Supporting Information
for
Hydrogen Detection Limits and Instrument Sensitivity of High-Resolution Broadband Neutron Spectrometers

Claudia Scatigno,[1,2,3,*] Matteo Zanetti,[1,4] Svemir Rudić,[1,*] Roberto Senesi,[5,6] Carla Andreani,[5,7] Giuseppe Gorini[8,9] and Felix Fernandez-Alonso[10,11,12,13]

1. ISIS Facility, STFC, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK.
2. Centro Fermi – Museo Storico della Fisica e Centro Studi e Ricerche "Enrico Fermi", Piazza del Viminale 1, 00184 Roma, Italy.
3. Università degli Studi di Roma "Tor Vergata", Dipartimento di Scienze e Tecnologie Chimiche, Piazzale Aldo Moro 7, 00185 Roma, Italy.
4. Consiglio Nazionale delle Ricerche, Dipartimento di Scienze Fisiche e Tecnologie della Materia, 00185 Roma, Italy.
5. Università degli Studi di Roma "Tor Vergata", Dipartimento di Fisica and Centro NAST, Via della Ricerca Scientifica 1, 00133 Roma, Italy.
6. CNR-ISM, Via del Fosso del Cavaliere 100, 00133 Roma, Italy.
7. CNR-IPCB, Via Campi Flegrei 34, Comprensorio "A. Olivetti", 80078 Pozzuoli, Naples, Italy.
8. Università degli studi di Milano-Bicocca, Piazza della Scienza 3, 20126 Milano, Italy.
9. Istituto di Fisica del Plasma "P. Caldirola", Consiglio Nazionale delle Ricerche, 20125 Milano, Italy.
10. Materials Physics Centre, CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastian, Spain.
11. Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastian, Spain.
12. Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.
13. IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain.

* Authors for correspondence.

Claudia Scatigno - Email: claudia.scatigno@cref.it
Svemir Rudić - Email: svemir.rudic@stfc.ac.uk

Abstract: The supporting information contains further details associated with the experimental measurements presented in the manuscript. In particular, the specifications and details of each analyte used can be found in Tables S1-S3. The LOD and LOQ values for elemental hydrogen analyte when ZrH_2, 2,5-diiodothiophene, and low density polyethylene are used as spectral calibrants, are given in Tables S5, S6, and S7, respectively. Finally, the SI contains the inelastic neutron scattering (INS) spectra of 2,5-diiodothiophene and low density polyethylene (LDPE) analytes as a function of sample mass, from which corresponding calibration curves i.e. analytical sensitivity (for a particular spectral range) were determined.

Table of contents

Table S1. Physical characteristics of the measured ZrH_2 samples denoted by letter Z. Samples were enclosed (or not) within aluminium sachet(s) and placed within standard TOSCA neutron spectrometer sample flat cell made from aluminium. Sample denoted by letter B refers to cell and sachet without the presence of analyte. Integrated proton current is a measure of 'time' taken to record the inelastic neutron scattering spectrum of each sample. $M_r(ZrH_2) = 93.2358$ $gmol^{-1}$.

Sample name	Sample mass (g)	Number of moles (μmol)	Spacing within Al cell (mm)	Number of Al sachets	Sample area (cm^2)	Integrated proton current (μA hours)
B1	-	-	1	1	4.0 x 4.8	1500.0
Z1	0.0091	98	1	3	1.0 x 1.0	2080.6
Z2	0.0175	188	1	3	1.0 x 1.0	1644.1
Z3	0.0348	373	1	3	1.0 x 1.0	1772.6
Z4	0.0710	762	1	3	1.0 x 1.0	2035.1
Z5	0.1504	1613	1	4	1.5 x 1.5	600.0
Z6	1.1000	11798	1	1	4.0 x 4.8	1430.6
Z7	3.5000	37539	1	1	4.0 x 4.8	700.7
Z8	5.3570	57456	1	0	4.0 x 4.8	286.7

Table S2. Physical characteristics of the measured 2,5-diiodothiophene samples denoted by letter D. Samples were enclosed within aluminium sachet(s) and placed within standard TOSCA neutron spectrometer sample flat cell made from aluminium. Sample denoted by letter B refers to cell and sachet without the presence of analyte. Integrated proton current is a measure of 'time' taken to record the inelastic neutron scattering spectrum of each sample. $M_r(C_4H_2I_2S) = 335.9198\ gmol^{-1}$.

