

# Quantitative Analysis of Small Metal Fragments by LA-ICP-MS

## Introduction

A number of well-established techniques, including spark source optical emission spectrometry (SSOES) and X-ray fluorescence (XRF), deliver accurate, precise and relatively fast analysis of steels, typically providing analysis of an area of several cm<sup>2</sup>. Both techniques require samples of a certain shape, a minimum size and particular surface preparation qualities. In most cases, analyses at the cm scale are perfectly acceptable and the provision of the required sample geometry presents no problem. There are, however, a number of situations in which these requirements can not be met:

- ▶ Analysis of small features or inclusions
- ▶ Analysis of fragments / millings / turnings
- ▶ Forensic applications
- ▶ Failure analysis of specific sample zones
- ▶ Composition changes - small sample areas

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is able to generate analyses from any size or shape of sample. This study shows the power of the technique to analyse very small and irregularly shaped sample sizes, using certified reference materials in the form of millings/turnings, as “unknown” samples.

## Calibration

Instrument calibration was achieved using 8 flat geometry steel setting-up samples (BAS UK), typically “certified” to 2 or 3 significant figures. Pieces cut from all 8 samples were mounted together in the ablation cell (Figure 1).

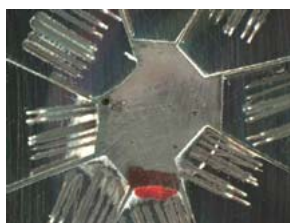


Figure 1: Eight BAS steel samples in the ablation cell

Ablation positions were defined on each piece and calibration data were acquired from all pieces in an unattended procedure. The samples included low-alloy and highly-alloyed steels. Some elements varied from ppm levels to high % levels (e.g. Cr). Fe content varied from 61% to 99%. In this challenging application, reference was made to an internal standard element (Fe) during calibration, but not during the analysis of samples. Close attention was paid to the use of identical laser ablation conditions for all standards and all samples, to ensure that instrument response was as uniform as possible throughout.

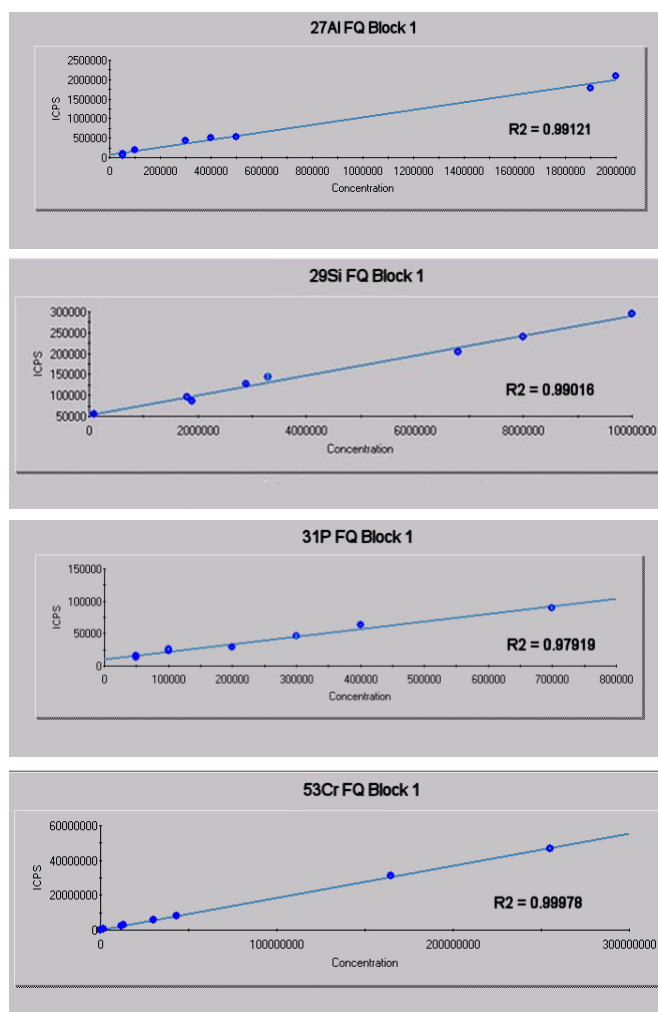


Figure 2: Four calibration curves for trace-to-major element content. Al, Si and P were chosen as examples of “less easy” elements. Many alloying elements show the correlation illustrated by the Cr curve. All calibrations were linear – an important characteristic of mass spectrometry, compared with SSOES.

## Bulk Sample Analysis

Having calibrated the instrument, the setting-up samples were re-analyzed as unknowns. As expected, analytical values were close to the reference values, as may be seen in Table 1.

