water. The resulting solutions were then analysed for Fe by ICP-AES. It was found that the best stability and the most reproducible values were obtained at the highest repetition rate available (400 Hz), a resistance of 2.2 $\Omega$ and a voltage of 500 V. It was observed that with voltages below 500 V the spark is too soft not to be dependent on the hardness of the steel sample. On the other hand, stronger conditions (higher voltage and lower resistance) will lead to higher ablation rates promoting the formation of large-sized particles which can no longer be used for ICP-MS measurements. Under the aforementioned operating conditions, which had to be applied in order to obtain stable and reproducible aerosols, the amount of sample eroded from iron and low-alloyed steel was about 75 μg min$^{-1}$, which is too high for use in ICP-MS analysis, producing signal drift and blocking the sampling cones.

The size distributions of the particles produced by the spark fall into several distinct types: irregularly shaped particles that are believed to be ablated material (most of the ablated particles were between 1 and 3 μm, although particles as large as 10 μm were observed); spheres $<1$ μm in diameter; and aggregates of spherical particles up to several micrometres in diameter that are formed from melted material. Figs. 2 and 3
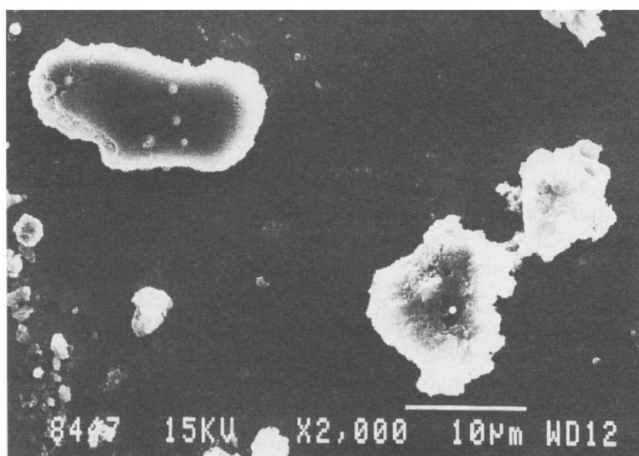
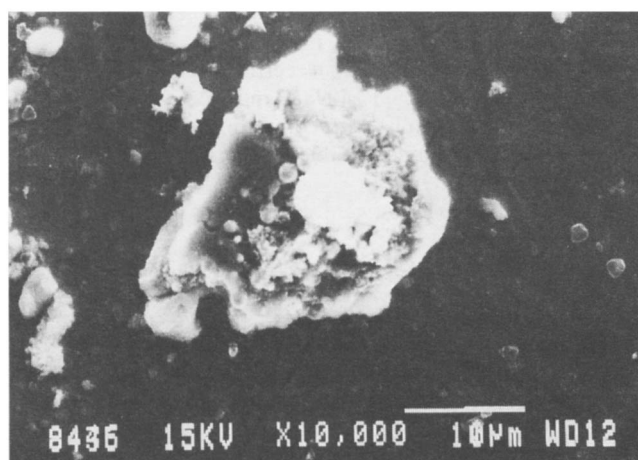**Fig. 2** Some of the spark sampling particles obtained from CRM SS-459/1



**Fig. 3** One of the largest ablated particles

show some of the spark sampling particles obtained from CRM SS-459/1. Repetition rate, spark current waveform and sample matrix may play an important role in determining the relative populations of these groups. Whenever there is evidence of melting, distillation effects will cause systematic error, requiring calibration standards and samples to be closely matched.

In order to regulate particle size and reduce the amount of aerosol reaching the ICP-MS system, a cyclone device was installed between the spark chamber and the ICP torch.[13] The cyclone operates by imparting a spiral motion to the aerosol, as a result of which, and owing to the higher angular momentum, particles of larger diameter tend preferentially to impact the walls of the chamber and therefore not reach the plasma. Control of the aerosol particle size by the cyclone leads to a more uniform particle size distribution, thereby improving the precision of measurements and preventing deposition of material on the sampling cones. A carrier gas flow rate of 1.0 ml min$^{-1}$ was found to be a good compromise for stable sparking, efficient analyte removal, optimum analyte excitation and lowest memory effects.

