Non-destructive Quantitation of Hydrogen via Mass-resolved Neutron Spectroscopy

Electronic Supplementary Information

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1 Sample Preparation

Low density polyethylene (LDPE) was purchased from Goodfellow, Cambridge Ltd., in two different batches. The first batch consisted of as-received LDPE sheets of average thickness 0.05 mm and average dimension of 300 mm by 300 mm. The second consisted of as-received LDPE sheets of average thickness of 0.25, 1.00, 2.30 and 4.80 mm and average dimension of 300 mm by 300 mm. The effective density of the LDPE sheet of each thickness was measured by weighing 10 different sheets assuming homogeneous density. Following this, the as-received LDPE sheets were cut to dimension 60 mm by 60 mm to fit the sample holder used for the experiments. Prior to assembly, all sheets were cleaned, degreased, and handled with gloves. Sandwicking 2 and 3 sheets of 0.05 mm thickness made possible to obtain samples of 0.10 and 0.15 mm thicknesses. To obtain 0.5 mm thickness samples two 0.25 mm sheets were sandwiched. To make the results of the quantitative analysis independent of the incident neutron-beam geometry, the figure of merit was chosen to be the number of moles of H per square centimeter (hereinafter referred to as mole/cm²).

2 MANSE

All experiments were performed on the VESUVIO spectrometer at the ISIS Pulsed Neutron and Muon Source, United Kingdom. At ISIS, neutrons are produced when an energetic proton beam from the synchrotron accelerator hits a heavy metal target - a process called 'spallation'. Thus, a convenient unit characterising the length of a given neutron experiment at ISIS is the total integrated proton charge per experiment. With the present VESUVIO setup and ISIS neutron beam specification, a unit-of-time of the VESUVIO measurement equals ca. 35 minutes.

At an inverted-geometry neutron spectrometer like VESUVIO, the sample is exposed to a polychromatic neutron beam characterized by an incident-energy spectrum $I(E_0)$. Incident neutrons having initial energy $E_0$ travel a distance $L_0$ from the pulsed source to the sample. After scattering at an angle $\theta$, neutrons of final energy $E_1$ travel a distance $L_1$ to the detector, as schematically shown in Fig. 1. A thin metal foil placed in front of the detectors absorbs neutrons over a narrow range of energies, thereby fixing $E_1$ of the detected neutrons at $E_1 = 4.9$ eV. With the time-of-flight (TOF) of each neutron measured, for each TOF channel (bin) there exists a unique relation between the TOF, neutron incident energy $E_0$, energy transfer, $E_0 - E_1$, and the momentum transfer $Q$.

The instrument is divided into three separate sections: (i) beam monitors (S1 and S2), (ii) forward (S135 - S198), and (iii) back scattering detector banks (S3 - S134). The incident- and transmitted-beam monitors consist of beads of $^6$Li-doped scintillator glass. In backscattering, there are a total of 132 $^6$Li-doped glass scintillation detectors. All NCS measurements described in this work were obtained form the analysis of TOF spectra recorded by forward-scattering detectors. In forward scattering, a total of 64 Yttrium-Aluminium-Perovskite-doped (YAP) $\gamma$-ray detectors are arranged into near-to-vertical columns of eight detectors (banks), four above and below the horizontal plane passing through the sample centre. There are 4 forward-scattering detec-

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Table 1  LDPE samples for MANSE analysis. Samples made by sandwiching 2 or 3 sheets of LDPE are marked with an asterisk. All table entries are listed as mean values and their errors as 1-STDs. For details, see the text.