Sample name	Sample mass (g)	Number of moles (µmol)	Spacing within Al cell (mm)	Number of Al sachets	Sample area (cm^2)	Integrated proton current (µA hours)
B2	-	-	1	1	4.0 x 4.8	600.0
D1	0.0180	54	1	3	1.0 x 1.0	1645.0
D2	0.0380	113	1	3	1.0 x 1.0	1988.2
D3	0.0810	241	1	3	1.0 x 1.0	2016.4
D4	0.5010	1491	1	1	3.0 x 3.0	900.7
D5	1.0033	2987	1	1	3.0 x 3.0	1712.0
D6	3.0005	8932	1	1	4.0 x 4.8	240.9

Table S3. Physical characteristics of the measured low-density polyethylene (LDPE) samples denoted by letter PE. Geometrically smaller samples (PE2, PE4, PE5) were placed within standard TOSCA neutron spectrometer sample flat cell made from aluminium, while others were kept within larger frame that allowed their examination without interference between neutron beam and the frame i.e. sample holder. Sample denoted by letter B refers to empty cryostat. Integrated proton current is a measure of 'time' taken to record the inelastic neutron scattering spectrum of each sample. Mass of samples kept within the frame was derived from their density and volume; Volume = Analyte thickness x Sample area. $M_r(CH_2)$ = 14.0264 $gmol^{-1}$.

Sample name	Sample density (g/cm^3)	Sample mass (g)	Number of moles (µmol)	Analyte thickness (mm)	Number of slabs into Al frame	Sample area (cm^2)	Holder type	Integrated proton current (µA hours)
B3	-	-	-	-	-	-	-	400.2
PE1	0.8400	0.0672	4791	0.05	1	4.0 x 4.0	Frame	2079.1
PE2	0.9420	0.2167	15447	2.30	1	1.0 x 1.0	Cell	400.1
PE3	0.8790	0.7032	50134	0.50	2	4.0 x 4.0	Frame	472.4
PE4	0.9420	0.8666	61786	9.20	4	1.0 x 1.0	Cell	300.1
PE5	0.9420	0.8666	61786	2.30	1	2.0 x 2.0	Cell	300.0
PE6	0.9090	1.4399	102653	0.99	1	4.0 x 4.0	Frame	600.0
PE7	0.9090	1.4544	103690	1.00	1	4.0 x 4.0	Frame	501.3

Table S4. Energy ranges across which the inelastic neutron scattering spectra were integrated. ES stands for entire spectrum and EL for elastic line, and this is true for all three analytes. FH stands for first harmonic, SH for second harmonic, and TH for third harmonic in the case of ZrH_2; ν1 - ν20 stands for vibrational modes of $C_4H_2I_2S$; Range1 - Range3 stands for energy ranges in the case of low density polyethylene (LDPE). INS denotes the sum of the ranges within the inelastic neutron scattering region, e.g. for ZrH_2 INS = FH + SH + TH, rather than integration across the whole INS range.

