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Unlocking the potential of NMR spectroscopy for precise and efficient quantification of microplastics

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Abstract

Precise, fast, and reliable identification and quantification of microplastic contamination are essential for determining their environmental concentrations for risk assessments. This study investigates the use of nuclear magnetic resonance (NMR) spectroscopy to quantify microplastics by analysing dilution series of polystyrene (PS), polyisoprene-cis (PI), polybutadiene-cis (PB), polylactic acid (PLA), polyvinyl chloride (PVC) and polyurethane (PU). Each polymer type was dissolved in a suitable solvent and an internal standard was utilized for quantification. Detection and quantification limits for each polymer type were established in two ways: (1) by using an equation based on proton signals and an internal standard with known concentration and (2) by using the LOQ based on the signal-to-noise ratio. Both data sets were compared and showed that using the internal standard (method 1) results in more accurate and lower concentration limits in the range of 0.2–8 $\mu\text{g mL}^{-1}$ for all six polymer types, while the LOQ based on the SNR (method 2) gives consistently higher concentration limits (1–10 $\mu\text{g mL}^{-1}$). The research shows the accuracy, efficacy, and reliability of quantitative NMR spectroscopy for polymer analysis in these concentration ranges compared to established quantifying methods, such as, PyGC/MS, FTIR, or Raman spectroscopy.

Keywords Microplastic, Quantification, QNMR, NMR spectroscopy, LOD, LOQ

Introduction

Global plastics production has reached 400.3 million tons per year [1], leading to widespread use of plastic items in modern life [1–3]. Plastics are a diverse group of materials, including commonly produced polymers like polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polyester (PET), polyurethane (PU) etc [1]. Microplastics (MPs, 1 μm to 5 mm [3, 4]) and nanoplastics (NPs, < 1 μm [5–8]), have become a topic of great concern regarding to human-health and environmental risk [2, 9]. Primary microplastics are produced as micro-sized particles [10], while secondary

microplastics are generated from the breakdown of larger plastic [11–14]. The omnipresence, small size, ingestion, uptake and translocation of MPs into tissues have made them a major environmental issue [4, 11–13], requiring further research to clarify the evidence for their toxicity [15]. Risk assessments require quantification of the substances in question and determination of dose-effects [16].

Knowledge of exposure levels and hazards form the basis of risk assessments [17, 18]. Rapid, reliable and cost-efficient quantification of MP concentrations in all sorts of matrices are thus needed for better risk assessments. Currently, there are several methods used to identify, qualify, and quantify MPs in environmental samples [19, 20]. These methods include optical methods such as scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy which are mainly used to qualitatively identify the type

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of polymer [20]. SEM provides high-resolution images of MP surface details up to 0.5 nm and therefore, can be used to analyse the weathering process of MPs in natural environments [21]. Besides the disadvantage of being an expensive and time consuming method, SEM is restricted in differentiating between plastics and other particles which leads to a high potential for misclassification of polymer types [22]. The perhaps best suited and most used method to identify plastic items $> 11.3 \mu\text{m}$, is FTIR [2, 23]. In comparison to μ -FTIR, Raman spectroscopy is more suitable to identify small MPs ($> 1 \mu\text{m}$) and deliver their chemical and structural characteristics [24]. Both methods, FTIR and Raman spectroscopy are non-destructive and determine the dimension of particles by visual images, which enables the quantification of MPs based on the particle dimensions and the density of the polymer in question [25]. Nevertheless, this quantification of MPs is not practical due to both optical methods in terms of being time-consuming, and often require intense and expensive sample preparation [26]. Due to inconsistent information on the abundance of microplastic particles given by different studies, comparability of results remain challenging [27–29]. Consequently, there is a need for more efficient and accurate methods for quantifying MP concentrations in environmental samples. Recently, thermoanalytical methods such as thermal desorption gas chromatography-mass spectrometry (TDS-GC-/MS) and pyrolysis gas chromatography-mass spectrometry (PyGC/MS) have been developed to qualitatively and quantitatively detect microplastics by their characteristic decomposition products [25, 30, 31]. These methods have disadvantages such as time-consuming and expensive sample preparations and having limitations such as destroying the sample, hence providing no information about size and shape of the MP particles [30]. To summarize, most of the current best-practice methods are expensive, time-consuming and, due to the high costs per sample, it has become customary to perform only one replicate analysis [26].