<table>
<thead>
<tr>
<th>Thickness [mm]</th>
<th>Average Density [g cm(^{-3})]</th>
<th>n [H mmol cm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050 ± 0.004</td>
<td>0.815 ± 0.030</td>
<td>0.582 ± 0.068</td>
</tr>
<tr>
<td>0.100± 0.005</td>
<td>0.815 ± 0.030</td>
<td>1.164 ± 0.101</td>
</tr>
<tr>
<td>0.150± 0.009</td>
<td>0.815 ± 0.030</td>
<td>1.746 ± 0.169</td>
</tr>
<tr>
<td>0.250 ± 0.007</td>
<td>0.861 ± 0.027</td>
<td>3.076 ± 0.182</td>
</tr>
<tr>
<td>0.500 ± 0.008</td>
<td>0.916 ± 0.030</td>
<td>6.542 ± 0.319</td>
</tr>
<tr>
<td>1.000 ± 0.006</td>
<td>0.948 ± 0.036</td>
<td>13.542 ± 0.596</td>
</tr>
<tr>
<td>1.250 ± 0.008</td>
<td>0.953 ± 0.041</td>
<td>17.017 ± 0.841</td>
</tr>
<tr>
<td>1.500 ± 0.008</td>
<td>0.946 ± 0.038</td>
<td>20.271 ± 1.598</td>
</tr>
<tr>
<td>2.300 ± 0.057</td>
<td>0.942 ± 0.020</td>
<td>30.951 ± 1.424</td>
</tr>
<tr>
<td>3.300 ± 0.058</td>
<td>0.971 ± 0.032</td>
<td>45.775 ± 2.313</td>
</tr>
<tr>
<td>4.800 ± 0.054</td>
<td>0.915 ± 0.020</td>
<td>62.743 ± 2.077</td>
</tr>
</tbody>
</table>

Fig. 1  Schematic layout of the VESUVIO spectrometer: a) incident neutron monitor; b) transmission neutron monitor; c) Au resonance filters; d) S135-S198 -forward scattering detectors; e) S3-S134 - backward scattering detectors; s) sample. For further details, see the text.

To obtain each TOF spectrum, a difference of two separate measurements is performed: (i) one with the foil out of the scattered neutron beam, and (ii) one with the foil in the beam. A motorised foil changing mechanism is in place for both forward and backscattering. Each individual experiment (run) is divided into 6 different periods. In each period, the gold foil is moved in front of a given detector bank leaving the adjacent detector facing directly the sample. With the number of neutrons detected per period fixed at 15 µAh of total accumulated proton current, a unit-of-time of the VESUVIO measurement (hereinafter referred to as the run) equals ca. 35 minutes, which is equivalent to 90 µAh of total integrated proton charge. Importantly, due to the difference-measurement nature of the method, the signal plotted in each MANSE spectrum corresponds to difference of counts and thus can be either positive or negative.

The MANSE data treatment scheme is explained in more detail elsewhere and thus here only a brief account will be given. Each MANSE spectrum is recorded by a detector placed at a particular scattering angle \(\theta\) and time-of-flight channel TOF \(t\). For a given mass \(M\) and a given detector, instrument calibration procedures establish a unique relation between the values of TOF for each channel \(t\), momentum transfer \(Q(\theta, t)\) and energy transfer \(E(t)\). Consequently, each MANSE spectrum can be represented as a histogram with bins given by the count rates, \(C(\theta, t) dt = C(\theta, t, E(t)) dt\), calculated for a number of \(t\) values.

Due to the impulsive nature of the scattering events of epithermal neutrons transferring high energy and momentum to the nu-
nuclei present in the sample, each MANSE spectrum, \( C(\theta,t)dt \), can be described as a linear combination of response functions of individual masses \( M \), \( C_M(\theta,t)dt = C_M[Q(\theta,t),E(t)] \). Each response function can then be expressed as a convolution of its own mass-dependent resolution function \( R_M \) and nuclear momentum distribution (NMD) expressed in a form of the so-called neutron Compton profile \( J_M \):

\[
J_M(x_M) = \frac{\exp(-x_M^2)}{\sqrt{2\pi}\sigma_M^2} \left[ 1 - \frac{k}{Q} H_3(x_M) \right]
\]

with \( x_M = (y_M)/(\sigma_M\sqrt{2}) \) where \( \sigma_M \) and \( y_M \) are the standard deviation of the NMD and the West-scaling variable for each \( M \), respectively. The West-scaling variable describes the magnitude of the projection of a nuclear momentum onto the momentum transfer direction and can be mathematically expressed through \( Q(\theta,t) \) and \( E(t) \) as: \(^2\eta,7,13-15\):

\[
y_M[Q(\theta,t),E(t)] = \frac{M}{h^2Q(t)} \left( E(t) - \frac{R^2[Q(\theta,t)]^2}{2M} \right)
\]

Consequently, the count rate, \( C(\theta,t) \), can be expressed as:

\[
C(\theta,t) = C[Q(\theta,t),E(t)] = A \frac{E_0[|E_0|]}{Q} \times \left[ \sum M c_M J_M(x_M) \otimes R_M(x_M) \right]
\]

where \( A \) is a proportionality constant.

