

Refine, Validate, and Report

Refinement is simply a way to improve the fit between the measured intensities and the intensities calculated from the model. The peaks in the difference map and the list of worst fitting peaks usually suggest which actions are appropriate to improve the next refinement. If the peaks in the difference map are in the locations of hydrogens, then add hydrogens. If the difference map peaks are near ($< 0.7 \text{ \AA}$) isotropically-refined atoms, then let those atoms refine anisotropically. If the difference map peaks are near anisotropically-refined atoms, then consider a disordered model. Although performing the tasks below in this order may seem slow, refinement that is carried out too quickly may lead to a false, local minimum but not the true global minimum. Each time continue to refine the model to convergence, $\max(|\text{shift}/\text{esd}|) < 0.05$.

1. Refine all atoms with isotropic displacement parameters and without hydrogens.
2. Refine heavy atoms with anisotropic displacement parameters.
3. Add hydrogens to carbons with a riding model. Use difference maps to locate hydrogen(s) bonded to atoms such as N or O.
4. Refine all non-hydrogen atoms anisotropically. (Steps 3 and 4 are sometimes switched.)
5. Change the weighting scheme to make the GoF or S value to be closer to 1.0. This step may need to be done several times.
6. Check for inappropriate peaks in the difference map or inappropriate displacement parameters. (This may suggest twinning or disorder.)
7. Check for the presence of secondary extinction.
8. Check for correct absolute structure.

It is often valuable to use some molecular editor program to speed up analysis of peaks in the Fourier maps. The programs Shelxle, Olex, ORTEP, and XP are among the more commonly used programs. The first three programs in the list are free to academics. The program Shelxle is recommended in this lab because it offers the user nearly complete control of the atom parameters file throughout the refinement process.

