Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Supplementary material

List of selected spectral lines characteristics – NIST 1411 glass.

Element	λ (nm)	Z	Ei (eV)	Ek (eV)	Ak (s-1)	gi (-)	gk (-)	C (%)
Mg II	279.55	12	0.00	4.43	2.60E+08	2	4	0.14
Ba II	493.41	56	0.00	2.51	9.53E+07	2	2	4.06
Mg II	280.27	12	0.00	4.42	2.57E+08	2	2	0.14
Sr II	421.55	38	0.00	2.94	1.28E+08	2	2	0.07
Ca II	393.37	20	0.00	3.15	1.47E+08	2	4	1.21
Ca II	396.85	20	0.00	3.12	1.40E+08	2	2	1.21
Ba II	455.40	56	0.00	2.72	1.11E+08	2	4	4.06
Si II	413.09	14	9.84	12.84	1.74E+08	6	8	27.09
Ca II	315.89	20	3.12	7.05	3.10E+08	2	4	1.21
Si I	288.16	14	0.78	5.08	2.17E+08	5	3	27.09
K I	766.49	19	0.00	1.62	3.78E+07	2	4	2.46
Na I	589.00	11	0.00	2.10	6.16E+07	2	4	7.52
Al I	309.27	13	0.01	4.02	7.29E+07	4	6	2.95
Al I	394.40	13	0.00	3.14	4.99E+07	2	2	2.95
Zn I	330.26	30	4.03	7.78	1.20E+08	3	5	2.58
Mg I	285.21	12	0.00	4.35	4.91E+08	5	3	0.14
Zn I	334.50	30	4.08	7.78	1.70E+08	5	7	2.58
Al I	396.15	13	0.01	3.14	9.85E+07	4	2	2.95
B I	249.77	5	0.00	4.96	1.68E+08	4	2	3.44
Mg I	389.19	12	7.17	10.36	1.77E+08	3	5	0.14
Mg I	285.21	12	0.00	4.35	4.91E+08	1	3	0.14
Ca I	422.67	20	0.00	2.93	2.18E+08	1	3	1.21

List of selected spectral lines characteristics – EB316 aluminum alloy.

Element	λ (nm)	Z	Ei (eV)	Ek (eV)	Ak (s-1)	gi (-)	gk (-)	C (%)
Mg II	279.55	12	0.00	4.43	2.60E+08	2	4	0.05
Mg II	280.27	12	0.00	4.42	2.57E+08	2	2	0.05
Sr II	421.55	38	0.00	2.94	1.28E+08	2	2	0.03
Si II	413.09	14	9.84	12.84	1.74E+08	6	8	11.98
Si I	288.16	14	0.78	5.08	2.17E+08	5	3	11.98
Al I	309.27	13	0.01	4.02	7.29E+07	4	6	87.00
Al I	394.40	13	0.00	3.14	4.99E+07	2	2	87.00
Zn I	330.26	30	4.03	7.78	1.20E+08	3	5	0.06
Zn I	334.50	30	4.08	7.78	1.70E+08	5	7	0.06
Al I	396.15	13	0.01	3.14	9.85E+07	4	2	87.00
Si I	288.16	14	0.78	5.08	2.17E+08	5	3	11.98

Mg I	285.21	12	0.00	4.35	4.91E+08	1	3	0.05
Fe I	404.58	26	1.48	4.55	8.62E+07	9	9	0.11
Fe I	406.36	26	1.56	4.61	6.65E+07	9	7	0.11
Cu I	324.75	29	0.00	3.82	1.40E+08	2	4	0.03
Cu I	327.40	29	0.00	3.79	1.38E+08	2	2	0.03
Mn I	403.08	25	0.00	3.08	1.70E+07	6	8	0.20
Mn II	294.92	25	1.17	5.38	1.96E+08	5	7	0.20
Ni I	301.20	28	0.42	4.54	1.30E+08	5	5	0.02
Ni I	352.45	28	0.03	3.54	1.00E+08	7	5	0.02
Ni II	231.60	28	1.04	6.39	2.88E+08	10	8	0.02

List of selected spectral lines characteristics – SUS-1R steel alloy.