Each coefficient \( c_M \) in Eq. 3 is proportional to the product of the number density \( N_M \) and the total (coherent plus incoherent) bound neutron cross section of a given nuclide \( x_M = 4\pi h^2/M \), as described above\(^16,17\). Thus, an integral in the TOF domain \( I_M = \int C_M(\theta,t)dt \) calculated over the entire recoil peak region is proportional to the number of nuclei of a given isotope present in the sample of interest. Moreover, one can take advantage of the linear constraints imposed on the coefficients \( c_M \) by the sample chemical formulation by imposing constraints of the type \( c_H/c_C \). Such linear constraints were imposed in fitting the LDPE sample under investigation with \( c_H/c_C = \frac{2 \times 82.02}{1 \times 5.551} = 29.5514 \), where the tabulated values of the total bound neutron cross section for H and C, equal to 82.02 and 5.551 barn, respectively, were taken\(^18\).

Due to high energy and momentum transfers of neutrons scattered off protons, the proton recoil-peak position in a TOF spectrum will shift from detector to detector. Moreover, the kinematics involved in neutron-proton collisions will influence differently the widths of resolution functions \( R_M \) for different detectors. Thus, a fit to a sum of normalised TOF spectra, recorded by a group of detectors placed at a wide range of scattering angles, must be performed using a sum of unit-area normalised functions, given by Eq.3, with each element of the sum calculated for a different set of instrument parameters representing different detector (the so-called CAAD method\(^13\)). If chosen detectors lie within a relatively narrow scattering angular range and distance from the sample, the CAAD sum can be replaced with a fit using a single function given by Eq. 1 with average values of instrument parameters for the detectors in the group. Such detector grouping will always introduce an additional distribution of geometrical parameters which, by virtue of error propagation, will broaden the resolution function \( R_M \) for every mass \( M \), a process that can be mathematically described by an effective unit-area normalised resolution function, \( R_{eff,M} \). Such an approach produces spectra with signal-to-noise ratios better than for single detectors and avoids complications associated with globally fitting spectra acquired by detectors covering a large kinematic range. Here, the MANSE spectra recorded in forward scattering were grouped in 8 groups representing 8 detector banks. The data was fitted on the bank-by-bank basis using Eq.1 with the resolution function, \( R_{eff,M} \), obtained by averaging instrument parameters within each group of detectors. Figure 2 shows the results of this procedure, as applied to data recorded at low (-40 degrees, detector bank 3) and high (-60 degrees, detector bank 1) scattering angles, for the thinnest (0.05 mm thickness) and thickest (4.3 mm thickness) LDPE sample investigated. All spectra shown in Fig. 2 consist of two recoil peaks: (i) the H recoil peak, centred at lower TOF values, and (ii) a C recoil peak, to the right of the H recoil peak.

