

Chapter 4.0

ABSORPTION CORRECTIONS

Methods available in WinGX

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4.0.1 Introduction

WinGX contains a number of options for absorption corrections [1], most of which are examined in the comparison below. The refined parameters principally affected by the systematic errors due by absorption are the anisotropic thermal parameters, more appropriately [2] called anisotropic displacement parameters (adp's). Since absorption primarily affects the low angle data, the net result is that the U^{ij} tensor refines to a smaller value than the "true" value. In severe cases, it may even result in negative eigenvalues (*i.e.* a non-positive definite U^{ij} tensor).

There are three basic methodologies for applying absorption corrections to reflection data. These are laid out in the menu scheme in **WinGX**, in decreasing order of theoretical rigour.

1. Exact numerical corrections - GAUSSIAN, ANALYTICAL, SPHERICAL, CYLINDRICAL & NEEDLE
2. Semi-empirical corrections - PSIABS, CAMEL-JOCKEY & MULTISCAN
3. Refined corrections - DIFABS, DELABS, XABS2 & SHELXA

4.0.2 Numerical methods

It is generally agreed that the best absorption corrections are provided by the analytical [3] or Gaussian quadrature [4] methods. These two methods require that the crystal faces are well defined and can be accurately indexed and measured. These conditions are not often met. It can be time consuming to index a specimen with numerous faces and difficult to measure accurately the distances between faces. For these reasons, these methods are used less than often than those which are experimentally easier to implement. The spherical and cylindrical corrections also provide numerically accurate corrections for crystals adopting the requisite morphology, but are not used very frequently, since grown crystals are not usually spheres or cylinders.

4.0.3 Semi-empirical methods

The semi-empirical methods rely on further intensity measurements. The multiscan method of Blessing [5] is of most use when there is a large redundancy in the data-set, as is usually the case for area-detector data. Equivalent intensities are analysed in terms of a multipolar spherical harmonic expansion and the method has been implemented in the programs PLATON [6], SORTAV [7] and SADABS [8]. A somewhat similar method called CAMEL-JOCKEY [9] uses a trigonometric series expansion of the diffractometer angles, but is little used since so many more experimental measurements are required, and is of historical interest only. For data measured using a point-detector, the most commonly used method is the azimuthal scan or psi-scan method of North *et al* [10], implemented in the program PSIABS. This method involves the measurement of the intensities of a (usually small) number of reflections with χ values close to 90° at different φ values. An averaged absorption surface is thus computed and used to calculate the

transmission factors. It works remarkably well, but is unsuitable for crystals with large μR values.

4.0.4 Refined corrections

The final type of absorption corrections are the so-called refined corrections DIFABS [11], XABS2 [12] and SHELXA [13], and these have fallen out of favour in the recent past. These rely on a refined model being available (hence the structure must be solved) and they calculate the absorption surface from the differences between the observed and calculated structure factors. The various programs differ in the exact mathematical functions used to model these differences, but all suffer from the same philosophical problem, in that the data is being modified to fit the model. One way round this philosophical problem would be to incorporate the parameters into a least-squares refinement.

4.0.5 A comparison of methods using NAWO4

A data-set for sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) is described here as a test data-set for absorption corrections. The compound was chosen because :

- it is commercially available in crystalline form
- the crystal used for the data collection has reasonable but not perfect facets so it may serve as an example of a “real” crystal specimen
- the linear absorption coefficient is very large
- only one heavily absorbing atom is present in the asymmetric unit

Crystal data for $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$: $a = 8.4797(5)$ $b = 10.5930(5)$ $c = 13.8527(10)$ Å, $V = 1244.33(1)$ Å³, orthorhombic, space group *Pbca*, $Z = 8$, $M_r = 329.8$, $T = 295$ K, $\mu(\text{Mo-K}\alpha) = 18.664$ mm⁻¹, crystal size 0.391x0.344x0.109 mm. 7543 reflections were measured, yielding 1811 unique reflections.

All refinements were carried out using SHELXL-93 and a number of criteria for assessing the results are given. The transmission factors obtained are given in Table 1 and the results of refinement are summarised in Tables 2 and 3. As expected, all methods offer a significant improvement over the uncorrected data in terms of the residuals. The best methods are clearly the analytical and Gaussian quadrature, which give virtually identical results. For all other methods, (except XABS2) the range of transmission factors is smaller, suggesting they may be under-correcting the data. The method which gives the second best set of figures in Table 2 is DIFABS. At this stage it is also useful to compare the adp's especially the degree of anisotropy given by the three principal mean-square displacements. The eigenvalues of the U^{ij} tensors of the W and Na atoms are listed in Table 3, and ORTEP views given in Figure 1. The accepted wisdom is that absorption errors cause the adp's to be somewhat smaller and more anisotropic than the “true” values (in this context the “true” value is assumed to be that obtained from the analytical correction.). Examination of the values obtained with no absorption correction bear this out. It can be seen that the adp for the W atom calculated using DIFABS is slightly smaller and more isotropic than the “true” value, but the

agreement is quite respectable. Moreover the adp's for the light Na atoms are also quite similar to their "true" value. These results suggest that the oft quoted problems with DIFABS are not always manifest. Rather unexpectedly in view of the large μR value, the psi-scan method gives values in Table 2 quite similar to DIFABS. However, the resultant adp's are much less acceptable. None of the remaining methods provide a satisfactory correction to the NAWO4 data. The next best correction is probably SHELXA (though it does give a large +ve residual), followed by multiscan and XABS2. The multiscan method of Blessing [5] surprisingly performs rather poorly for the NAWO4 data, even though there is a large degree of redundancy. It may be that the transmission paths have not been sampled adequately in this example.