The efficiency of the cyclone device was tested by trapping the particles reaching the ICP torch; these particles were removed from the end of the tube which transports the analyte from the cyclone to the ICP, aided by the argon gas flow, by introducing the end of the tube into an acidic solution (5 ml of *aqua regia* + 20 ml of water). After completion of the dissolution process by heating, the iron content of these solutions was determined by ICP-MS and found to be

$4.0 \pm 0.3$ µg min$^{-1}$. This indicates that the sampling efficiency obtained with the sparking technique from iron and low-alloyed steel samples, and using the cyclone device, is comparable to that obtained in the analysis of solids after dissolution. Moreover, the particles collected on a Nuclepore filter located downstream of the cyclone device were chiefly < 1 µm in diameter; only occasionally were spherical particles measuring a few micrometres in diameter observed under the sparking conditions applied (Fig. 4). It was concluded that complete vaporization of such particles in the ICP is likely to occur.

### ICP-MS Measurements

Plots of intensity *versus* time for all the analytes in CRM SS-459/1 are shown in Figs. 5 and 6. As the software displays the emission of only six elements simultaneously, two groups of five analytes are presented in each figure together with the [58]Fe isotope, used as internal standard. All the elements gave similarly shaped signals which remained near the maximum value for the duration of the burn. As shown in Figs. 5 and 6 the intensity reached its maximum value after 30 s and remained essentially constant at least for the duration of the spark ablation-ICP-MS measurement (60 s). This result shows that little, if any, differential sampling was occurring.

Consequently, and under the spark conditions selected ($f = 400$ Hz, $V = 500$ V, $R = 2.2$ Ω and Ar flow rate = 1.0 l min$^{-1}$), a pre-spark time of 30 s was found to be sufficient to obtain steady-state analyte volatilization and excitation.

For quantitative analysis, spark emission spectrometry has traditionally used the ratio of the analyte emission intensity to
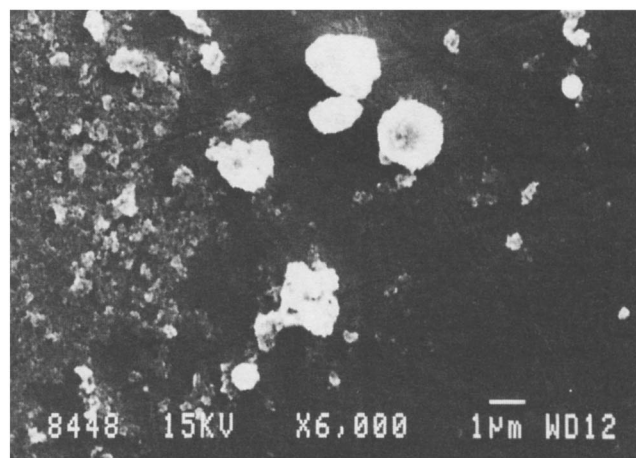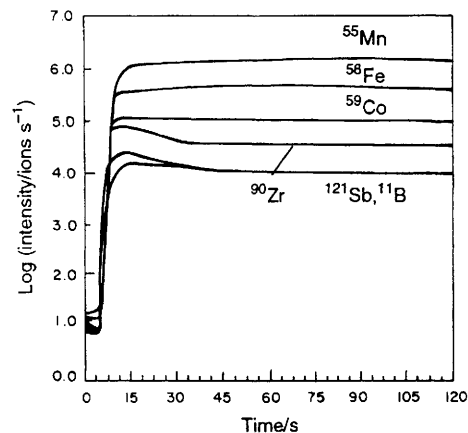


**Fig. 4** Size of particles downstream of the cyclone



**Fig. 5** Intensity *versus* time profiles for [58]Fe, [55]Mn, [59]Co, [90]Zr, [121]Sb and [11]B from CRM SS-459/1
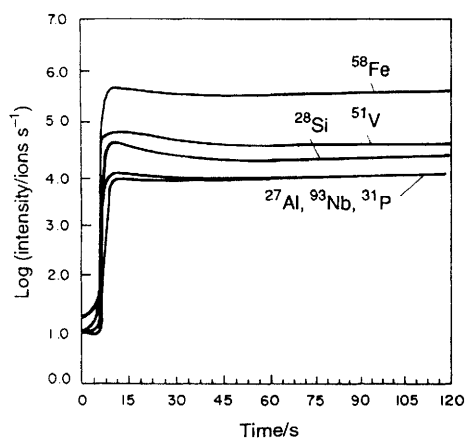
**Fig. 6** Insensity *versus* time profiles for $^{58}$Fe, $^{51}$V, $^{27}$Al, $^{93}$Nb, $^{28}$Si and $^{31}$P from CRM SS-459/1

