A model for uncertainty influences on static magnetisation measurements on magnetic nanoparticles

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Abstract. Liquid suspensions of magnetic nanoparticles play a crucial role in current biomedical research and applications. While their magnetic characteristics are of importance for their utilization, no measurement standard exists and an uncertainty budget for static magnetisations measurements of MNP is lacking. Here we present the structure of the uncertainty budget for static magnetisation measurements by stratifying the measurement process and data analysis into seven levels of rising complexity. The main uncertainty contributions of each level are stated and briefly described. This paves the way towards a reliable quantitative uncertainty budget that could be used for interlaboratory comparisons as well as for the development of a measurement standard.

1. Introduction
Magnetic nanoparticles (MNP) are widely used for in-vitro diagnostics and in many other different technical and biomedical applications because of their ability to interact in a controlled manner with an external magnetic field. To ensure quality, efficacy and safety of MNP applications, their magnetic characteristics must be determined in a reliable way. There exists a vast amount of publications on different aspects of static magnetisation measurements [4-12]. However, a commonly accepted measurement and analysis protocol for static magnetisation measurements is still not available. This impedes interlaboratory comparisons and the development of measurement standards at ISO level. Also, an uncertainty budget following the rules of the GUM is still pending for static magnetisation measurements on MNP. This situation is a consequence of the small effective magnetic moments of MNP samples, especially if the MNP are highly diluted. Background effects are then in the same order of magnitude and influence the measurement results in a complex and not easily understandable way. Here, we describe the structure of a reliable uncertainty budget for $M(H,T)$ magnetisation measurements introducing seven different levels of rising complexity. We characterize important uncertainty influences at each level.

2. Setup of a SQUID magnetometer for magnetisation measurements of highly diluted MNP
We refer to measurements by a superconducting quantum interference device (SQUID) magnetometer [8]. In this device, the sample is moved step by step through a gradiometric pick-up coil that is connected to a SQUID as shown in Fig. 1a. The magnetic moment of the sample creates a magnetic flux through the pick-up coil. On each position, a measurement of the flux is performed. Furthermore, the device provides external magnetic fields (up to +/-5 T) and temperatures in the range from 1.7 K to 400 K to the sample.
The sample is placed in a sample container located in the centre of the sample holder. For liquid MNP suspensions, commonly a polycarbonate capsule is used as the sample container and a polycarbonate straw is used as the holder.

![Figure 1](image_url)  
**Figure 1.** Measurement scheme. a) device setup with a sample in a sample container being moved through a gradiometric pickup coil connected to a SQUID. b) a typical SQUID response to a sample being moved along \( z \).

3. Measurement procedure and different levels of analysis

The main uncertainty contributions of the measurement and analysis process (see Fig. 2) will be described in the following using seven different levels of rising complexity:

1. Measurement of the magnetic flux of a sample at a fixed position as shown in Fig. 1a). A magnetic sample creates a magnetic flux in the pickup coils which are connected to the SQUID sensor via a flux transformer. There, the magnetic flux is transformed to a voltage signal which in turn is amplified. As a single measurement alone, it is not yet interpreted. Nevertheless, it contributes to the final uncertainty by intrinsic noise of SQUID and amplifier electronics and by external environmental flux contributions. Parts of this noise contribution are reduced by averaging repeated measurements.

2. Measurement of the magnetic flux profile along a straight line repeating step 1., moving the sample in defined steps through the pick-up coils (\( z \)-scan). The result is the so-called SQUID response shown in figure 1b). Here, the main uncertainty contribution is the positioning accuracy of the steps in \( z \)-direction. Additionally, linear drifts in the SQUID response are rejected by subtraction of a linear background (detrending), also the mean value of the SQUID response is subtracted. Non-linear background signals will further influence the final measurement result.