Label	Integrated range (meV)		Analyte
ES1000	-0.235	1000.000	All
ES500	-0.235	500.000	All
EL	-0.235	0.245	All
FH	130.000	150.000	ZrH_2
SH	255.300	299.500	ZrH_2
TH	380.500	448.600	ZrH_2
INS	130.000	448.600	ZrH_2
ν1	4.070	5.670	$C_4H_2I_2S$
ν2	6.250	7.020	$C_4H_2I_2S$
ν3	7.020	7.680	$C_4H_2I_2S$
ν4	8.880	10.620	$C_4H_2I_2S$
ν5	11.900	15.910	$C_4H_2I_2S$
ν6	22.330	24.040	$C_4H_2I_2S$
ν7	26.630	28.930	$C_4H_2I_2S$
ν8	28.930	30.640	$C_4H_2I_2S$
ν9	42.370	45.560	$C_4H_2I_2S$
ν10	54.740	57.870	$C_4H_2I_2S$
ν11	63.860	68.210	$C_4H_2I_2S$
ν12	78.040	80.030	$C_4H_2I_2S$
ν13	88.890	92.060	$C_4H_2I_2S$
ν14	95.840	100.150	$C_4H_2I_2S$
ν15	104.350	110.150	$C_4H_2I_2S$
ν16	111.940	115.880	$C_4H_2I_2S$
ν17	115.810	119.820	$C_4H_2I_2S$
ν18	128.480	132.550	$C_4H_2I_2S$
ν19	145.680	150.860	$C_4H_2I_2S$
ν20	154.680	161.760	$C_4H_2I_2S$
Range1	123.000	173.000	LDPE
Range2	173.000	186.000	LDPE
Range3	347.000	396.000	LDPE

Table S5. LOD and LOQ (in µmol) for elemental hydrogen analyte when ZrH_2 is used as spectral calibrant. Column denoted with '0' shows values derived with the help of backward scattering detectors, '1' shows values derived with the help of forward scattering detectors, while '2' shows values derived with the help of all available detectors i.e. backward and forward together.

Label	LOD_H			LOQ_H		
	0	1	2	0	1	2
ES1000	842	727	632	2806	2422	2106
ES500	561	409	341	1871	1365	1136
EL	105	50	61	349	166	204
FH	168	177	128	561	591	428
SH	651	662	414	2171	2206	1379
TH	873	843	708	2910	2810	2362
INS	305	387	283	1018	1288	943

Table S6. LOD and LOQ (in µmol) for elemental hydrogen analyte when 2,5-diiodothiophene is used as spectral calibrant. Column denoted with '0' shows values derived with the help of backward scattering detectors, '1' shows values derived with the help of forward scattering detectors, while '2' shows values derived with the help of all available detectors i.e. backward and forward together.

Label	LOD_H			LOQ_H		
	0	1	2	0	1	2
ES1000	1048	405	555	3493	1349	1850
ES500	612	373	414	2038	1244	1381
EL	46	26	48	152	88	159
ν1	389	664	95	1295	2215	316
ν2	444	459	256	1479	1530	853
ν3	720	688	490	2401	2295	1635
ν4	306	296	221	1019	986	737
ν5	536	1017	617	1785	3391	2056
ν6	1548	3705	1626	5161	12350	5419
ν7	961	1227	605	3202	4089	2015
ν8	319	977	343	1063	3257	1144
ν9	632	410	288	2108	1368	960
ν10	995	892	764	3317	2972	2548
ν11	484	505	337	1612	1685	1124
ν12	2559	2251	2332	8531	7504	7773
ν13	983	912	877	3276	3040	2924
ν14	363	232	267	1211	775	891
ν15	535	548	313	1783	1826	1043
ν16	661	474	438	2204	1581	1459
ν17	1328	1301	788	4427	4338	2628
ν18	1436	767	1008	4787	2557	3358
ν19	940	724	622	3133	2414	2072
ν20	2758	1471	1655	9192	4905	5516
INS	484	356	340	1615	1188	1135

Table S7. LOD and LOQ (in µmol) for elemental hydrogen analyte when low density polyethylene (LDPE) is used as spectral calibrant. Column denoted with '0' shows values derived with the help of backward scattering detectors, '1' shows values derived with the help of forward scattering detectors, while '2' shows values derived with the help of all available detectors i.e. backward and forward together.