an appropriate spectral line intensity of a matrix element as an internal standard. This approach is also used in spark sampling ICP spectrometry. In this work, relative intensities were ratioed to the $^{58}$Fe isotope, used as internal standard. It was necessary to use the iron isotope of lowest abundance (relative abundance = 0.33) because the other iron isotopes produced too high a signal. The potential spectral overlap interference produced by the possible presence of Ni is foreseen by applying the programmed corrections of the ELAN 5000

software. The use of intensity ratios enables the relative standard deviations ($s_r$) of repetitive sparkings at one location and of sparkings at different locations on the same sample to be decreased. The $s_r$ values ranged from 3 to 7% when the relative intensities were compared; however, when the $^{58}$Fe isotope was used as internal standard most of the $s_r$ values were lower than 3%.

After verifying the linearity of the mass intensity counts *versus* analyte concentrations, within the interval of the concentrations considered, only two samples were employed for calibration, *i.e.*, 'low' and 'high'. The BAM CRM 098/1 (pure iron) was used as the 'low' standard and the BAS CRM carbon steel (SS-456/1 to SS-460/1) with the highest content of the corresponding analyte as the 'high' standard.

The measuring conditions were chosen such that a sequence of the 11 isotopes analysed, in the peak hop scanning mode, resulted in a replicate time of 1 min.

Using the above calibration graphs, the remainder of the samples of the series SS-456/1 to SS-460/1 were analysed as unknowns. The agreement between the certified values and the results obtained, listed in Table 2, proved the accuracy of the developed method.

By plotting intensities *versus* certified values for all the CRMs used, *viz.*, BAM CRM098/1 and BAS CRMs SS-456/1 to SS-460/1, linear graphs with correlation coefficients greater than 0.996 were obtained. Table 3 shows the parameters of these graphs.

Detection limits (DLs) were calculated as three times the

**Table 2** Certified values and results obtained (%, $n=6$) for the analysis of BAS CRMs SS-456/1 to SS-460/1. Values in parentheses are standard deviations. Values for BAM CRM 098/1, used as the 'low' calibration sample, are given in $\mu g\ g^{-1}$

| Element | | CRM 098-1* | CRM 456/1† | CRM 457/1† | CRM 458/1† | CRM 459/1† | CR < 460/1† |
|---|---|---|---|---|---|---|---|
| Si | Certified | 'Low'‡ | 0.225 (0.009) | 0.060 (0.005) | 0.547 (0.020) | 'High'‡ | 0.090 (0.005) |
| | Found | 4.8 (1.6) | 0.24 (0.01) | 0.051 (0.002) | 0.54 (0.02) | 0.58 (0.01) | 0.098 (0.006) |
| Mn | Certified | 'Low' | 0.207 (0.004) | 0.285 (0.006) | 0.498 (0.025) | 'High' | 0.665 (0.022) |
| | Found | 0.8 (0.6) | 0.20 (0.01) | 0.30 (0.01) | 0.40 (0.01) | 0.97 (0.02) | 0.67 (0.01) |
| P | Certified | 'Low' | 0.0169 (0.0015) | 0.0107 (0.0010) | 0.0330 (0.0025) | 'High' | 0.0405 (0.0040) |
| | Found | 0.6 | 0.018 (0.001) | 0.010 (0.001) | 0.032 (0.002) | 0.054 (0.002) | 0.043 (0.002) |
| Al | Certified | 'Low' | 0.0078 (0.0002) | 'High' | 0.0229 (0.0007) | 0.0277 (0.0005) | 0.0135 (0.0008) |
| | Found | 2.8§ | 0.009 (0.001) | 0.111 (0.004) | 0.023 (0.002) | 0.028 (0.002) | 0.012 (0.001) |
| B | Certified | 'Low' | 0.0015 (0.0002) | 0.0027 (0.0005) | 0.0063 (0.0008) | 'High' | 0.0029 (0.0003) |
| | Found | <0.1 | 0.0015 (0.0002) | 0.0025 (0.0002) | 0.0061 (0.0002) | 0.0118 (0.0005) | 0.0028 (0.0002) |
| Co | Certified | 'Low' | 0.0551 (0.0027) | 0.0233 (0.0009) | 'High' | 0.1120 (0.0015) | 0.0135 (0.0008) |
| | Found | <0.1§ | 0.052 (0.001) | 0.023 (0.001) | 0.21 (0.01) | 0.109 (0.004) | 0.014 (0.001) |
| Nb | Certified | 'Low' | 0.0059 (0.0002) | 0.0231 (0.0007) | 0.0530 (0.0012) | 0.0150 (0.0003) | 'High' |
| | Found | 0.02§ | 0.006 (0.001) | 0.022 (0.001) | 0.052 (0.003) | 0.014 (0.002) | 0.066 (0.004) |
| V | Certified | 'Low' | 0.0240 (0.0004) | 'High' | 0.1060 (0.0015) | 0.0793 (0.0010) | 0.0612 (0.0007) |
| | Found | 0.31§ | 0.022 (0.001) | 0.166 (0.006) | 0.108 (0.004) | 0.080 (0.004) | 0.060 (0.004) |
| Zr | Certified | 'Low' | 0.0203 (0.0002) | 0.0053 (0.0002) | 0.0510 (0.0010) | 'High' | 0.055 (0.0001) |
| | Found | 0.05§ | — | 0.006 (0.001) | 0.050 (0.003) | 0.072 (0.003) | 0.006 (0.001) |
| Sb | Certified | 'Low' | 0.0115 (0.0007) | 0.0378 (0.0018) | 'High' | 0.0071 (0.0004) | 0.0040 (0.0002) |
| | Found | <0.1§ | 0.012 (—) | 0.038 (0.002) | 0.072 (0.003) | 0.0063 (0.0002) | 0.0038 (0.0004) |

