**Information for potential collaborators**

This text is intended to inform both current and potential collaborators of the practical possibilities and limits of Gas Electron Diffraction (GED) as practised here in Bielefeld, as well as the compound requirements and the steps that need to be taken before a sample can be measured. For those considering whether an electron diffraction study might provide interesting or useful insight, please refer to Section 1 below entitled “Which types of compounds are best suited to a GED investigation?”. Those looking for instructions of how to prepare a sample for measurement and additional requirements, please refer to Sections 2 and 3.

1. Which types of compounds are best suited to a GED investigation?

In principle, any compound that is volatile enough, without decomposing, can be studied by GED. Whilst the experiment has certain practical difficulties, it is relatively straight-forward to understand the experimental limits: if the compound can be purified and evaporated or sublimed without decomposing, its diffraction pattern can be obtained. The analysis of the data, however, is not as transparent and it is worthwhile thinking about what information might be obtained from the diffraction data and the value of such information.

1.1. A short introduction to the principles of GED illustrated by way of an example.

GED is a direct way of determining the distribution of the distances between atoms in a molecule, which is related to the recorded intensity pattern by way of a Fourier transformation. (See Figure 1.)

![Figure 1](https://example.com/figure1.png)

**Figure 1** – Various forms of gas electron diffraction data. (Click here for enlarged version.)

The difficulty in determining a structure is introduced by the fact that the distance between each atom pair is not fixed, rather, it varies due to vibrations and is more accurately described by a probability distribution, which to a good approximation can be assumed to be Gaussian. For similar distances these probability distributions overlap and, as a result, are either indistinguishable or are highly correlated in the refinement.

The extent of this problem can be seen from the example of \( \text{Me}_3 \text{SiCH}_2 \text{ONO}_2 \), the data for which is shown in Figures 1 and 2. This compound has 20 atoms giving a total of 190 inter-atomic distances, which are represented by the vertical lines in the RDC (their heights are proportional to the product of the atomic numbers). Due to symmetry (\( \text{C}_3 \)), the number of distinct distances is reduced to 112, but this would still be more than enough to determine the 31 internal coordinates required for a full
description of the molecule. However, the experimental radial distribution curve (blue line in Figure 2) exhibits only nine distinct peaks and three shoulders, each of which can be interpreted as a refinable parameter. The breadth and shapes of the peaks may also provide information regarding the molecular structure, but these are also correlated to the amplitudes of vibration which are sometimes refined, but more often have to be constrained to calculated values that may be inaccurate.

**Figure 2** – Radial-distribution curve and molecular structure of Me₃SiCH₂ONO₂. The distances that are the major contributors to a single peak are indicated on the RDC. (Click here for an enlarged version.)

In our example, some local symmetry was assumed (e.g. for the methyl groups), allowing the structure to be described in terms of 14 independent parameters and there appeared to be some information in the diffraction data for all of these parameters. However, the least-squares refinement was not entirely stable due to the low data-to-parameter ratio and six of the most uncertain parameters were restrained to calculated values, so that eight parameters were refined without any external information:

Bonded distances: Si-C (average), C-O, N-O (CH₂), N-O (terminal),

Angles: Me-Si-Me, Si-C-O, C-O-N, O-N-O (terminal)

### 1.2. Suggested guidelines for getting the most out of GED.

As may be apparent from the example above, the biggest problem for the analysis of GED data is the question of how to handle the vibrational motion. When the compound is relatively rigid the approximation that the vibrations can be described in terms of normal modes holds and accurate amplitudes of vibration can be calculated and used in the refinement. Large-amplitude motion is said to occur when there is a frequency of vibration less than 200-300 cm⁻¹ and can often lead to unsolvable structures, as the distribution of inter-atomic distances can be incompatible with a three-dimensional structure. This is not always the case though and serious problems are usually only encountered when the calculated frequencies are as low as 50 cm⁻¹. In such situations functional groups may, effectively, be freely rotating, so that the probability distribution for the atom pair is not well described by a Gaussian function. In addition, multiple conformers can compound the problem and the effect of large-amplitude anharmonic motion is often impossible to distinguish from the presence of multiple conformers.
In summary, the rigidity of the compound determines, to a large extent, the accuracy to which its structure can be determined and, if possible, molecules with a ‘floppy’ chain-type structure should be avoided, as should those with a number of possible conformers. Lastly, it is worth mentioning that the accuracy of GED is probably comparable to a high-quality ab initio structure (CCSD(T) with a triple-zeta or larger basis) and if such a structure is available, a GED study is not likely to provide additional information. Having said that, calculations at this level depend can only be done for single-reference problems, and it is always a good idea to check the convergence of calculations and the accuracy of their predictions against experiment.

2. Basic requirements for the compound to be studied.

Purity: GED cannot differentiate between the diffraction produced by a specific compound and that produced by an impurity in the sample (although a large proportion of impurity will be evident during the refinement stage). Any impurity may unknowingly distort the obtained structure, thus it is imperative that the sample is of high purity, ie. > 95 %, or with no observable impurities in a conventional NMR spectrum.

Vapour Pressure: Some idea about vapour pressure is useful for the measurement. Of course, in many cases this might not be possible to measure, but ordinarily we require approximately 5-10 mbar at the experimental temperature. Heavier elements scatter electrons more strongly and therefore do not require so high a vapour pressure. Whilst higher vapour pressures than this are not problematic it is still useful to have some prior knowledge of their dependence on temperature.

Quantity: The structure analysis requires data at two nozzle-to-detector distances and for each of these, an absolute minimum of about 100 mg is required, ie. at least 200 mg. However, the measurement usually requires some optimisation of the temperature and exposure parameters, so we recommend two portions of at least 250 mg (one for each measurement).


All compounds: If possible, please provide the following information:

- H\textsuperscript{1} NMR spectrum or some reliable assessment of purity
- Storage instructions
- An approximate lifetime of stability
- Any unusual handling procedures or precautions
- Instructions for disposal

Compounds which are not sensitive to air: These can be delivered in any standard container.

Air-sensitive compounds: Please transfer into a flask containing a vacuum fitting and tap. We generally use Young-type flasks as shown below: