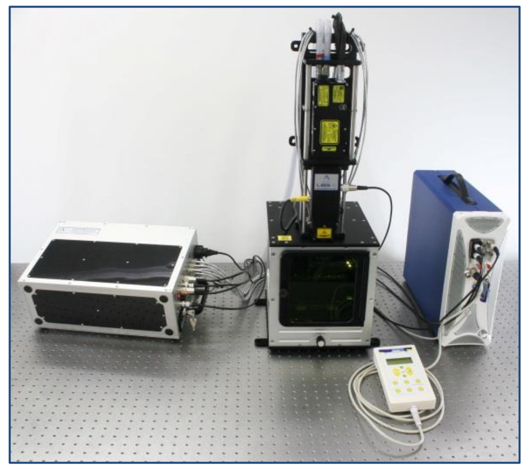
Technical Note 4:
A comparison of the analytical performance of an Echelle Multiplex Unit (EMU) spectrometer with a low-cost multi-channel spectrometer using an APL modular LIBS system

APPLIED PHOTONICS
LASER SPECTROSCOPY SOLUTIONS

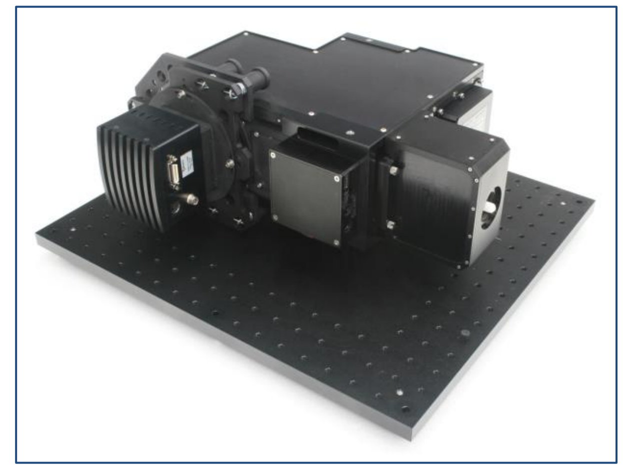
Introduction

This technical note describes a performance comparison of two different spectrometer configurations utilising an APL benchtop modular LIBS instrument. One configuration used a low-cost, medium-resolution, multi-channel spectrometer (APL SpectroModule-6, fitted with six Avantes AvaSpec HR 2048 compact spectrometers) referred to in this note as SM-6, and the other configuration used a high-resolution echelle spectrometer (Catalina Scientific EMU 120/65 fitted with a Raptor Photonics Falcon Blue EMCCD camera) referred to in this note as EMU. The two LIBS instrument configurations were used to generate calibration curves for Cr, Ni and Si where ten Certified Reference Materials (CRMs) were used as calibration standards. As far as possible, measurement conditions were replicated in both series of experiments so as to achieve a more meaningful comparison of the performance of each of the two spectrometers. The analytical performance of the two configurations of LIBS equipment were compared in terms of the respective calibration curves and associated analytical figures of merit (Limit Of Detection-LOD, Relative Standard Deviation-RSD etc.) derived from the experimental data.

SpectroModule-6
Multiple Czerny-Turner optical configuration
Six input fibres of 200 or 400 µm core diameter (connects to all six channels of LIBS-6 module)
Wavelength range approx. 185 - 900 nm
Resolving power: ≈ 4,800 @ 285 nm, ≈ 6,000 @ 360 nm, ≈ 5,600 @ 450 nm
Spectrum file size ≈ 150 KB
Low cost
Compact and rugged



APL modular LIBS system (LIBS-6 module, Quantel Ultra laser 100 mJ 1064 nm laser and XYZ-750 sample chamber) with SpectroModule-6 LIBS spectrometer

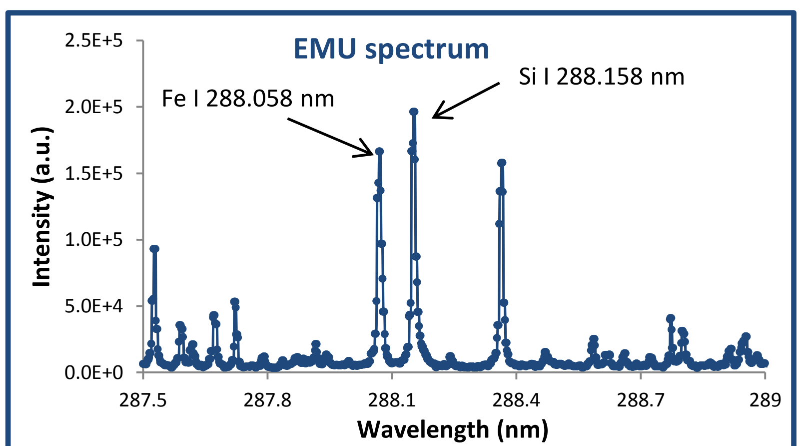


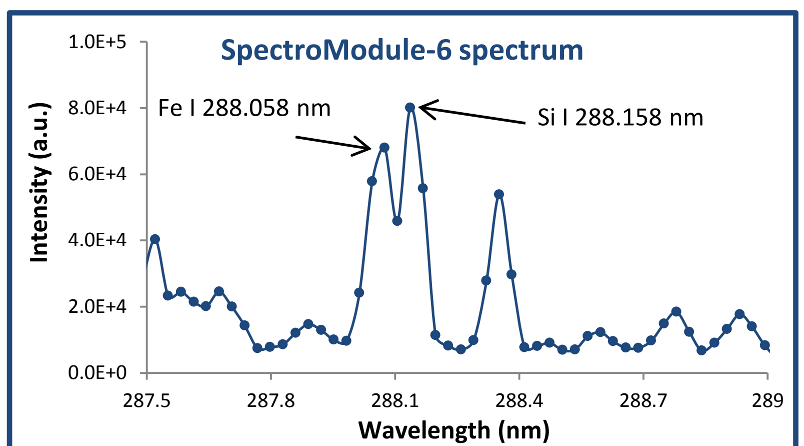
EMU 120/65 high-resolution echelle spectrometer fitted with a EMCCD camera

EMU 120/65 spectrometer and EMCCD camera
Echelle optical configuration
Single input fibre of 400 µm core diameter (connects to one channel of LIBS-6 module)
Wavelength range approx. 190 - 1100 nm
Average resolving power: ≈ 42,000
Image file size ≈ 4MB
High optical throughput – up to f/2
Adjustable gain capability

Spectral resolution comparison

The detection of Si in an Fe matrix, a well-known problem in LIBS due to the proximity between the Si emission line at 288.158 nm and the Fe emission line at 288.058 nm, was selected as an example to illustrate the resolving power of each system. The figures below display the performance of the EMU and the SM-6 when it comes to spectrally resolving two (or more) adjacent emission lines.

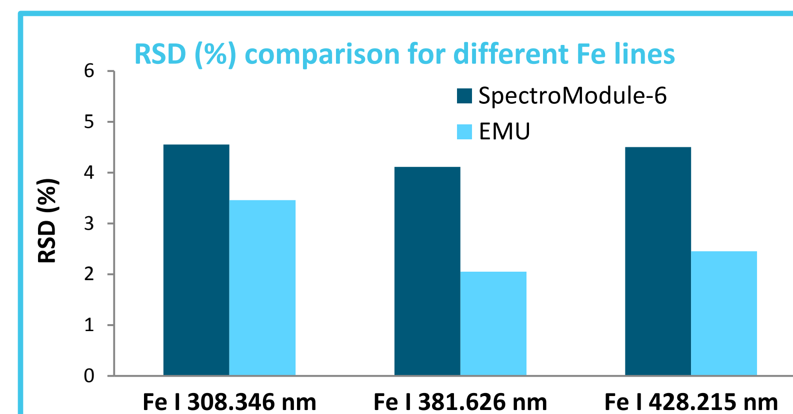




The spectrum acquired with the EMU displays a better resolution together with an increase in the number of sampling points. The latter would allow for more reliable data processing including the definition of peak limits, calculation of area under the peaks, baseline definitions, spectrum deconvolution, etc.