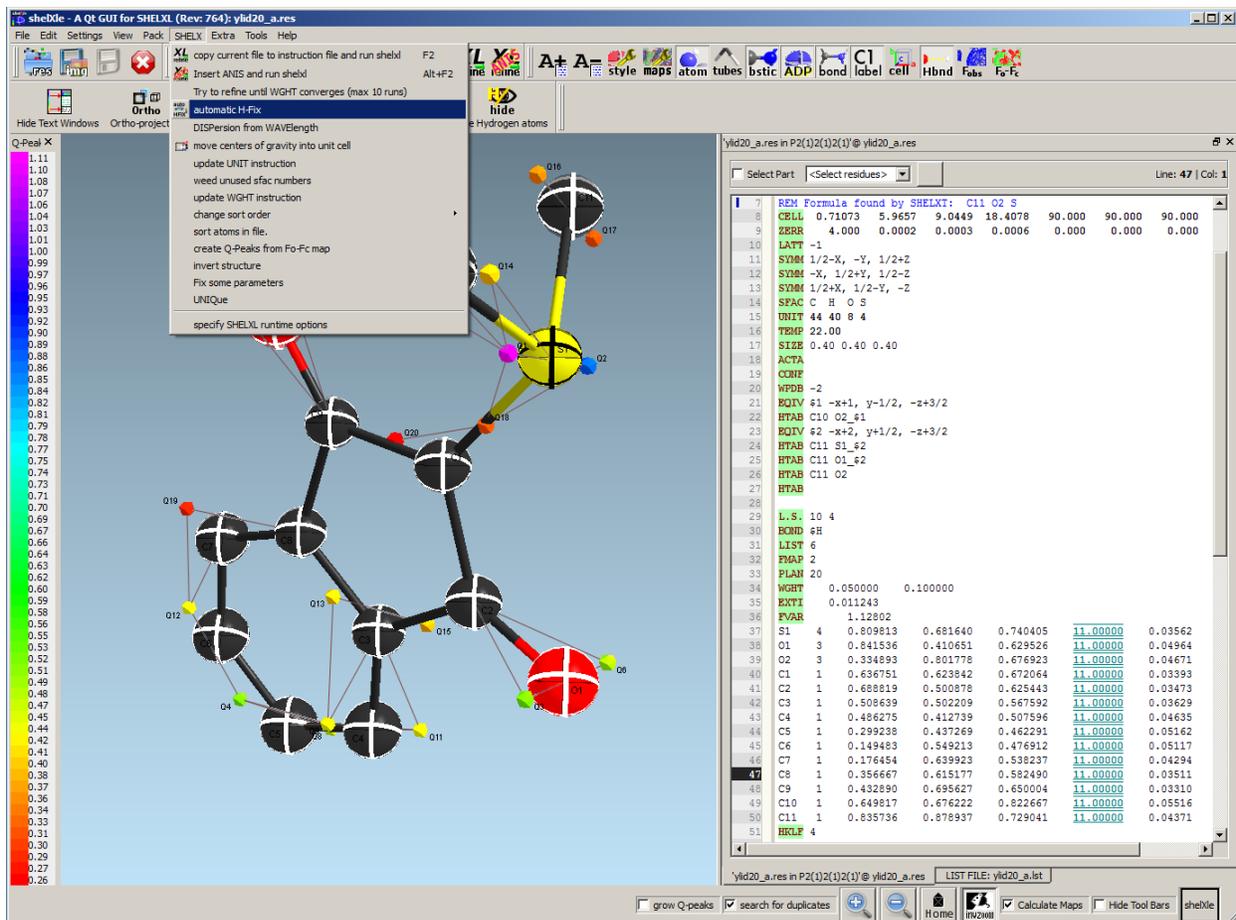
After an initial model of atoms has been provided by some structure solution method, it is best to properly label and sort the atoms in the model file. In Shelxle, atoms are labeled in the "Rename mode" routine. There is complete control over the Part number, the atom type and number and significant control of any suffix. Once all atoms are labeled, select the "SHELX > Sort atoms" routine to carry out the sorting. The order of sorting can be changed with the "SHELX > Change sort order" menu. Atoms can also be sorted by hand in the *.res file displayed on the right-hand panel. New peaks in the difference map are shown as small, flat-surfaced blocks. The "Q-Peak Legend" button toggles a color coding of the heights of peaks in the difference map.

In the *.res file, be sure to add the following four commands after the UNIT instruction and before any atoms:

```
ACTA
CONF
WPDB -2
```

HTAB

The ACTA command tells the refinement program to generate a *.cif file for archiving and communicating the crystal structure. The CONF command asks the program to calculate all obvious torsion angles. The WPDB command tells the program to generate a file in “protein data bank” format, because some folks that will see the structure in the future may wish to make drawings of the structure with programs that require this type of file. The HTAB command asks the program to calculate possible hydrogen bonds.