In the limit of single scattering, experimental spectra can be fitted with a linear combination of mass-dependent line shapes, given by Eq. 3 and shown as solid lines in panels (a) and (b) in Fig. 2. With increasing sample thickness the agreement between fitting curves and experimental data worsens due to contributions from multiple scattering in the sample (as shown in panels c and d in Fig. 2). The multiple scattering contribution (MS) of epithermal neutrons for the case of VESUVIO spectrometer was described thoroughly by Mayers et al.\(^19\) In Figure 2, MS is visible as a positive signal plateau left from the centre of the H recoil peak for the thickest sample (panels c and d). As described in Ref.\(^19\), MS is flat from the shortest recorded TOF value of 50 μs up to the centre of the proton recoil peak. Following this, the magnitude of MS decreases approximately in a linear manner to reach zero value in the region of H and C recoil-peak overlap. Thus, to a good degree of accuracy, the MS contribution at the C recoil peak can be neglected for all scattering angles and LDPE sample thickness values considered and the C recoil-peak shape can be very well described within the single-scattering limit. Using this approximation, the integrated H intensities from LDPE MANSE data (denoted as \( I_H \)) were calculated, for each detector bank, by numerical integration of H recoil peaks over the TOF interval 50 – 550 μs after subtraction of the C contribution fitted to recorded...
Fig. 2 MANSE data for LDPE recorded at 300 K. Data recorded at low (-40 degrees, left panels) and high (-60 degrees, right panels) scattering angles are shown for the thinnest (0.05 mm, top panels) and thickest (4.8 mm, bottom panels) LDPE sample. The fit of the experimental data (red trace) is performed using Eq. (1). The individual contributions to the fit from H and C recoil peaks are shown as red and blue traces, respectively. In the limit of single scattering (thin samples) experimental spectra can be fitted with a linear combination of mass-dependent line shapes, given by Eq. 3 and shown as solid lines in panels (a) and (b). For thicker samples the single scattering limit is no longer valid due to the presence of multiple scattering contribution visible as a positive signal plateau left from the centre of the H recoil peak for the thickest sample (panels c and d).

MANSE data in the single-scattering limit using Eqs. 3 and 1. The total integrated intensities were then obtained by direct summation of $I_H$ over all forward-scattering detectors (hereafter denoted as $I_{HT}$).

### 3 The choice of the blank

The choice of the suitable system to represent the blank measurement is of utmost importance for a number of reasons. Firstly, as mentioned in the seminal work by Currie, an estimate is necessary of the critical data acquisition time, beyond which an apparatus will start counting noise as analyte. Currie established a graphical method to find this critical data acquisition time. Namely, two histograms, representing the probability distribution functions of the apparatus responses to the blank and a given analyte concentration respectively, should overlap at a given critical value of the analyte concentration. The probability distribution function of the responses to a given analyte concentration, when integrated up to this critical value, should then give no more than one percent probability. In other words, a detection limit can be established corresponding to the smallest concentration of the analyte that will yield a net count above system background detected with 99% probability with only 1% probability of falsely concluding that a blank observation represents an analyte signal.

The manner in which the expectation value and the standard deviation of the blank are obtained can vary depending on the type of spectroscopic measurement under consideration. In single-channel measurements (for example, in alpha and beta radiation-counting applications) a non-radioactive blank count is often performed for this purpose prior to the sample assay. However, in multichannel spectroscopic measurements, such as those employing the neutron TOF detection, it is common to specify 'sidecar' regions on either side of the peak region of interest (ROI) which can be used to estimate the continuum counts beneath the peak. MANSE has a unique place amongst these multichannel measurements due to the fact that neutron scattering off each isotope occupies largely exclusive fraction of the accessible $E - Q$ plane. Thus, MANSE produces a series of peaks for different isotopes whose ROIs are almost mutually exclusive, particularly at high scattering angles. MANSE detection of H amount in bulk is even more special as this isotope scatters epithermal neutrons only in the forward direction (in the single-scattering limit) and the H peak ROIs correspond to the lowest time-of-flight channels, kinematically forbidden to other elements, as illustrated in Fig. 3. Figure 3 shows calculated profile of the spectral response, $C(Q(\theta, t), E(t))$, associated with atomic-recoil excitations in the polyethylene sample. The calculation was performed for indirect-geometry configuration of the VESUVIO spectrometer with the final energy fixed at $E_1 = 4908$ meV and the scattering angle of 70 degrees, and using the CH$_2$ formula unit. Atomic-recoil exci-
Fig. 3 Calculated profile of the spectral response, $C(Q(\theta, t), E(t))$, associated with atomic-recoil excitations of H (red shaded area under the peak with label H) and C (blue shaded area under the peak with label C) in the polyethylene. The H and C recoil peaks lie on the instrument trajectory crossing the H recoil line (solid red line) and the C recoil line (blue solid curve). See text for details.