\* Values in $\mu g\ g^{-1}$.
† Values in %.
‡ 'Low' and 'high': samples used for calibration.
§ Values obtained by flow injection-ICP-MS.

**Table 3** Parameters of the calibration graphs obtained for BAM CRM 098/1 and BAS CRMs SS-456/1 to SS-460/1

| Element | Slope | Intercept | Root mean square | Correlation coefficient | Concentration range (%) |
|---|---|---|---|---|---|
| Si | 3.200 | 0.13828 | 0.07115 | 0.9985 | 0.00048–0.58 |
| Mn | 12.441 | 2.57871 | 0.04035 | 0.9971 | 0.00008–0.97 |
| P | 0.591 | 0.00398 | 0.00248 | 0.9965 | 0.00006–0.054 |
| Al | 3.768 | 0.00368 | 0.00431 | 0.9990 | 0.00028–0.111 |
| B | 0.354 | 0.00109 | 0.00017 | 0.9970 | 0–0.0118 |
| Co | 2.723 | 0.01239 | 0.01053 | 0.9990 | 0–0.21 |
| Nb | 6.157 | 0.00296 | 0.00625 | 0.9989 | 0–0.066 |
| V | 4.335 | 0.00696 | 0.01585 | 0.9985 | 0.00003–0.166 |
| Zr | 7.492 | 0.00190 | 0.00633 | 0.9977 | 0–0.072 |
| Sb | 1.636 | 0.00309 | 0.00178 | 0.9995 | 0–0.072 |

**Table 4** DLs (3s) and precision (s_r, n = 6) at concentrations levels of ten times the DL

| Element | DL/µg g$^{-1}$ | $s_r$ (%) |
|---------|----------------|-----------|
| Si | 1.5 | 2.5 |
| Mn | 0.12 | 2.5 |
| P | 2.5 | 1.8 |
| Al | 0.32 | 2.2 |
| B | 2.1 | 1.2 |
| Co | 0.15 | 0.9 |
| Nb | 0.08 | 1.8 |
| V | 0.10 | 0.7 |
| Zr | 0.11 | 0.6 |
| Sb | 0.30 | 0.6 |

**Table 5** Comparison of DLs (µg g$^{-1}$) obtained for Al, Nb and V by ICP-MS and ICP-AES

| Element | DL (3s): ICP-MS | DL (2s): ICP-AES* |
|---------|-----------------|-------------------|
| Al | 0.32 | 3.0 |
| Nb | 0.08 | 4.5 |
| V | 0.10 | 2.0 |