3. Determination of the magnetic moment assuming a point-like sample. The SQUID response obtained in step 2. is interpreted by a curve fit using a single dipole model. Calibration of the result in terms of magnetic moment is done using a reference sample of known susceptibility (commonly palladium). Sources of uncertainty are the off-centre uncertainty of the \( x,y \)-position and the absolute \( z \)-positioning at each measurement point of the SQUID response \([3, 6, 8]\), the accuracy of the curve fit and the susceptibility of the reference sample. For a palladium reference, a susceptibility uncertainty of \(<0.5\%\) is documented \([9]\).

4. Determination of the sample magnetic moment considering interfering magnetic moments of sample holder and sample container, and additionally, influences due to sample misalignment in step 3. The magnetic moments of MNP samples at low concentrations might be in the range of background signals. As an example, at 5 T and 300 K, a magnetic moment of \( 0.6 \cdot 10^{-6} \text{ Am}^2 \) is measured for 30 µL of nanomag-D (micromod Partikeltechnologie GmbH, Germany) MNP at an iron
A concentration of 0.5 mg/mL. The diamagnetic magnetic moment of the sample container measured under same conditions amounts to \(-0.9 \times 10^{-6}\) Am² and the sample holder contributes a moment of \(3 \times 10^{-7}\) Am². The main uncertainty lies in the background signal of the sample container which is normally obtained using a separate empty container. Additionally, magnetic contaminations as well as sample misalignment can influence the background subtraction [4, 7, 10]. For liquid MNP suspensions the magnetic contribution of the solvent (water, oil) should be considered either by using literature values \((-1.0 \times 10^{-6}\) Am² in the example) or by performing reference measurements.

Figure 2. Ishikawa diagram outlining the main uncertainty contributions during the interpretation of magnetisation measurements of MNP.

5. Recalibration of the magnetic moment of the sample obtained in step 4 incorporating the sample geometry. In the previous steps, only a point like dipole was assumed. To account for extended sample geometries, correction factors are obtained by mathematical modelling [5, 13]. Alternatively, a comparison with a reference sample of equal shape and known magnetic moment can be used. Uncertainty contributions result from the mismatch between model and given sample geometry. Difficulties may arise for composite bodies and irregular shaped sample geometries.

6. Measurement of a series of magnetic moments repeating steps 1-5, while varying other measurement parameters like external magnetic field \(H\) and sample temperature \(T\). The magnetisation curve \(M(H,T)\) is constructed which shows the dependency of the magnetic moment of the sample on these parameters. Here, the result is influenced by the uncertainty of the varying parameters \(H\) and \(T\). As an example, there might occur flux pinning in the superconductor creating \(H\). A detailed discussion can be found in the device manual and in several publications [8, 10, 11]. Another important uncertainty influence on this level is the change of the MNP formation within the suspension caused by the external parameters. MNPs might form chains or fall out during the measurement as a result of changes in \(H\) or \(T\) [1].

7. Interpretation of the magnetisation curve from step 6 using sophisticated physical models for MNP, e.g. to determine mean particle size (Langevin function), particle size distribution [2] or anisotropy parameters. Uncertainty contributions stem from idealisations in the model assumptions...
(MNP as ideal spheres) and the selection of the physical model (Langevin valid for isotropic MNP, only), as well as from other external parameters (chemical MNP composition, MNP concentration). Typically, these models omit the uncertainties in $H$ or $T$, which results in further uncertainties in $M$.

4. Conclusion

We presented a comprehensive analysis of the uncertainty contributions in static magnetisation measurements of MNP with small magnetic moments. This is a prerequisite to a complete quantitative uncertainty budget following the GUM. Consequently, the numerical values of uncertainties should be determined by experiments, by analytical modelling, or by stochastic estimation using Monte Carlo methods for each of the seven levels. The resulting uncertainty of each step enters the input of the uncertainty analysis of the consecutive higher level.

In the context of the current development of a series of international standards for magnetic nanomaterials by ISO/TC229 “Nanotechnologies”, this contribution supports the development of a measurement standard for MNP characterisation. It will also be useful in the analysis of interlaboratory comparisons of $M(H,T)$ measurements of MNP, that will serve for the establishment of MNP reference materials with defined magnetic properties.

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