Measurement precision (RSD)

Comparison of the Relative Standard Deviation (RSD). A certified steel sample was analysed and the RSD of 10 replicate measurements was computed for several well-resolved Fe lines. In both cases, RSDs less than 5% were obtained with slightly improved reproducibility for the EMU spectrometer.



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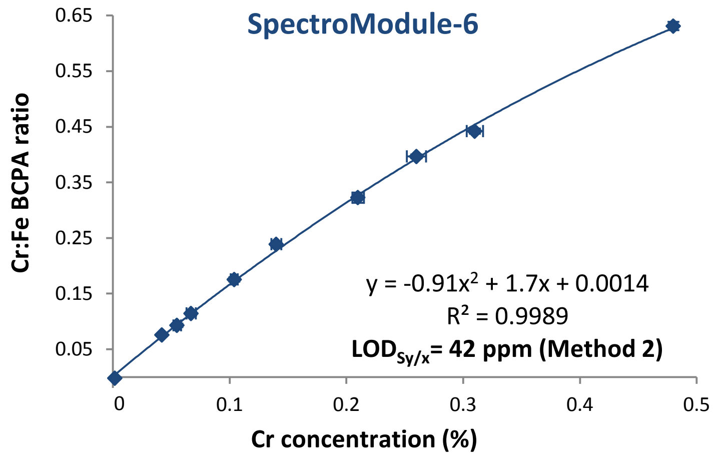
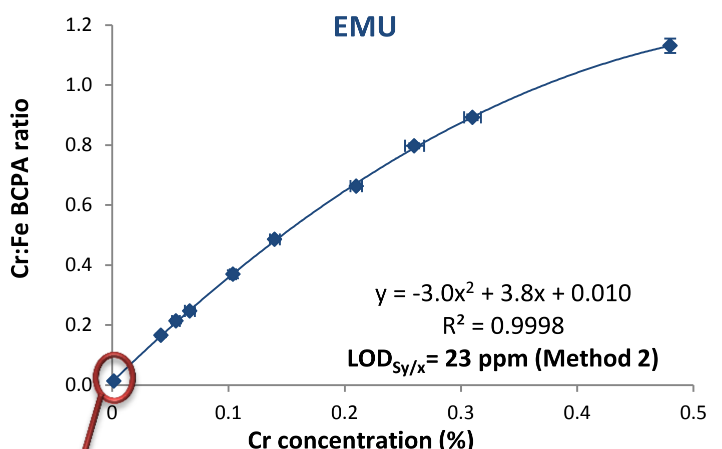
Calibration curves

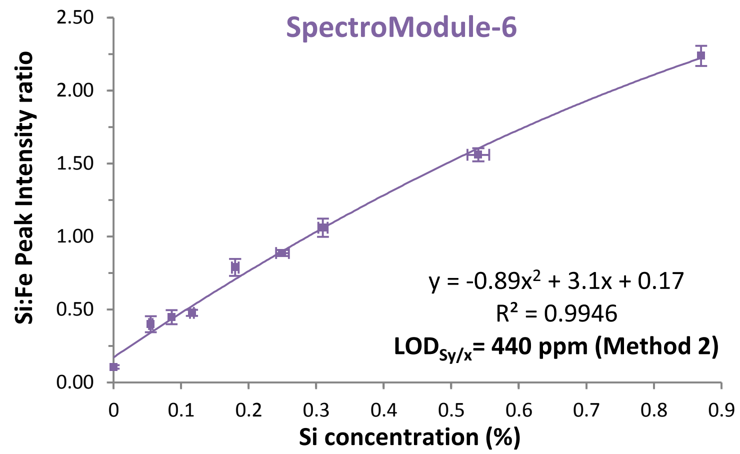
For the construction of the calibration curves, 10 replicate measurements per sample were acquired (50 cleaning/100 accumulation laser shots per measurement). The power density at the sample was estimated to be 15 GW/cm^2 and air was used as purge gas. All calibration curves were constructed using APL LIBSoft software; some with the Baseline-Corrected Peak Area ratio approach (BCPA ratio) and some with the peak intensity ratio approach, selecting always the one that gave the best result. The LOD was estimated using the standard error of the regression, $s_{y/x}$ (i.e. Method 2 as described in *Technical Note 1*). For more details on the experimental parameters for each spectrometer refer to *Technical Notes 2* and *3*.