Label	LOD_H			LOQ_H		
	0	1	2	0	1	2
ES1000	421	453	340	1405	1510	1133
ES500	410	426	398	1366	1419	1326
EL	1530	217	885	5100	725	2949
Range1	234	427	275	780	1423	917
Range2	658	692	516	2193	2307	1720
Range3	1720	1344	1262	5734	4479	4207
INS	772	540	593	2572	1800	1976

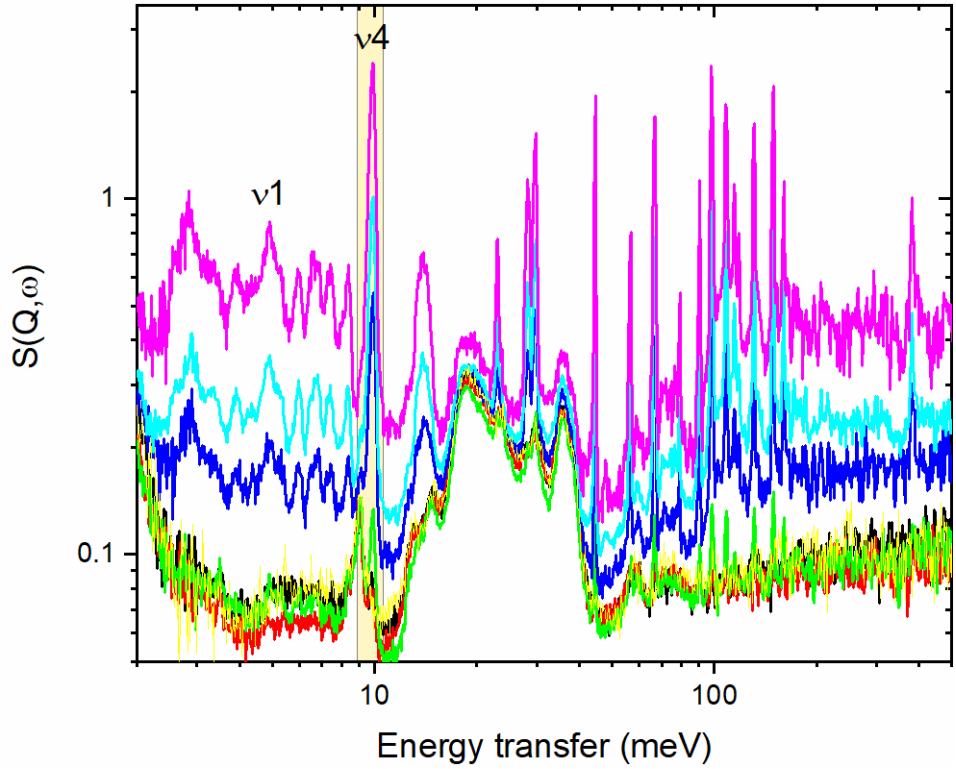

Figure S1. Inelastic neutron scattering spectra of 2,5-diiodothiophene as a function of sample (D1-D6) mass. The yellow trace corresponds to the INS spectrum of an empty aluminium cell and sachet. The spectra were recorded at temperature of 10 K. ν1 and ν4 vibrational modes mentioned in the text are specifically denoted, as well as the energy range used for integration of ν4 peak.