Fig. 4 Integrated intensities of different systems chosen as blank and background shown for different numbers of accumulated runs along with their respective 1-STD confidence bands: (i) 'sidecar' region (550–600 µs) in MANSE spectra of LDPE - filled green diamond symbols and green shaded area; (ii) thin plain slabs of H-free high-grade purity vanadium - olive filled square symbols along and olive shaded area; (iii) thin plain slabs of H-free high-grade purity lead - orange upward triangles along with transparent orange shaded area; (iv) empty instrument - black filled squares along with grey shaded area; (v) empty aluminium sample container - red filled circles along with red shaded area. See text for details.

As shown in Fig. 2, for the particular case of MANSE spectra of LDPE, the 'sidecar' regions can be easily chosen on the right-hand-side of the ROI, which in this case is the TOF region occupied by the H and C recoil peaks ranging from 50 to 400 µs. It is this 'sidecar' TOF region of the LDPE spectra, on the right of the C peak in the MANSE spectrum of LDPE that extends from 47 to 48 Å\(^{-1}\) on the $Q$ axis and on the negative side of the energy transfer axis, $E$. Using the mapping between the $Q$ and $E$ and TOF values, given by the instrument calibration, one obtains a desired 'sidecar' region from 550 to 600 µs. The integral intensity of this 'sidecar' region, calculated for different numbers of accumulated runs, starts the catalogue of different systems chosen as blank and background, shown in Figs. 4 and 6, and is shown as filled green diamond symbols along with transparent green 1-STD confidence band. Apart from these data, Fig 4 shows, in form of scattered plots with colour-matched 1-STD confidence bands, data for other candidates for a blank measurement, thin plain slabs of H-free high-grade purity vanadium and lead, shown as olive filled square symbols and orange upward triangles respectively. As for the systems representing the background, empty instrument and empty aluminium sample container integrated intensities are shown as black filled squares and red filled circles, respectively.

Perhaps the most natural candidate for a blank measurement for the case of the LDPE is a sample of pure graphite. The sample was carefully prepared by enclosing fine-mesh high-purity graphite powder in an aluminium sachet, and subsequently, in an aluminium container, thus forming a thin plane-slab sample, in which neutron scattering off carbon and aluminium are both within the single-scattering limit. Ensuring the single-scattering limit was necessary in order to avoid counting scattering intensity due to neutrons multiply scattered off carbon in the ROI of the H peak. As clearly seen from the inset of Fig. 5, the sample transmission for epithermal neutrons is ca. 95% (5% scattering power). In this limit, the magnitude of the multiple scattering can be well approximated treating multiple scattering as series of nearly elastic collisions, with dominating contribution from double scattering. Taking the scattering power of 5% and neglecting the multiple scattering of the order higher than double, one can estimate the magnitude of the double scattering to be $0.05^2 = 0.25\%$. Consequently, the MANSE spectrum of the graphite sample can be very well described within the single-scattering limit using Eqs. 3 and 1. Figure 5 shows the sum of graphite sample MANSE forward scattering spectra recorded at VESUVIO together with the sum of the fitting lines, for the total signal (black solid line), the C recoil peak (red solid line and shaded area) and aluminium container and sachet recoil peak (green solid line and shaded area). Clearly,
both the ROI of the H recoil peak in the region from 100 to 300 \( \mu s \) and the ‘sidecar’ region from 550 to 600 \( \mu s \) are clear of any scattering intensity from the sample and container.

The integral intensities, obtained by the direct numerical integration of graphite MANSE spectra, together with their respective 1-STD confidence bands, are shown in Fig. 6. The integral intensities were obtained by three different computational routes: (i) (wine filled pentagons and wine shaded area) integration of the raw spectra of a pure graphite sample in the ‘sidecar’ region from 550 to 600 \( \mu s \), (ii) (gray filled stars and grey shaded area) integration of the raw spectra in the ROI of H, from 100 to 300 \( \mu s \), and (iii) (dark yellow filled circles and shaded region) integration of reduced spectra in the ROI of H, whereby the reduced spectra were obtained by subtracting, from the total raw spectra, the fitting curves to C recoil peaks calculated in the single-scattering limit using Eqs. 3 and 1. This last computational route was chosen in order to mimic the calculation of the H integrated intensities of the LDPE, shown in Sec. 4, in the limit of vanishing concentration of the analyte.

Taken together, all data shown in Figs. 4 and 6, starting from 10 accumulated runs onwards, converge towards the zero value, whereas their respective 1-STD confidence bands are bounded by the value of four. It is perhaps worth noting that, in case of blank and empty instrument spectra, this convergence is oscillatory in nature, whereby the integral intensities adopt both small positive
and small negative values. It is a simple consequence of the fact that each MANSE spectrum of the blank and empty instrument is obtained as a difference of the foil-out and foil-in spectra, both containing close-to-zero numbers of counts. On the whole, it can be safely assumed that the expectation value of the integrated intensity for a blank measurement is zero and its standard deviation is no bigger than four counts. These values will be thus used in all subsequent calculations of the limit of detection and the limit of H quantitation of the MANSE method. Importantly, this result demonstrates the consistency of all three computation routes adopted for the calculation of the integral intensities of the blank and the right choice of the ROIs, both for the ‘sidecar’ region and the ROI of H.

4 The limit of detection and the limit of quantitation of hydrogen

The limits of detection (LOD) and quantitation (LOQ) of H (for definition of LOD and LOQ, see Section 3.3 of the main article) were obtained by calculating cumulative (as a function of the number of accumulate runs) average and standard deviation values of integrated intensities of the LDPE sample of 0.25-mm thickness with n of 3.076 mmol/cm² (see Table 1) and the blank measurement (see Fig. 4). The H integrated intensities were obtained by numerically integrating the histograms representing the H recoil peaks obtained in forward scattering by subtracting, from the total MANSE spectra, the fitting curves to C recoil peaks calculated in the single-scattering limit using Eqs. 3 and 1. The standard deviations of the H integrated intensities were obtained by adding in quadrature the errors of individual histogram bins. The integrated intensities of the blank were calculated by integrating numerically the histograms representing MANSE spectra of H-free high-grade purity vanadium and lead thin plane slabs, shown in Fig. 4. The integration was performed in the TOF region corresponding to the the ROI of the H recoil peak. The standard deviations of the integral intensities of the blank samples were also obtained by adding in quadrature the errors of individual histogram bins.

It is clear in Fig. 7 that an experiment consisting of 10 accumulated runs gives already a reasonably good statistics with relatively short acquisition time. From 10 accumulated runs onwards, the value of the scattering intensity reaches the asymptotic value of 961 counts and is bounded by 1-STD confidence interval of 24 counts. Based on these two values, the sensitivity of the MANSE method, S, can be calculated as \( S = \frac{(3.076 - 0) \text{ mmol/cm}^2}{(961 - 0) \text{ count}} = 0.0032 \text{ mmol/cm}^2/\text{count} \). Using the value of the sensitivity, \( S = 3.2 \mu\text{mol/cm}^2/\text{count} \), and the standard deviation of the blank measurement, 4 counts, one obtains LOD of 0.0032·3.4 = 38.4 μmol/cm² and LOQ of 0.0032·10.4 = 128 μmol/cm².

5 Determination of the LDPE sample transmission

In order to quantify the contribution from multiple scattering and γ-background to the total H integrated intensity, the transmission levels of a series of LDPE samples of various thicknesses between 0.05 and 4.8 mm were calculated and compared to the transmission measured with empty instrument. The plot of the LDPE sample transmission vs. H concentration in units of mol/cm² is shown in Fig. 8. The plot shows, along with data points, an exponential decay fitting curve together with 95% and 99% confidence bands (as solid red line, red shaded area, and light red shaded area, respectively). Fitting the sample transmission, \( T \), with an exponential decay of the form, \( T = \exp(-\lambda \gamma) \), yields \( \lambda = 17.4 \pm 0.5 \text{ mm/cm}^2 \). Given this exponential relation, transmission scales linearly with the H concentration in the region between 0 and ca. 7 mmol/cm² (LDPE sample thickness in the region between 0 and 0.5 mm), a clear signature that the neutron scattering from the LDPE sample is within the single-scattering limit.

This linear region is shown in Fig. 8 as the pink shaded area. A linear fit of the LDPE sample transmission as a function of \( n \) is shown in the inset in Fig. 8 as the black solid line.

References

1 www.isis.stfc.ac.uk/instruments/vesuvio.
**Fig. 8** LDPE sample transmission vs. \( n \). See text for details.