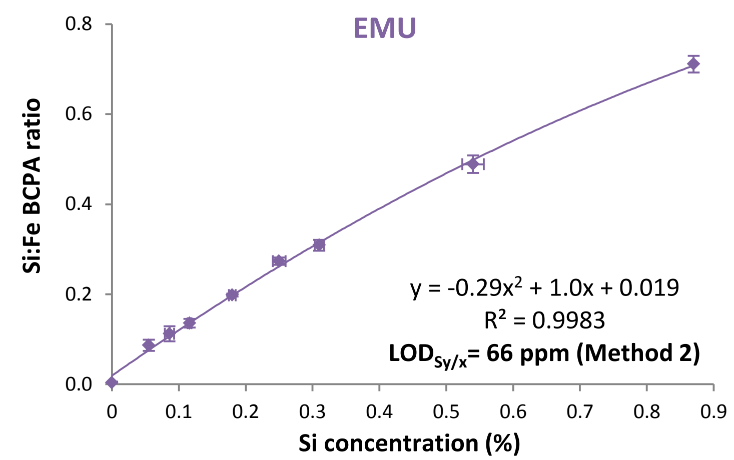
Cr calibration curve
Analyte/Matrix emission line: Cr I 425.435 nm/Fe I 428.240 nm



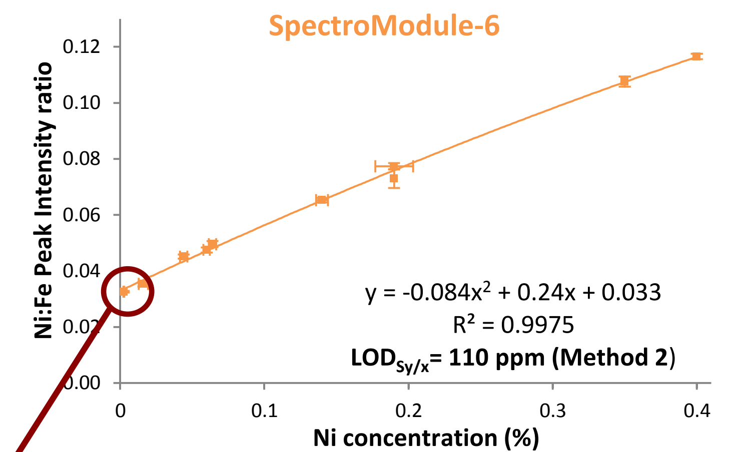


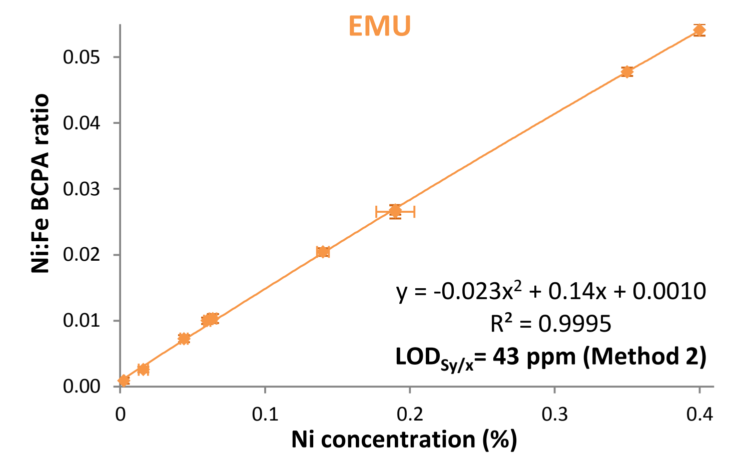
Si calibration curve
Analyte/Matrix emission line: Si I 288.158 nm/Fe I 308.374 nm