Small pieces of a certified reference material (NBS) were used to assess the ability of this technique to analyze very small samples. The largest dimension of each sample turning was of the order of a few millimetres and the thickness was usually of the



**NEW WAVE**  
RESEARCH



	Al		P		V		Cr		Nb		Mo		Sn	
	Cert	LA	Cert	LA	Cert	LA	Cert	LA	Cert	LA	Cert	LA	Cert	LA
A/8	.04	.04	.005	.01	.005	.001	.02	.03	.01	---	.005	.002	.005	.001
D/11	.19	.19	.01	.02	.12	.11	3.0	3.1	.05	.05	1.3	1.3	.01	.01
C/17	.05	.05	.07	.08	.42	.42	.18	.20	.02	.03	.11	.11	.06	.07
H/5	.2	.16	.04	.06	.33	.33	1.3	1.1	.11	.09	.42	.45	.03	.03
G/5	.005	.006	.03	.04	.06	.07	16.5	12.9	.005	.003	2.2	2.2	.01	.02
E/4	.03	.04	.01	.02	.03	.04	4.3	3.6	1.1	1.2	.97	.98	---	.002
B/6	.01	.02	.005	.01	.01	.01	1.2	1.2	.005	.006	.20	.21	.01	.01
F/4	.005	.004	.02	.03	.05	.05	25.5	23.4	.005	.001	3.5	3.4	.01	.02

Table 1: Comparison of LA-ICP-MS values with certified values (bulk samples). All data % (w/w)

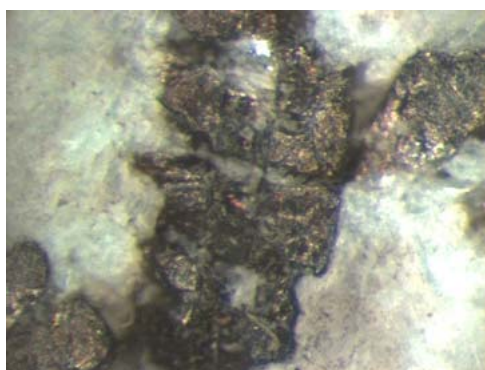


Figure 3: Small steel turning (width ~1mm) mounted on boric acid.

Sample i.d.		Al	Si	Mn	Ni	Cr	V	Mo	Cu	Sn
SS5 (bulk)	Ref	.057	.625	1.11	.565	.96	.265	1.41	.24	.007
	Sample	.065	.70	1.05	.61	.98	.25	1.28	.24	.007
	SD	.006	.028	.057	.036	.052	.014	.073	.014	<.001
NBS d33 milling	Ref	---	1.55	1.80	1.03	1.15	---	---	---	---
	Sample	.37	1.59	1.66	1.1	1.2	.003	.02	0.09	0.01
	SD	.015	.017	.030	.010	.011	<.001	<.001	.003	<.001

Table 2: Comparison of LA-ICP-MS values with certified values (steel fragment and bulk analyses). All data % (w/w)

order of a few hundred microns (a couple of hair thicknesses). For proper analysis, depth penetration rate and sampling time should be coordinated to avoid penetration of very thin samples. The pre-ablation period was therefore limited to a few seconds to preserve the sample integrity. Small samples such as these require mounting to prevent them moving under the acoustic shock of each laser pulse and so they were presented to the laser chamber on pressed boric acid mounts. Preparation of the mounts was very simple. The turnings were placed in the bottom of a compression die and boric acid powder was added on top. This was compressed, resulting in a firm boric acid pellet with the steel turnings exposed for ablation at one of its circular surfaces (Figure 3).

## Summary

Many small sample geometries may be analyzed by LA-ICP-MS with accuracy and precision independent of sample form. Sample preparation is minimal and any shape of sample may be simply mounted for presentation to the laser sampling system.

## Acknowledgements

Dr. Walter Grillo and Dr. Massimo Godano  
Fiat, Turin, Italy



www.new-wave.com

### USA

New Wave Research, Inc  
48660 Kato Road  
Fremont CA 94538-7339  
Tel: 510-249-1550  
Tel: 800-566-1743  
Fax: 510-249-1551  
Email: [Lasers@new-wave.com](mailto:Lasers@new-wave.com)

### Japan

New Wave Research, KK  
5F Chojiya Building, 1-36-4,  
Shinjuku-ku, Shinjuku  
Tokyo, 160-0022 Japan  
Tel: +81-3-3351-0131  
Fax: +81-3-3351-0121  
Email: [NewWaveKK@new-wave.com](mailto:NewWaveKK@new-wave.com)

### Taiwan

New Wave Research G. C. Co., Ltd.  
2FL, No. 118, Shinhu 3 Rd.,  
Neihu Dist., Taipei  
Taiwan 114  
Tel: 886-2-8792-7585  
Fax: 886-2-8792-7584  
Email: [NewWaveGC@new-wave.com](mailto:NewWaveGC@new-wave.com)

### Europe

New Wave Research Co. Ltd.  
Suite B Oak Park Business Centre  
Alington Road  
Eynesbury, St Neots  
Cambs PE19 6WA, England, UK  
Tel: 44-(0)1480 403325  
Fax: 44-(0)1480 476899  
Email: [NewWaveEU@new-wave.com](mailto:NewWaveEU@new-wave.com)

### Shanghai

Room 606, Dragon Pearl Complex  
2123, Pudong Road, Pudong,  
Shanghai, China  
Tel: 86-21-5860-9889  
Fax: 86-21-5860-0424