Trace Element Peak Fitting

Introduction

The goal of this procedure is to fit several trace element emission lines to retrieve their peak areas and from that their concentrations. The trace elements that are considered for quantification are lithium (Li), rubidium (Rb), strontium (Sr), and barium (Ba). Only peak areas are computed for chromium (Cr) and manganese (Mn). In Table 1 we describe the wavelength of the emission lines we consider for these elements, the wavelength range that is considered and the wavelengths of the interfering emission lines, when present.

Element	Wavelength (nm)	Wavelength range (nm)	Interfering lines (nm)
Li	670.97	668.5 – 673.5	670.12, 671.95
Rb	780.24	779.3 – 781.0	
Sr	421.67	421.4 – 422.25	422.055
Ba	455.5	454.4 – 456.2	454.6, 455.09, 455.38, 455.68
Cr	425.19	424.5 – 425.9	424.862, 425.55
Mn	403.19,403.42,403.5	402.8 – 403.9	

Table 1: characteristics of the trace elements

To fit these emission lines we use an IDL code named MPFIT developed by Craig B. Markwardt [1]. It uses a Levenberg-Marquardt minimization scheme and can be found here http://purl.com/net/mpfit.

Fitting details and area computation.

Each emission line is fit using a Voigt function, and a parabolic function is used for the baseline.

Constraints are added during the fit:
- The amplitude of the line is positive
- The location of the line is bounded by [λ-dλ: λ+dλ] where λ is the initial location of the line and dλ is the maximum wavelength step in the wavelength range listed in Table 1.
- The Gaussian width (σ) and the Lorentzian width (γ) of the Voigt profile are bounded by [0.5*dλ: 5.0*dλ].

Special case for Ba:
Since the Ba line is embedded with four other lines and is often weak, the above described constraints are not sufficient to obtain a good fit. With that algorithm the computed Ba area still varies a lot due to the interfering lines. To solve this issue, we add an additional constraint that ties the emission locations to the location of a more intense nearby emission line. This is justified by the fact that the locations of each line are quantified and perfectly known (NIST database for reference), while the ChemCam wavelength calibration is not quite perfect. This additional constraint gives much more stable results.

The quality of the fit is determined in two steps:
- If MPFIT returns a status value less than 0, an error occurred and the area is set to NaN.
- Else if a combination of the Chi^2 and the error on the area is larger than a certain threshold then the fit is poor

- In that case we retry to fit using the tied version described above.
- If the fit is still poor the area is set to -999.
- Else the area is returned.

To retrieve the area, we compute the fit function on a X-axis having 1000 points and bounds that are $\pm 10*(\sigma + \gamma)$. The area is then computed using a trapezoidal rule

Concentration computation.

The concentrations are computed for Li, Rb, Sr, and Ba. They are retrieved using regression laws that were determined using a laboratory database (more than 400 samples) [2] that displays diverse compositions that are more relevant for Gale crater than the previous ChemCam database [3]. These models are based on univariate calibration curves. For each element, the best model is selected depending on the results obtained by using the ChemCam calibration targets onboard Curiosity [4]. The Limit of Detection (LoD) is also determined for these elements

Root Mean Square Error (RMSE) computation.

For each element, the RMSE is determined as a function of the concentration. This is done by using the following procedure:
- Apply a moving average on the quadratic error using 10, 20, 30 & 40 points
- Take the square root to get RMSE
- Sample the range of values in deciles
- Compute the square root of the mean of quadratic error for each decile.
- Identify ranges with similar RMSE.
- Fit a power law through these errors to get their function in terms of the concentrations.

The LoDs and the laws to compute the RMSE in function of the concentration are displayed in Table 2.

Element	RMSE (ppm)	LoD (ppm)
Li	0.0279*ct + LoD	4.6
Rb	3.e-4*ct^2 + 0.0289*ct + LoD	26.0
Sr	0.2*ct + LoD	87.0
Ba	1.e-4*ct^2 + 0.1131*ct + LoD	121.0

Table 2: LoDs and RMSE laws for the quantified minor elements where 'ct' is the concentration

Outputs.

Two tables are generated.
- The first one (Trace Element Area (TEA)) contains the areas for the trace elements. A -999 value is listed when the fit went wrong (Table 3).
- Six additional comment columns are added (one for each element) that have:
  - Blank
  - "poor fit" when the fit failed

- The second one (Trace Element Concentration (TEC)) contains the concentration and its related RMSE. A -999 value is listed when the fit went wrong. In the case the concentration is lower than the LoD ,the RMSE is set to the LoD (Table 4).