Element	**λ (nm)**	**Z**	**Ei (eV)**	**Ek (eV)**	**Ak (s-1)**	**gi (-)**	**gk (-)**	**C (%)**
Fe I	368.75	26	0.86	4.22	8.00E+06	7	9	88.91
Fe I	372.26	26	0.09	3.42	4.97E+06	3	5	88.91
Fe I	372.76	26	0.96	4.28	2.24E+07	7	5	88.91
Fe I	373.49	26	0.86	4.18	9.01E+07	11	11	88.91
Fe I	373.71	26	0.05	3.37	1.41E+07	7	9	88.91
Fe I	374.34	26	0.99	4.30	2.60E+07	9	3	88.91
Fe I	374.95	26	0.91	4.22	7.63E+07	9	9	88.91
Fe I	375.82	26	0.96	4.26	6.34E+07	11	7	88.91
Fe I	376.38	26	0.99	4.28	5.44E+07	1	5	88.91
Fe I	376.55	26	3.24	6.53	9.51E+07	13	15	88.91
Fe I	382.04	26	0.86	4.10	6.67E+07	11	9	88.91
Fe I	382.78	26	1.56	4.80	1.05E+08	11	5	88.91
Fe I	387.25	26	0.99	4.19	1.05E+07	5	5	88.91
Fe I	389.97	26	0.09	3.27	2.58E+06	5	5	88.91
Fe I	390.29	26	1.56	4.73	2.14E+07	7	7	88.91
Fe I	404.58	26	1.48	4.55	8.62E+07	9	9	88.91
Fe I	406.36	26	1.56	4.61	6.65E+07	9	7	88.91
Cr I	425.44	24	0.00	2.91	3.15E+07	7	9	1.70
Si I	288.16	14	0.78	5.08	2.17E+08	5	3	0.8
Mo I	379.83	42	0.00	3.26	6.90E+07	7	9	0.90
Ni I	301.20	28	0.42	4.54	1.30E+08	5	5	2.90
Ni I	352.45	28	0.03	3.54	1.00E+08	7	5	2.90
Ni II	231.60	28	1.04	6.39	2.88E+08	10	8	2.90
Cu I	324.75	29	0.00	3.82	1.40E+08	2	4	0.70
Cu I	327.40	29	0.00	3.79	1.38E+08	2	2	0.70
Co I	345.35	27	0.43	4.02	1.10E+08	10	12	0.30

Physical and mechanical properties of the samples. HV is hardness by Vickers, R reflectivity, Lv latent heat, Cp specific heat, Tb is boiling point. The material properties were measured and subtracted from material tables.

	Glass	Steel	Al alloy
HV (-)	980	180	95
R (%)	0.78	0.96	0.90
Lv(J/kg)	750	247	396
Cp(J/g °C)	0.84	0.47	0.22
Tb(°C)	3265	2870	2480

Signal-to-Background ratio derivation

The particular spectral line intensity in absence of self-absorption for plasma in local thermodynamic equilibrium (LTE) is given by following expression [40]:

$$ {}^{q}I_{ij}^{S} = \left(\frac{h\nu}{4\pi}\right) {}^{q}n^{S} \frac{A_{ij}^{S} g_i^{S}}{{}^{q}U^{S}(T)} \exp\left(\frac{-E_i^{S}}{k_B T_{exc}}\right), \quad (2) $$

where ${}^{q}I_{ij}^{S}$ (eV cm^{-3} s^{-1}) is the intensity of atomic or ionic line of element S, *q* is the ionization stage, *i,j* are the indexes of the higher and lower energetic quantum states of the same ionization stage *q*, ${}^{q}n^{S}$ (cm^{-3}) is the total number density of species *S*, A_{ij}^{S} (s^{-1}) is the transition probability of upper level of species *S*, g_i^{S} (dimensionless) is degeneracy of the upper level, E_i^{S} (eV) is the excitation energy of upper level, T_{exc} (K) is the excitation temperature, k_B (eV K^{-1}) is the Boltzmann constant, h (eV.s) is the Planck constant and $qU^{S}(T)$ $(dimensionless)$ is internal partition function of selected species at temperature T_{exc} (K):

$$ qU^{S}(T) = \sum_i g_i e^{\frac{-E_i^{S}}{k_B T}}. \quad (3) $$

The Saha equilibrium relation between the number density of neutral and singly ionized species is given by:

$$ n_e \frac{IIn^{S}}{In^{S}} = \frac{(2\pi m_e k_B T_{ion})^{\frac{3}{2}} 2IIU^{S}(T)}{h^3 IU^{S}(T)} e^{\frac{-E_{ion}^{S} - \Delta E_{ion}}{k_B T_{ion}}}, \quad (4) $$

where n_e (cm^{-3}) is the electron density, In^{S} and IIn^{S} (cm^{-3}) are the number densities of neutral and singly ionized species *S*, $IU^{S}(T)$ and $IIU^{S}(T)$ are the partition functions of respective species *S* indicated by superscript *I* and *II*, E_{ion}^{S} (eV) is the ionization energy of the respective element, ΔE_{ion} the lowering in ionization energy and m_e (g) is the electron mass. By using Saha equation (4), the equation (2) becomes:

$$ {}^{q}I_{ij}^{S} = \left(\frac{h\nu}{4\pi}\right) n_e \, {}^{II}n^{S} T_{ion}^{-3/2} \frac{A_{ij}^{S} g_i^{S}}{2 \, {}^{II}U^{S}(T)} \frac{h^3}{(2\pi m k_B)^{3/2}} \left[\exp\left(\frac{E_{ion}^{S} - \Delta E_{ion}}{k_B T_{ion}} - \frac{E_i^{S}}{k_B T_{exc}} \right) \right]. \quad (5) $$

As stated above the plasma continuum radiation results from recombination of ions and electrons and from interactions of free electrons with the electrical fields of ions (Bremsstrahlung). The expression for the continuum emission coefficient $I_c(\lambda)$ in terms of wavelengths is given by equation (6) [35]:

$$I_c(\lambda)=\left(\frac{16\pi e^6}{3c^2\left(6\pi m^3 k_B\right)^{1/2}}\right)\frac{n_e\,{}^{II}n^S}{\lambda_c^2 T_{ion}^{1/2}}\left[\xi\left(1-\exp\frac{-hc}{\lambda k_B T_{ion}}\right)+G\exp\frac{-hc}{\lambda k_B T_{ion}}\right], \quad (6)$$

where *G* and ξ are the correction factors. *G is* the free-free Gaunt factor and ξ corrects free-bound continuum radiation. The values of *G* and ξ has been calculated for several gases as a function of temperature and electron density. Finally the signal to continuum ratio (SBR) is given by:

$$SBR(\lambda)=\left(\frac{h^4 3^{3/2} c^3}{256\pi^3 e^6 k_B}\right)\frac{A_{ij}^S g_i^S}{{}^{II}U^S(T)}\left(\frac{\lambda}{\Delta\lambda_{meas}}\right)\frac{1}{T_{ion}}\frac{\exp\left(\frac{-E_i^S}{k_B T_{exc}}\right)\exp\left(\frac{-E_{ion}^S-\Delta E_{ion}}{k_B T_{ion}}\right)}{\left[\xi\left(1-\exp\frac{-hc}{\lambda k_B T_{ion}}\right)+G\exp\frac{-hc}{\lambda k_B T_{ion}}\right]}. \quad (7)$$

Determination coefficient R^2:

$$R^2=1-\frac{SS_{res}}{SS_{tot}},$$

$$SS_{tot}=\sum_i (y_i-\underline{y})^2,$$

$$SS_{res}=\sum_i (y_i-f_i)^2,$$

where y_i is the *i*-th value from the observed dataset, $\underline{y}$ *is the mean of observed data,* f_i is the predicted value associated with y_i. SS_{tot} is the total sum of squares (proportional to the variance of the data) and SS_{res} is the sum of squares of residuals.

Average determination coefficient and standard deviation for 30 best performing ANN architectures. Activation function of all ANN was logistic function.

Number of neurons		Determination coefficient R2	
Layer 1	Layer 2	mean	sd
45	23	0.967	0.005
43	18	0.967	0.004
50	37	0.966	0.008
23	41	0.966	0.002
46	19	0.965	0.004
47	30	0.965	0.002
43	15	0.965	0.004
40	16	0.965	0.002
35	25	0.965	0.001
42	18	0.964	0.004
47	31	0.964	0.003
46	26	0.964	0.005
32	44	0.964	0.008

49	32	0.964	0.003
23	35	0.963	0.002
50	23	0.963	0.004
43	29	0.962	0.004
20	42	0.962	0.011
46	25	0.962	0.004
31	25	0.962	0.007
32	42	0.961	0.005
37	23	0.961	0.007
37	26	0.961	0.007
29	15	0.960	0.003
47	21	0.960	0.003
34	29	0.960	0.002
36	30	0.960	0.006
37	33	0.960	0.005
23	33	0.959	0.006
44	30	0.959	0.006

Selected spectral lines with selected quantum parameters and R^2 (reference vs predicted SNR).