Table 1. Transmission factors

METHOD	T minimum	T maximum	Ratio
Multiscan	0.0169	0.1202	6.03
DIFABS	0.0151	0.0820	5.43
XABS2	0.0181	0.1733	9.57
Analytical	0.0208	0.1475	7.09
Gaussian	0.0206	0.1479	7.17
Psi-scans	0.0053	0.0307	5.79
SHELXA	0.1072	0.5722	5.33

Table 2 Refinement results

METHOD	R(merge)	R(sigma)	R1	wR2	$\Delta\rho(max)$	$\Delta\rho(min)$	NIEQ*
none	0.1495	0.0946	0.0989	0.2363	24.01	-7.31	818
Multiscan	0.0654	0.0408	0.0652	0.1639	10.49	-4.87	303
DIFABS	0.0632	0.0368	0.0348	0.0945	5.84	-1.81	388
XABS2	0.1175	0.0772	0.0606	0.1611	10.24	-5.86	769
Analytical	0.0382	0.0242	0.0208	0.0552	2.47	-1.60	210
Gaussian	0.0383	0.0242	0.0210	0.0555	2.41	-1.59	210
Psi-scans [‡]	0.0663	0.0387	0.0371	0.1063	4.99	-3.42	342
SHELXA	0.0817	0.0492	0.0501	0.1316	11.73	-2.74	549

* NIEQ = number of inconsistent equivalent reflections flagged by SHELXL-93

[‡] No theta correction, unit weights

Table 3 Eigenvalues (\AA^2) of the U^{ij} tensors for the W and Na atoms*

METHOD	W			Na1			Na2		
	λ_1	λ_2	λ_3	λ_1	λ_2	λ_3	λ_1	λ_2	λ_3
none	0.0175	0.0096	0.0082	0.0267	0.0208	0.0148	0.0311	0.0163	0.0134
Multiscan	0.0188	0.0168	0.0149	0.0300	0.0253	0.0206	0.0277	0.0242	0.0231
DIFABS	0.0131	0.0124	0.0107	0.0245	0.0202	0.0168	0.0240	0.0193	0.0174
XABS2	0.0107	0.0099	0.0062	0.0202	0.0167	0.0151	0.0213	0.0185	0.0116
Analytical	0.0148	0.0134	0.0101	0.0241	0.0200	0.0196	0.0252	0.0215	0.0158
Gaussian	0.0148	0.0134	0.0101	0.0241	0.0199	0.0197	0.0251	0.0215	0.0158
Psi-scans	0.0154	0.0128	0.0069	0.0267	0.0228	0.0113	0.0255	0.0197	0.0145
SHELXA	0.0167	0.0110	0.0101	0.0249	0.0211	0.0171	0.0270	0.0199	0.0158

* The standard uncertainties on the eigenvalues are ~ 0.0001 for W and -0.0007 for Na

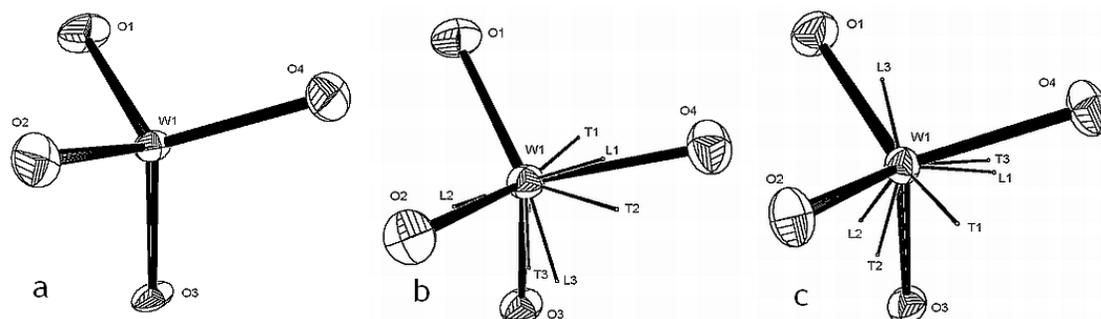


Figure 1. ORTEP views of the WO_4^{2-} anion, obtained with refinements with (a) no absorption correction, (b) analytical absorption correction and (c) DIFABS absorption correction.

4.0.6 References

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