The screenshot shows the shelXle GUI with a molecular structure and a list of refinement parameters. The structure is a complex organic molecule with several atoms labeled O1 through O18. A menu is open over the structure, showing options like "Automatic H-Fix" and "Specify SHELXL runtime options". The list of parameters on the right includes:

```
7 REM Formula found by SHELXT: C11 O2 S
8 CELL 0.71073 5.9657 9.0449 18.4078 90.000 90.000 90.000
9 ZERR 4.000 0.0002 0.0003 0.0006 0.000 0.000 0.000
10 LATT -1
11 SYMM 1/2-X, -Y, 1/2+Z
12 SYMM -X, 1/2+Y, 1/2-Z
13 SYMM 1/2+X, 1/2-Y, -Z
14 SFAC C H O S
15 UNIT 44 40 8 4
16 TEMP 22.00
17 SIZE 0.40 0.40 0.40
18 ACTA
19 CONF
20 WPDF -2
21 EQIV #1 -x+1, y-1/2, -z+3/2
22 HTAB C10 O2_s1
23 EQIV #2 -x+2, y+1/2, -z+3/2
24 HTAB C11 S1_s2
25 HTAB C11 O1_s2
26 HTAB C11 O2
27 HTAB
28
29 L S 10 4
30 BOND #H
31 LIST 6
32 FMAP 2
33 PLAN 20
34 WGT 0.050000 0.100000
35 EXTI 0.011243
36 FVAR 1.12802
37 S1 4 0.809813 0.681640 0.740405 11.00000 0.03562
38 O1 3 0.841536 0.410651 0.629526 11.00000 0.04964
39 O2 3 0.334893 0.801778 0.678923 11.00000 0.04671
40 C1 1 0.636751 0.623842 0.672064 11.00000 0.03939
41 C2 1 0.688819 0.500878 0.625443 11.00000 0.03473
42 C3 1 0.508639 0.502209 0.567592 11.00000 0.03629
43 C4 1 0.486275 0.412739 0.507596 11.00000 0.04635
44 C5 1 0.299238 0.437269 0.462291 11.00000 0.05162
45 C6 1 0.149483 0.549213 0.476912 11.00000 0.05117
46 C7 1 0.176454 0.639923 0.538237 11.00000 0.04294
47 C8 1 0.356667 0.615177 0.582490 11.00000 0.03511
48 C9 1 0.432890 0.695627 0.650004 11.00000 0.03310
49 C10 1 0.649817 0.676222 0.822667 11.00000 0.05516
50 C11 1 0.835736 0.878937 0.725041 11.00000 0.04971
51 HELLF 4
```

Hydrogens can be added using the “Shelx > Automatic H-fix” option shown above. Refine until converged then refine non-hydrogen atoms anisotropically.

When all atoms have been added and refinement has converged, leave the Shelxle program, open a command prompt window, and perform one final round of refinement with a *.ins file in which the “LIST 6” command has been changed to a “LIST 4”. This change generates a *.cif with the data needed by checkcif to validate the structure.

Checklist for a Completed Structure

1. Intensity data should have been collected to at least 0.82Å resolution with at least 98% completeness. If the intensities fall to background values and were truncated at lower resolution, describe this in the *.cif file.
2. Be sure that all bond lengths, angles, and torsion angles are *chemically* reasonable!
3. The last difference map should be relatively flat. No peaks or valleys in the map should be $> 0.1 * Z_{\max}$.
4. The anisotropic displacement parameters should be only slightly prolate (cigar shaped) or oblate (plate shaped). RIGU, DELU, SIMU, or ISOR restraints may be needed.
5. If the sample crystallizes in a non-centrosymmetric space group, check that the absolute structure has been correctly determined.
6. The final refinement must be converged -- largest $|\text{shift}| / \text{esd} < 0.05$.
7. The weighting scheme should be adjusted so that the $\text{GoF} = S \approx 1.0$.
8. The final R_1 and wR_2 should be reasonably low for the data. $R_1 < 0.05$ for a good structure; $R_1 < 0.10$ for an acceptable structure. $wR_2 < 2 * R_1$.

Validate the Structure

First, edit the *.pcf file with the following changes.

1. Change the space group symbol by removing all parentheses if present and adding spaces between symmetry operations that apply in different directions.
2. The `_cell_measurement_reflns_used` should be a number > 400 . If not, then find the information that needs to be updated from the *project._ls* file (found near the bottom of the file). Also correct the `_cell_measurement_theta_min` and `_max` values. Note that the *._ls* file records 2θ values, but the *.cif needs θ values.
3. Change the `_exptl_absorpt_correction_type` value to 'multi-scan'.
4. Change the `_diffrn_measurement_device_type` to 'Bruker Photon II CMOS'.
5. Change all references to programs in the `_computing` items by opening the nearest programs.txt file; selecting all contents; copying all contents; in the *.pcf file, selecting all lines beginning with `_computing`; then pasting the information from the programs.txt file.
6. Close and save the *.pcf file and close the programs.txt file.

Second, edit the *.cif file with the following steps. Open the file with the ENCIFER program.