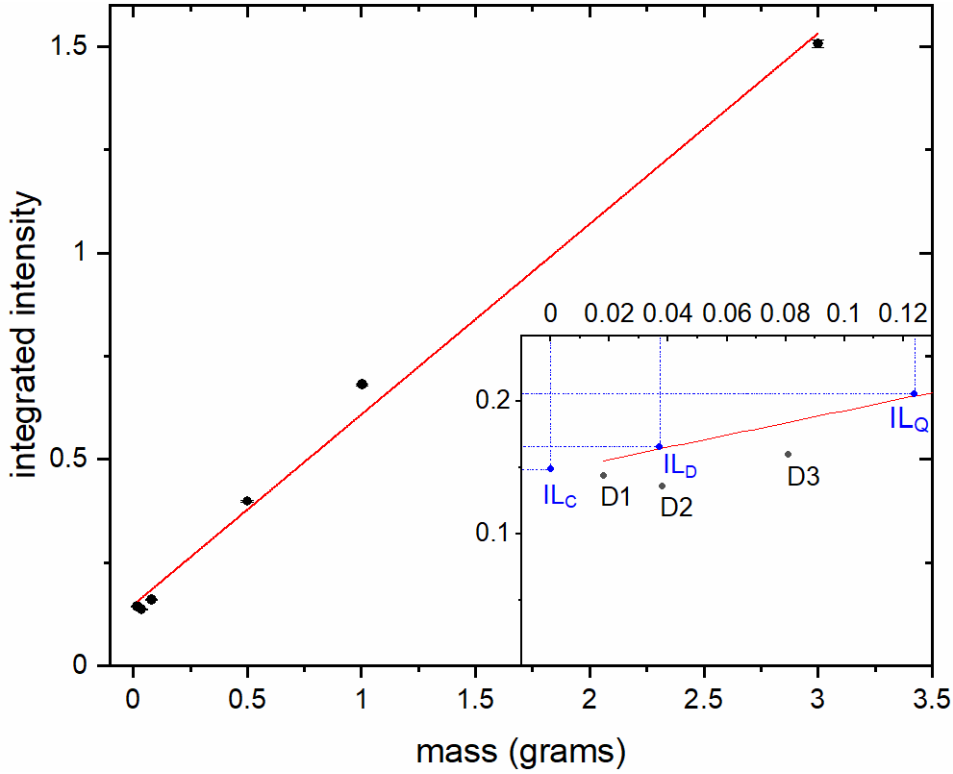

Figure S2. Integrated intensity of 2,5-diiodothiophene ν4 vibrational mode as a function of sample mass. Red line is a linear fit through the experimental points used to derive analytical sensitivity. The inset in the bottom right corner shows low mass part of the calibration curve, as well as derived intensity count values of the blank (IL_C), detection (IL_D) and quantification (IL_Q).

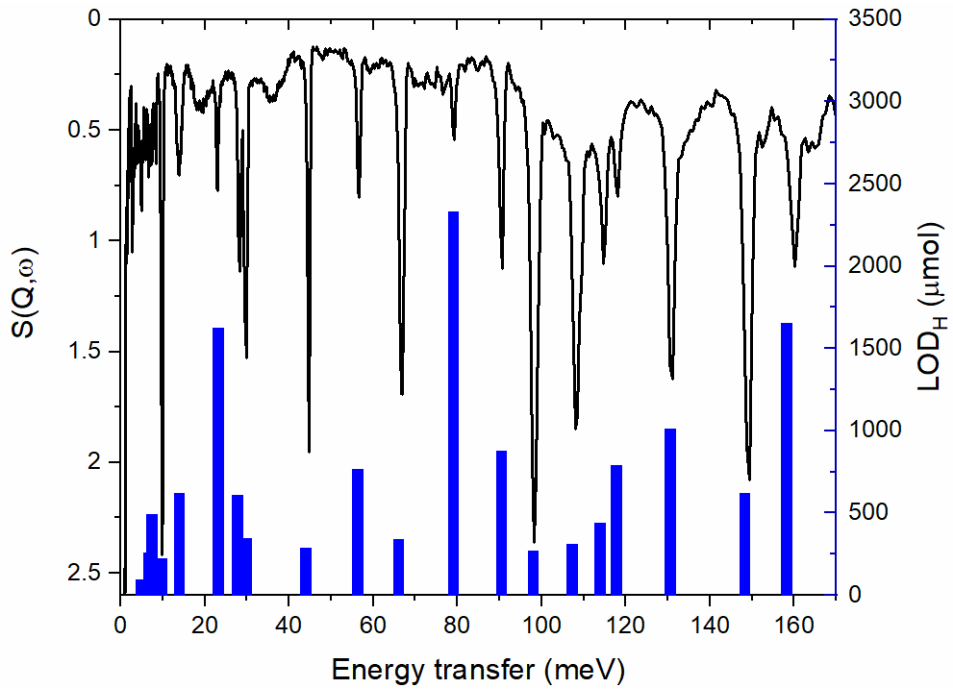

Figure S3. LOD of elemental hydrogen in 2,5-diiodothiophene analyte as measured on TOSCA neutron spectrometer for a particular vibrational mode is shown as histogram. INS spectrum of 2,5-diiodothiophene is superimposed for ease of reference.