- Four additional comment columns are added (one for each element) that have:
  - Blank
  - "poor fit" when the fit failed
  - " < LoD" when the concentration is below the LoD

File	Target	Li	Cr	Mn	Rb	Sr	Ba	Li Comment	Cr Comment	Mn Comment	Rb Comment	Sr Comment	Ba Comment
CL5_555507542CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-1	0.00032042	6.35E-05	4.07E-05	-999	1.09E-05	4.43E-06				poor fit		
CL5_555507611CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-2	0.00057206	6.04E-05	5.88E-05	3.04E-05	1.30E-05	5.55E-06						
CL5_555507675CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-3	0.00031441	6.05E-05	5.57E-05	0.0001373	1.05E-05	8.52E-06						
CL5_555507778CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-4	0.00030176	3.43E-05	3.82E-05	-999	2.38E-05	5.36E-06				poor fit		
CL5_555507973CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-5	0.0004668	5.87E-05	6.04E-05	0.00011369	1.35E-05	9.97E-06						
CL5_555508036CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-6	0.00048898	5.53E-05	5.47E-05	0.00011263	9.32E-06	3.99E-06						
CL5_555508141CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-7	0.00050409	4.94E-05	5.77E-05	6.30E-05	3.40E-05	6.81E-06						
CL5_555508337CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-8	0.00048228	6.35E-05	5.83E-05	0.0001891	3.63E-05	4.64E-06						
CL5_555508400CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-9	0.00049266	4.11E-05	5.55E-05	-999	1.20E-05	4.83E-06				poor fit		

Table 3: Example of output for the Trace Element Area (TEC) file

File	Target	Li (ppm)	rmse (ppm)	Rb (ppm)	rmse (ppm)	Sr (ppm)	rmse (ppm)	Ba (ppm)	rmse (ppm)	Li Comment	Rb Comment	Sr Comment	Ba Comment
CL5_555507542CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-1	11.3	4.9	-999	-999	19.6	87	8.4	121		poor fit	< LoD	< LoD
CL5_555507611CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-2	20.8	5.2	8.5	26	23.7	87	10.6	121		< LoD	< LoD	< LoD
CL5_555507675CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-3	11.1	4.9	38.7	27.6	18.9	87	16.3	121			< LoD	< LoD
CL5_555507778CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-4	10.6	4.9	-999	-999	45.3	87	10.2	121		poor fit	< LoD	< LoD
CL5_555507973CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-5	16.8	5.1	31.9	27.2	24.6	87	19.1	121			< LoD	< LoD
CL5_555508036CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-6	17.6	5.1	31.6	27.2	16.7	87	7.6	121			< LoD	< LoD
CL5_555508141CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-7	18.2	5.1	17.6	26	67.5	87	13	121		< LoD	< LoD	< LoD
CL5_555508337CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-8	17.4	5.1	53.5	28.4	72.8	87	8.8	121			< LoD	< LoD
CL5_555508400CCS_F0642790CCAM01780P3.CSV	Huckins_Ledge-9	17.8	5.1	-999	-999	21.8	87	9.2	121		poor fit	< LoD	< LoD

Table 4: Example of output for the Trace Element Concentration (TEC) file

References

[1] Markwardt, C. B. 2009, "Non-Linear Least Squares Fitting in IDL with MPFIT," in proc. *Astronomical Data Analysis Software and Systems XVIII*, Quebec, Canada, ASP Conference Series, Vol. 411, eds. D. Bohlender, P. Dowler & D. Durand (Astronomical Society of the Pacific: San Francisco), p. 251-254 (ISBN: 978-1-58381-702-5.

[2] Clegg S.M., Wiens R.C., Anderson R.B., Forni O., Frydenvang J., Lasue J., Pilleri A., Payre V., Boucher T., Dyar M.D., McLennan S.M., Morris R.V., Graff T.G., Mertzman S.A., Ehlmann B.L., Bender S.C., Tokar R.L., Belgacem I., Newsom H., McInroy R.E., Martinez R., Gasda P., Gasnault O., and Maurice S. (2017) Recalibration of the Mars Science Laboratory ChemCam instrument with an expanded geochemical database. Spectrochim. Acta B, 129, 64-85.

[3] Wiens R.C., Maurice S., Lasue J., Forni O., Anderson R.B., Clegg S., Bender S., Barraclough B.L., Deflores L., Blaney D., Perez R., Lanza N., Ollila A., Cousin A., Gasnault O., Vaniman D., Dyar M.D., Fabre C., Sautter V., Delapp D., Newsom H., Melikechi N., and the ChemCam team (2013) Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover. Spectrochim. Acta B, 82, 1-27, http://dx.doi.org/10.1016/j.sab.2013.02.003. LA-UR-13-23023.

[4] Payré, V., and 16 colleagues (2017), Alkali trace elements in Gale crater, Mars, with ChemCam: Calibration update and geological implications. Journal of Geophysical Research (Planets) 122, 650-679.