1. Comment out the `_shelx_SHELXL_version_number` line by adding “#” as the first character in the line.
2. Change the `_chemical_formula_moiety` by deleting the “?” at the end of the line and adding a new line with the chemical moiety formula in the format shown below the `_chemical_formula_sum` item. Remember for each covalently-bonded unit to put carbon first, then hydrogen, then all other atom types in alphabetical order. Separate covalently-bonded groups with a comma. For groups with a number other than “1”, put parentheses around the formula and insert the number of groups before the leading parenthesis.
3. Change the value of `_exptl_absorpt_correction_T_min` from “?” to the `T_min` value listed at the end of the *.abs file.

4. Change the value of `_exptl_absorpt_correction_T_max` from “?” to the `T_max` value listed at the end of the `*.abs` file.
5. Change the value of `_exptl_absorpt_process_details` from “?” to ‘SADABS (Sheldrick, 2015c)’. Note use “TWINABS” instead of “SADABS” if that program was used.
6. Comment out the `_exptl_absorpt_special_details` line.
7. Change the `_atom_sites_solution_primary` from “?” to “dual”.
8. Change the `_atom_sites_solution_secondary` from “?” to “difmap”.
9. If the space group is not centrosymmetric then change the value for `_chemical_absolute_configuration` from “.” to appropriately describe how the correct absolute structure was determined, codes can be seen by selecting this data name and opening the dictionary (icon of a book with a question mark on front) for this data name.
10. Check syntax using *Tools > Check*, correct any problems, save the `*.cif`, and close the program.

Third, run the `cif2tab` program. The first stage of this program combines the information in the `*.pcf` with the `*.cif`. The second stage of `cif2tab` creates a file with tables of data for a report. In the “C” menu item of `cif2tab` type the name of the compound presented by the user.

Validate the structure by running the `checkcif` program available at: <http://checkcif.iucr.org/>
Locate your `*.cif` data file, select output as PDF and click Send CIF for checking.

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A service of the
International Union of Crystallography

checkCIF reports on the consistency and integrity of crystal structure determinations reported in CIF format.

Please upload your CIF using the form below.

File name:
Choose File ylid20.cif

Select form of checkCIF report

HTML

PDF (recommended for CIFs that might take a long time to check)

Select validation type

Full validation of CIF and structure factors

Validation of CIF only (no structure factors)

Output Validation Response Form

Level A alerts only

Level A and B alerts

Level A, B and C alerts

None

Send CIF for checking

Information about this version of checkCIF ...

Useful links

Prepublication check for submissions to IUCr journals

Details of checkCIF/PLATON tests

CIF dictionary

Download CIF editor (pubCIF) from the IUCr

Download CIF editor (enCIFer) from the CCDC

If there are no syntax problems, a new page will appear with a link to “Download checkcif report”. Save this file with your data files. If there are issues that can be resolved, modify the *.ins file, refine again, change the *.cif as outlined above, run ciftab, and then checkcif. Continue until no more resolvable issues remain.

If there are A- or B-level alerts, modify the cif by adding a line with `_vrf_platon_alert_code` then add two lines with “;” on each line. Between the semicolon lines, add one line with “Problem: *platon problem description*” and another line with “Response: *your response to this issue*”. Note if there is more than one Platon alert with the exact same alert code, then append “_a”, “_b”, etc, to the `_vrf_` lines so that they will be different data items.

