Quantitative Elemental Analysis of Metal Ions in Aqueous Solutions by Electrodeposition-assisted Laser-induced Breakdown Spectroscopy (EA-LIBS)

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One of the key feasibility issues with molten salt reactors is the corrosion of the structural materials. The integrity of structural materials should be verified to operate reactors in optimal conditions, but it is hard to analyze the structural materials directly in operating reactors. Therefore, we developed an electrodeposition-assisted laser-induced breakdown spectroscopy (EA-LIBS) system to evaluate the degree of corrosion in structural materials by measuring the concentration of corrosion products in coolants. EA-LIBS is an elemental analysis method that electrochemically deposit target metal ions in a solution to a working electrode and analyze it by laser spectroscopic sensing techniques. EA-LIBS system was tested in an aqueous solution evironnment before proceeding in a high-temperature molten salt environment. $NiCl_2$ and $FeCl_2$, which are typical corrosion products in molten salt reactors, were dissolved into deionized water with enough supporting electrolyte, Na2SO4. Then, electrodepositions of Ni(II) and Fe(II) were performed to the glassy carbon electrodes at -0.9 V (vs. SCE reference electrode) for two miniutes. These electrodes were analyzed by LIBS under optimal conditions of laser energy, delay time, and gate width. To assess the detection sensitivity of the EA-LIBS system, calibration curves for nickel and iron were obtained and limit of detections (LODs) were calculated. LODs for nickel and iron were 1.475 ppm and 9.033 ppm, respectively, and both are much smaller than the actual concentration of 20-150 ppm of the MSR coolant. Then, electrochemical and spectroscopic data was analyzed in terms of concentrations of each element in a solution. The results showed charges applied to the electrode during deposition had a linear relationship with concentrations of metal ions in a solution, which implies that the total amount of deposition could be obtained by measruing the charge. Similarly, ratio of nickel and iron LIBS peak intensities is proportional to the concentration of each element. It is expected that the metal ions in a solution could be measured both qualitatively and qunatitatively by combining this information.

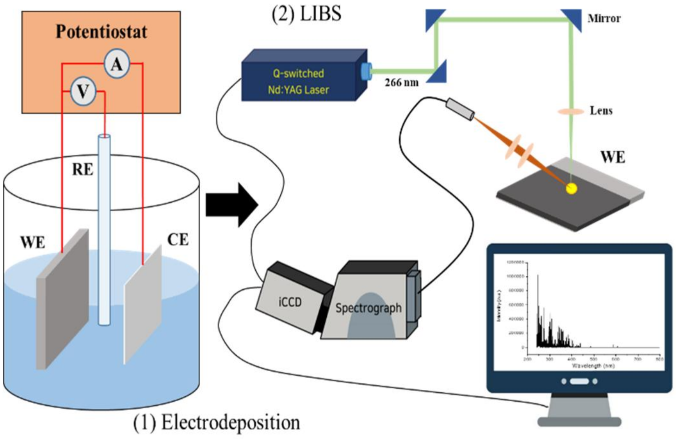
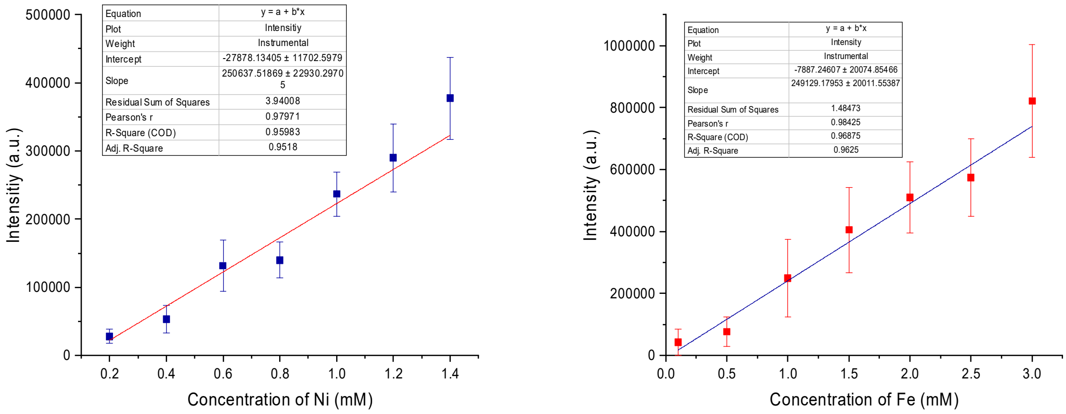