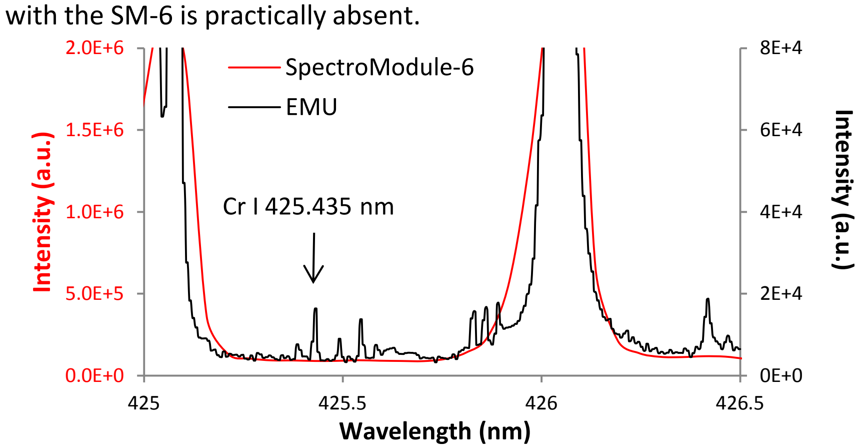


Ni calibration curve
Analyte/Matrix emission line: Ni I 351.505 nm/Fe I 381.584 nm





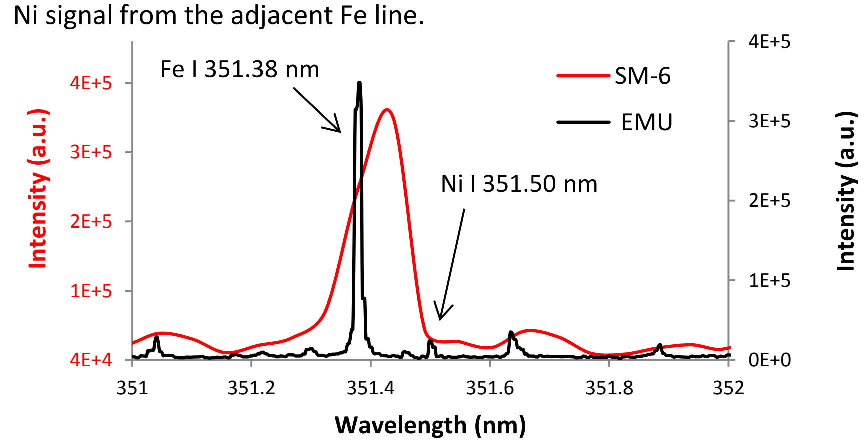
Comparison of the spectra obtained for a sample with 16 ppm Cr. The Cr emission line at 425.435 nm is clearly visible with the EMU, while with the SM-6 is practically absent.



Conclusions

The choice of spectrometer used with LIBS depends on many factors including price, performance etc. If the resolution demands of the LIBS application are not too high, the SpectroModule-6 spectrometer, or even a single channel version of it, could provide the required analytical performance and at a relatively low cost. For more demanding applications of LIBS, the high performance (resolution, throughput, etc.) of the EMU spectrometer provides an excellent solution.

The Ni calibration curve does not pass close to the origin due to the lower resolving power of the SM-6 that results in a contribution to the Ni signal from the adjacent Fe line.



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