A copy of the final checkcif.pdf for this structure is attached as an appendix.

checkcif.pdf - Adobe Acrobat Reader DC

File Edit View Window Help

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ylid20

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. [CIF dictionary](#) [Interpreting this report](#)

Datablock: ylid20

Bond precision: C-C = 0.0024 A Wavelength=0.71073

Cell: a=5.9657 (2) b=9.0449 (3) c=18.4078 (6)
 alpha=90 beta=90 gamma=90

Temperature: 295 K

	Calculated	Reported
Volume	993.27 (6)	993.27 (6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C11 H10 O2 S	C11 H10 O2 S
Sum formula	C11 H10 O2 S	C11 H10 O2 S
Mr	206.25	206.25
Dx, g cm-3	1.379	1.379
Z	4	4
Mu (mm-1)	0.294	0.294
F000	432.0	432.0
F000'	432.69	
h,k,lmax	7,11,23	7,11,23
Nref	2298 [1357]	2297
Tmin, Tmax		0.892, 0.892
Tmin'		

Correction method= # Reported T Limits: Tmin=0.892 Tmax=0.892
 AbsCorr = MULTI-SCAN

Data completeness= 1.69/1.00 Theta(max)= 27.568

R(reflections)= 0.0248 (2241) WR2(reflections)= 0.0694 (2297)

S = 0.977 Npar= 127

The following ALERTS were generated. Each ALERT has the format
 test-name_ALERT_alert-type_alert-level.
 click on the hyperlinks for more details of the test.

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Alert level C

PLAT480 ALERT 4 G	Long H...A H-Bond Reported H11B .. S1 ..	2.89 Ang.
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Alert level G

PLAT913 ALERT 3 G	Missing # of Very Strong Reflections in PCF ...	1 Note
PLAT933 ALERT 2 G	Number of OMIT Records in Embedded .res File ...	1 Note
PLAT978 ALERT 2 G	Number C-C Bonds with Positive Residual Density.	9 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
 0 ALERT level B = A potentially serious problem, consider carefully
 1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 3 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 2 ALERT type 2 Indicator that the structure model may be wrong or deficient
 1 ALERT type 3 Indicator that the structure quality may be low
 1 ALERT type 4 Improvement, methodology, query or suggestion
 0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C or E* or *IUCrData*, you should make sure that **full publication checks** are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

checkcif.pdf - Adobe Acrobat Reader DC

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DataBlock: yM20 - ellipsoid plot

NOMOVE FORCED

Prob = 50
Temp = 295

PLATON-Jul 20 19:39:17 2017 - (70316)

Z 123 yLLd20 P 21 21 21 R = 0.02 RES= 0 -137 X

Prepare the Report (optional)

Prepare Drawings

Three types of drawings need to be prepared, a capped stick drawing, a thermal ellipsoid drawing with all non-hydrogen atoms labelled, and a packing drawing. If the structure is disordered, then make a labelled thermal ellipsoid drawing for each of the disordered groups of the molecule.

There are several free programs for making drawings. The program mercury is available from the makers of the Cambridge Structural Database at <https://www.ccdc.cam.ac.uk/Community/csd-community/freemercury/>

In mercury, be sure to set the background to white by right-clicking in the background and select Display options and in the next menu select the single color of white, then Close.

Select your desired file with File > Open menu, choosing either the *.cif or *.res files. Set the style of your drawing with Display > Style. Note that parameters such as bond radii, etc., may also be changed in one of the Display > Style > Settings options.

The drawing should be oriented to describe the issue you wish to present, and if possible, with the narrowest arrangement of atoms from left to right in order to fit in the two-column format adopted by most journals. Also, orient the drawing to have the fewest overlaps of atoms. The orientation can be changed either with x-, x+, y-, y+, z- or z+ buttons or by holding the left mouse button down and rotating the mouse. The relative size of the drawing can be changed by holding the right mouse button down and moving the mouse. Translations of the drawing can be changed by holding the center mouse button and moving the mouse.

Drawings are saved by selecting File > Save As, then select the proper directory and file name. Save the files as *.jpg or *.png file types. Because several drawings need to be saved, it is recommended that you save them with different file names such as *project_a*, *project_b*, etc. Adjust the number of pixels to the best choice for your drawing and click Save. Always check your drawing by opening a command prompt window, setting the current directory to the directory of the files, and typing *project_a.jpg* or *project_b.png*. If necessary, make adjustments to the drawing and save the drawing again.