Fig. 1. Experimental setup of EA-LIBS for trace detection of Ni(II) and Fe(II).



Equation	y = a + b*x
Plot	Intensitiy
Weight	Instrumental
Intercept	-27878.13405 ± 11702.5979
Slope	250637.51869 ± 22930.2970 5
Residual Sum of Squares	3.94008
Pearson's r	0.97971
R-Square (COD)	0.95983
Adj. R-Square	0.9518

Equation	y = a + b*x
Plot	Intensity
Weight	Instrumental
Intercept	-7887.24607 ± 20074.85466
Slope	249129.17953 ± 20011.55387
Residual Sum of Squares	1.48473
Pearson's r	0.98425
R-Square (COD)	0.96875
Adj. R-Square	0.9625

Fig. 2 EA-LIBS calibration curves for nickel and iron.

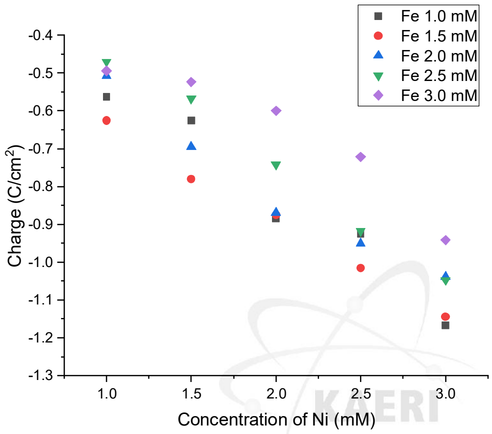


Fig 3. Plot of charge applied to the electrode system versus the concentration of Ni(II) and Fe(II).

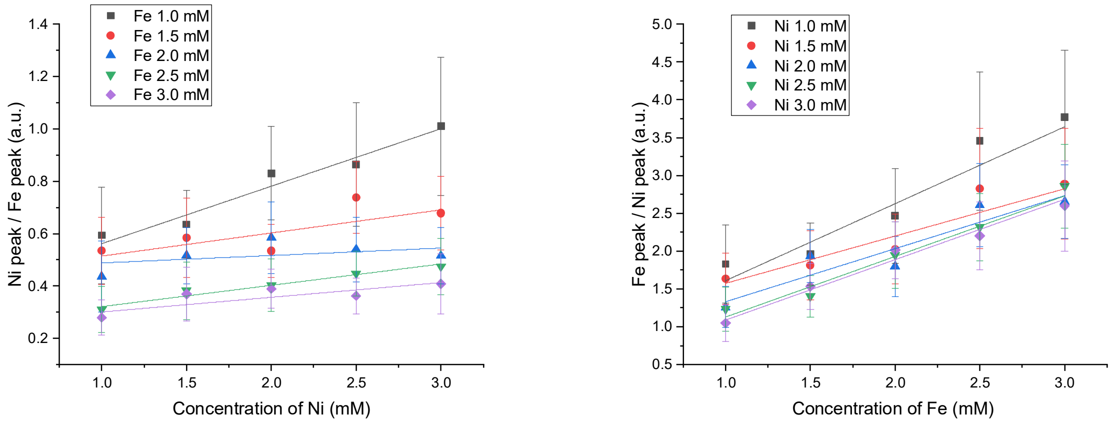


Fig 4. Plot of ratio of EA-LIBS peak intensities of Ni and Fe versus the concentration of Ni(II) and Fe(II).