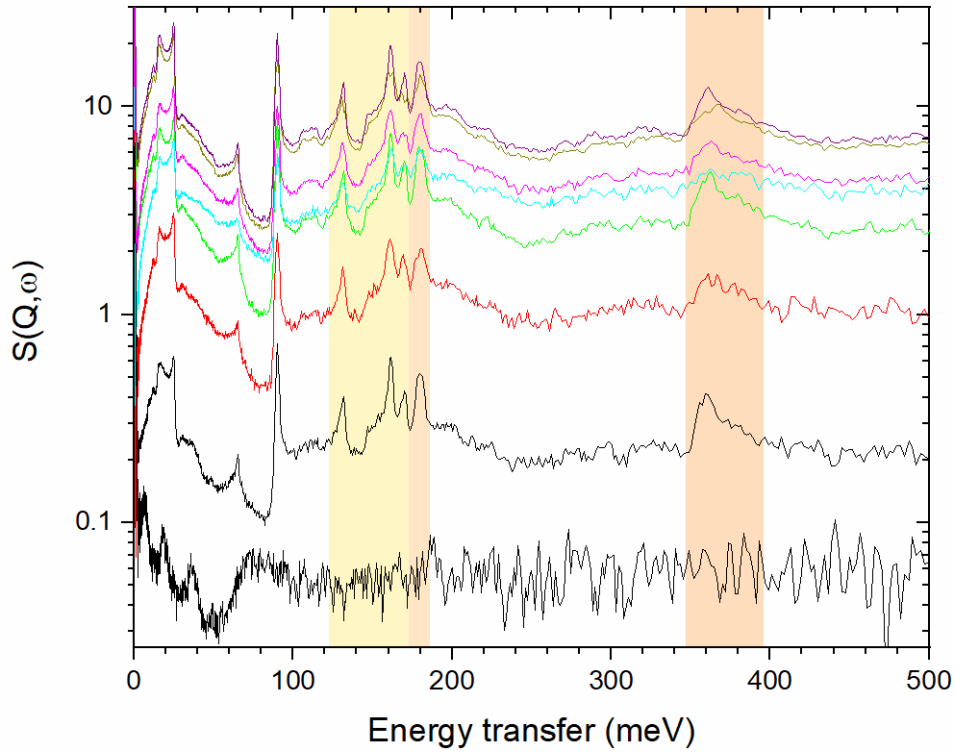

Figure S4. Inelastic neutron scattering spectra of low-density polyethylene as a function of sample (PE1-PE7) mass. The lowest intensity trace corresponds to the INS spectrum of the empty cryostat. The spectra were recorded at temperature of 10 K. The highlighted spectral ranges in terms of increasing energy transfer correspond to Range 1, 2, and 3, respectively, as in indicated in Table S4.

