MAD: Multiple wavelength Anomalous Dispersion

There are two approaches to abstracting information from a MAD experiment. One is to use all information in a set of simultaneous equations, mathematically satisfying perhaps, but using a different intuition then our geometrical approach. Another is to treat the experiment as a combination of isomorphous changes in the scattering power of the "heavy" atoms along with associated anomalous scattering differences. This uses the same conceptual machinery already developed for the SIRAS method, and, indeed, one of the commonly used computer programs for MAD phasing was originally developed for SIRAS.

Theoretically, all that is really needed is data at two wavelengths. Recall that in SIRAS a difference in isomorphous scattering along with one pair of anomalous scattering sets is sufficient. However, not only does redundancy of taking data at more than 2 wavelengths help in this experiment where one is interested in small differences between large numbers, three wavelengths can be selected to optimize the phasing information (and often data at 4 wavelengths is taken for further assurance).

Three wavelengths can be chosen, in terms of the SIRAS analysis, such that one pair has maximal "isomorphous" differences, and an intermediate wavelength gives maximal anomalous differences. At the absorption edge of an element, inner electrons come into resonance with the incident x-ray energy, these electrons scatter more strongly and with a different phase shift (i.e. more like 90 phase lag) to the incident wave. There also are slightly fewer electrons scattering with the usual 180 phase lag, so the usual scattering falls off while the anomalous scattering increases as the absorption edge is crossed. The effect is specific to the element but is subject to slight shifts because of interactions with surrounding atoms, so good practice is to run a scattering scan across the wavelength region and determine exactly the scattering profiles for the crystal under study.

Scattering from an element can be expressed as f(total) = fo + f' + f" where fo is the expected scattering for that element at the angle of the measurement, f' is the change in the usual 180 deg. phase lagged scatter, and f' is the amount of scatter with a 90 deg. phase lag. (2 components at 90 deg. of course, can represent all scattering.)

f' hits a minimum just at the absorption edge where f" is rapidly changing, and f" has a sharp maximum at the high energy side of the edge. Let L1 be the point of minimum usual scattering, L2 the point of maximal anomalous scattering, and L3 be remote from the edge where the usual scattering is no longer depressed. Then most of the phasing power can be extracted from the experiment just by taking the difference between L1 and L3 as the "isomorphous" part (averaging the Bijvoet pairs taken at those wavelengths) and the Bijvoet pair at L2 for the anomalous signal. Of course, with 3 sets of Bijvoet pairs there are other ways to combine the data sets to enhance the accuracy, but most of the power is gained from those optimal combinations.

Modern "area" detectors and high intensity x-rays from a synchrotron source on frozen crystals, allow for efficient collection of the Bijvoet pairs and redundancy to provide accurate intensity measurements.