The default color of the hydrogen atoms will be difficult to see with the white background so select Display > Colours > Atoms. Choose the “Select color” option and then pick a color that is not currently being used (gray is recommended).

When labeling atoms, first select the size and colour of the labels by Display > Labels > Label Colour or Label Size. To display the atom labels, select the “Label atoms” button in the options panel at the bottom of the screen or check the box before “Show Labels for” on the menu bar. All atoms are labeled. To remove labels from hydrogens select the option “Non-hydrogen atoms”. Move labels so that they do not overlap atoms or bonds by selecting the “Move Labels” option in the Picking Mode display and moving the label so that it is near the appropriate atom and is not touching any atom or bond.

To prepare the packing drawing remove “Labeling” and remove hydrogens except hydrogens involved in hydrogen bonds and set the style to Ball and Stick. The radii of the atoms and the bonds can be adjusted to taste. The packing diagram should be drawn by selecting the Packing button in the lower Display menu. The size, colour, and position of the cell axis labels can be adjusted in the same manner as the atom labels were adjusted.

Preparing the Report

Open the *.rtf file using the Word® program. Set the Show/Hide button to show all white space characters. Select the View > Ruler check box.

Delete the first blank space of the document. For each of the labeled drawings and for the packing drawing type a <ctrl>-<enter> followed by the up arrow. Now select “Insert > Object > Text from file” and select the E:\template.doc file. Select and cut the footnote on the third page and delete the two blank characters on this page. Use the page down and/or scroll down buttons to move to the bottom of Table 1. Paste the footnote at the bottom of Table 1.

Move to the first page of the document. Fill in the sample name, lab identification, user name, “moiety” chemical formula, date, and the sponsor of the project. At the bottom of page 1 insert the capped-stick drawing. Skip page 2 for now. On page 3, 4, etc. insert the labelled thermal ellipsoid drawing(s) and the packing drawing, with one drawing per page.

In the Experimental section make the following changes. Add any information about twinning or occupancies of disordered atoms in the first paragraph. Also, delete reference “(4)” in the first sentence if the OLEX2 program was not used. Truncate each of the crystal dimensions to show only two digits after the decimal points. In the fifth sentence, change “Semi-empirical from equivalents” to just “empirical”. In the first sentence of the second paragraph, set the first letter of the crystal system to lower case and change all letters in the space group name to italics. If there were no hydrogens bonded to nitrogens or oxygens, then delete the sentence describing these hydrogens. Replace question marks in the weighting factor expression with the proper terms used in refinement. (These terms are in the *.cif.) If the space group is centrosymmetric, then delete the last two sentences of paragraph 2.

In the Acknowledgements include your name in the last line.

Edit the references to represent the references used in determining the structure.

In Table 1, change the first letter in the name of the crystal system to lower case. Change all letters in the space group name to italics. Change the first letter in the Absorption correction type to lower case. If the Extinction coefficient is listed as “n/a” then delete this line.

On Table 3, select all bond distances, and then select Page Layout > Columns > 2. Then select all bond angles, then select Page Layout > Columns > 2, then move the tab shown on the ruler from 2” to 2.25”. If there are no symmetry operations used to generate atoms in Table 3, then

delete the line referring to the operations. If there are symmetry operations, then add a space after each comma (,) in the operations.

If there is a Table 6 or 7, then check the line below the table to see if there are symmetry operations used to generate atoms. If there are no operations, delete this line. If there are operations, then put a blank space after the commas in the operations.

Delete the last page (which is blank).

Page through the document and record the page numbers for the start of Tables 3, 4, 5, 6, and 7. On the Table of Contents, page 2, correct the page numbers for these tables or delete lines for missing tables. Also, if there is more than one labelled drawing, add a line for each additional drawing and update the page numbers for all items in the Table of Contents.

If desired, Insert a page number at the bottom center of each page.

Finally, save this document and save the document as the *.pdf. Exit the word processing program.