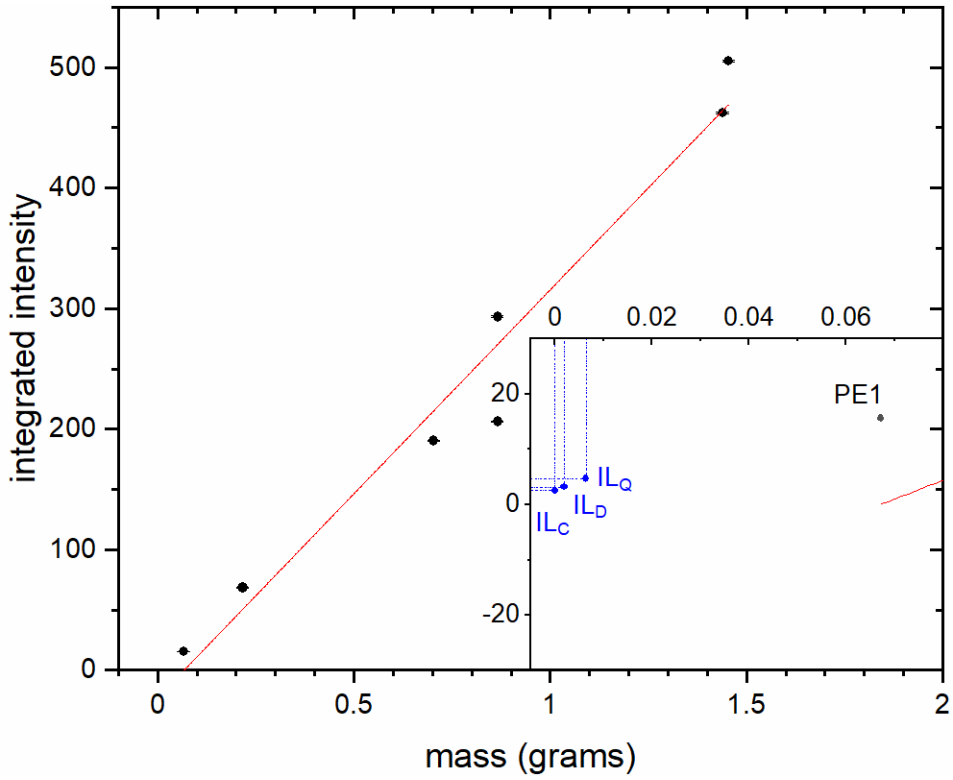

Figure S5. Integrated intensity of low-density polyethylene 'Range1' as a function of sample mass. Red line is a linear fit through the experimental points used to derive analytical sensitivity. The inset in bottom right corner shows low mass part of the calibration curve, as well as derived intensity count values of the blank (IL_C), detection (IL_D) and quantification (IL_Q).

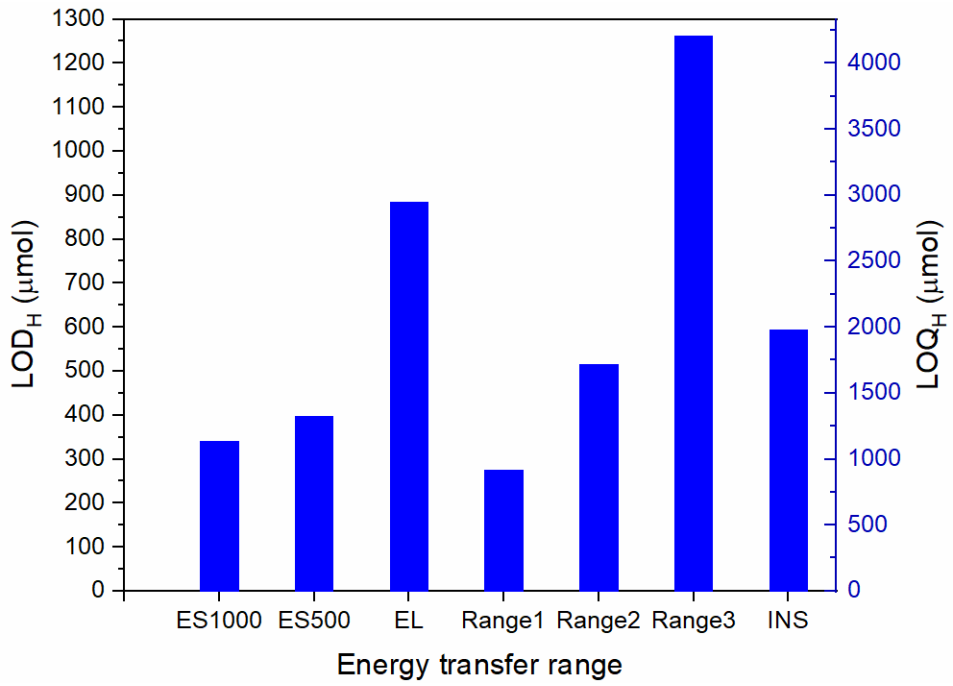

Figure S6. LOD and LOQ of elemental hydrogen in low-density polyethylene as measured on TOSCA neutron spectrometer for a particular spectral energy range, are shown as histogram.