* Values from ref. 11.

standard deviation of the signal intensities corresponding to the pure iron sample BAM CRM098/1. Since this iron sample is not of 100% purity, this will give reasonable values for elements present below the true DL. For elements present at higher concentrations the procedure will give DLs larger than the true values. Table 4 lists the DLs and the $s_r$ values for concentration levels of ten times the DL. The $s_r$ values were calculated from six repetitive sparkings at various locations on the sample. These values are comparable to those obtained by continuous nebulization from a 0.05% m/v iron solution. Table 5 compares the DLs (2s) obtained with spark ablation-ICP-AES[11] for Al, Nb and V, with the DLs (3s) achieved in this work.

Conditions for the two methods differ; in particular, spark source parameters (R, V and f), carrier gas flow rate and pressure and internal standardization are associated with unique considerations, and were optimized for each technique in order to improve the quality of the analysis. The sparking conditions used for ICP-AES measurements were stronger (700 V, 0 Ω, 400 Hz) and the eroded analyte was transported directly to the plasma torch, with a view to improving sensitivity and power of detection.

## CONCLUSION

A study of the analysis of bulk samples using spark ablation to generate the aerosol has shown the potential of this sampling system for ICP-MS analysis, and has confirmed that it is a useful means for the direct analysis of conducting materials. However, one of the fundamental difficulties of introducing solid particles into an ICP-MS instrument is the possibility of solid deposition on the sampling cone; in this work it was found that the use of an appropriate cyclone device makes it possible to control the particle size and aerosol uptake rate to a degree comparable to that achieved with continuous nebulization from an Fe solution with the maximum recommended level of total solids. The major advantages of the spark ablation sampling system in comparison with continuous nebulization are the ease with which samples can be prepared, sample dissolution is not required and, the air, solvent and solute do not contribute to the spectral background; however, the spark efficiency depends on the sample matrix, requiring the use of matrix-matched calibration samples. Detection limits comparable to those obtained with continuous nebulization and satisfactory precision values, better than 2.5% at concentrations of ten times the DL, have been obtained.

In conclusion, spark ablation is a valid sampling system for the simultaneous determination of P, Si, Mn, Nb, Al, V, B, Co, Zr and Sb in low-alloyed steels by ICP-MS.

## REFERENCES

1 Kuss, H. M., Bossmann, D., and Müller, M., *At. Spectrosc.*, 1994, **15**, 148.
2 Vaughan, M. A., and Horlick, G., *J. Anal. At. Spectrom.*, 1989, **4**, 45.
3 Paul, M., and Völlkopf, U., *Fresenius' Z. Anal. Chem.*, 1989, **334**, 680.
4 Moore, J. A. F., McGuire, M. J., and Hart, P. A., *Plasma Source Mass Spectrometry II*, Royal Society of Chemistry Special Publication, Royal Society of Chemistry, Cambridge, 1993, p. 150.
5 Gustavsson, I., and Larson, H., in *Proceedings of 3rd International Conference on Progress of Analytical Chemistry in the Iron and Steel Industry*, ed. Nauche, R., Commission of European Communities, Brussels, 1992, p. 193.
6 Kuss, H. M., Bossman, D., and Müller, M., in *Proceedings of 3rd International Conference on Progress of Analytical Chemistry in the Iron and Steel Industry*, ed. Nauche, R., Commission of European Communities, Brussels, 1992, p. 201.
7 Kuss, H. M., Müller, M., and Bossman, D., *Chem. Listy*, 1992, **86**, 623.
8 Scheeline, A., and Coleman, D. M., *Anal. Chem.*, 1987, **59**, 1185A.
9 Jiang, S. J., and Houk, R. S., *Anal. Chem.*, 1986, **58**, 1739.
10 Jakubowski, N., Feldmann, I., Sack, B., and Stuewer, D., *J. Anal. At. Spectrom.*, 1992, **7**, 121.
11 Gomez Coedo, A., Dorado Lopez, M. T., Jimenez Seco, J. L., and Gutierrez Cobo, I., *J. Anal. At. Spectrom.*, 1992, **7**, 11.
12 Jarvis, K. E., Gray, A. L., and Houk, R. S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*, Blackie, London, 1992, p. 280.
13 Stefan, I., and Vujicic, G., *Spectrochim. Acta, Part B*, 1992, **47**, 61.