Element	Wavelength	Ek	Ak	gk	Determination coefficient R2	
					mean	sd
Fe I	406.36	4.61	6.65E+07	7	0.890	0.071
Ba II	455.40	2.72	1.11E+08	4	0.880	0.051
Mg I	280.27	4.42	2.57E+08	2	0.874	0.124
Si I	413.09	12.84	1.74E+08	8	0.869	0.111
Al I	396.15	3.14	9.85E+07	2	0.856	0.025
Al I	394.40	3.14	4.99E+07	2	0.815	0.210
Zn I	330.26	7.78	1.20E+08	5	0.800	0.146
Mg I	279.55	4.43	2.60E+08	4	0.777	0.251
Al I	309.27	4.02	7.29E+07	6	0.773	0.100
Ca I	315.89	7.05	3.10E+08	4	0.727	0.090
Si I	288.16	5.08	2.17E+08	3	0.682	0.326
Cu I	324.75	3.82	1.40E+08	4	0.677	0.089
Fe I	404.58	4.55	8.62E+07	9	0.655	0.187
Fe I	387.25	4.19	1.05E+07	5	0.654	0.092
Na I	589.00	2.10	6.16E+07	4	0.619	0.041
B I	249.77	4.96	1.68E+08	2	0.588	0.478
Mn I	294.92	5.38	1.96E+08	7	0.560	0.140
Zn I	334.50	7.78	1.70E+08	7	0.529	0.271
K I	766.49	1.62	3.78E+07	4	0.519	0.173
Fe I	390.29	4.73	2.14E+07	7	0.508	0.279
Sr II	421.55	2.94	1.28E+08	2	0.477	0.056

Mg I	285.21	4.35	4.91E+08	3	0.449	0.127
Mg I	389.19	10.36	1.77E+08	5	0.431	0.282
Cu I	327.40	3.79	1.38E+08	2	0.429	0.245
Fe I	389.97	3.27	2.58E+06	5	0.421	0.186
Fe I	374.95	4.22	7.63E+07	9	0.399	0.127
Ca I	393.37	3.15	1.47E+08	4	0.377	0.216
Fe I	376.38	4.28	5.44E+07	5	0.322	0.086
Ba II	493.41	2.51	9.53E+07	2	0.295	0.343
Ca I	396.85	3.12	1.40E+08	2	0.286	0.276
Al I	394.40	3.14	4.99E+07	2	0.283	0.068
Fe I	372.76	4.28	2.24E+07	5	0.277	0.060
Fe I	382.04	4.10	6.67E+07	9	0.252	0.225
Fe I	382.78	4.80	1.05E+08	5	0.202	0.084
Al I	309.27	4.02	7.29E+07	6	0.195	0.108
Cr I	425.44	2.91	3.15E+07	9	0.191	0.197
Ni I	352.45	3.54	1.00E+08	5	0.186	0.300
Mn I	403.08	3.08	1.70E+07	8	0.141	0.098
Fe I	376.55	6.53	9.51E+07	15	0.137	0.077
Fe I	375.82	4.26	6.34E+07	7	0.130	0.101
Fe I	373.49	4.18	9.01E+07	11	0.115	0.159
Zn I	334.50	7.78	1.70E+08	7	0.100	0.133
Fe I	373.71	3.37	1.41E+07	9	0.081	0.056
Fe I	368.75	4.22	8.00E+06	9	0.073	0.047
Co I	345.35	4.02	1.10E+08	12	0.069	0.044
Ni I	301.20	4.54	1.30E+08	5	0.067	0.053
Fe I	374.34	4.30	2.60E+07	3	0.066	0.018
Zn I	330.26	7.78	1.20E+08	5	0.062	0.047
Ni I	231.60	6.39	2.88E+08	8	0.055	0.052
Fe I	372.26	3.42	4.97E+06	5	0.041	0.020