Recent research highlights that there is a significant demand for further development of both qualitative and quantitative analysis methods due to the insufficient knowledge of MP concentrations in a range of environmental matrices. Over the last 10 years, quantitative nuclear magnetic resonance (qNMR) spectroscopy has gained popularity as a method for quantitatively detecting and analysing various substances [32, 33], including microplastic particles [34–37]. qNMR has several advantages including being fast and cost-effective, size-independent, sensitive, precise and simple to perform [32, 33]. One potential limitation of qNMR for analysing microplastic particles is that the particles must be dissolved in a suitable solvent [38], which leads to a loss of

information on particle size, colour and shape. Additionally, high-resistant polymer types like PP and PE can only be dissolved at high temperatures [39–41] which currently causes a restriction for the use of qNMR for now. A limiting factor for qNMR is the limit of detection (LOD) and limit of quantification (LOQ). LOD refers to the minimum concentration of an analyte in a sample that can be identified but not necessarily quantified under the specified test conditions. In contrast, LOQ is defined as the lowest concentration of an analyte in a sample that can be reliably quantified [42, 43]. For future use of qNMR in MP quantification it is important to determine these limitations for each polymer type, which will determine the suitable areas of use for the rapid and inexpensive qNMR method.

Recent studies reported the validation of NMR acquisition of single polymers at different concentration levels in environmental samples [34–37]. In contrast, this study focuses on the detection and quantification of NMR spectroscopy for various polymer types by using standard qNMR parametric settings to ensure equality throughout different polymer types, aiming for the same precision and accuracy for all polymers. To our knowledge, qNMR spectroscopy has not been tested and optimized to reach the most accurate and lowest concentration limits possible for a wider range of polymer types. This study compares two different approaches to determine the concentration limits of the pure polymers PS, PLA, PVC, PU, PI and PB by comparing two methods: (1) using the internal standard with known concentration and the specific proton signals of each polymer type and (2) by using the same output data to determine the concentration limits based on the signal-to-noise ratio (SNR).

Materials and methods

Microplastic particles

Microplastic particles were utilized as model particles for detection and quantification by qNMR: PS, PLA, PU beads with a size distribution of 3–5 mm were purchased from GoodFellow Cambridge Ltd., England; PVC powder with a size distribution of $< 50 \mu\text{m}$ and a purity of $> 99.7\%$ was acquired from Werth-Metall, Germany; the natural rubber Polyisoprene-cis (PI) and the synthetic rubber Polybutadiene-cis (PB) were purchased from Sigma Aldrich. Although commercially available particles were utilized as polymer particles, they were deliberately not established standards.

Sample preparation

Deuterated chloroform (CDCl_3 , 99.8 atom % D) from Sigma-Aldrich was used for dissolving PS, PI, PB and PLA. For dissolving PVC and PU, deuterated tetrahydrofuran (THF-d_8 , ≥ 99.5 atom % D) purchased by

Sigma-Aldrich and VWR International, LLC. was used. All polymer types in their corresponding solvents were dissolved at room temperature. A stock solution of the different polymer types was used to prepare a dilution series of varying concentration levels. The dilution series of PS and PVC were prepared with concentrations in the range of 0.1 to 100 $\mu\text{g mL}^{-1}$ and PB, PLA, PI and PU with concentrations in the range of 0.01 to 100 $\mu\text{g mL}^{-1}$. All dilution series were represented with one replicate of each concentration level. The highest concentration level served as a reference. In order to quantify the amount of polymers in the sample, an internal standard of dimethyl sulfone (DMSO_2) purchased by TraceCERT[®], Sigma-Aldrich with a known concentration was added to each polymer sample. To conduct NMR measurements, a volume of 600 μL of the sample solution was transferred into NMR tubes with a diameter of 5 mm (Bruker Bio-Spin, 4'' NMR tubes) and subsequently analysed.

¹H qNMR – quantitative analysis

All NMR experiments were performed using a Bruker Ascend 600 MHz spectrometer with an AVANCE NEO console and a QCI-P CryoProbe[™]. Measurements were performed at 298 K. In qNMR measurements, the acquisition parameters for all MP particles were standardized, with receiver gain and pulse width calibrated automatically for each sample. The spectral width was set at 29.76 ppm, number of scans at 8, spectral size at 262,144 points, acquisition time at 3.67 s, and delay at 60 s for each sample.

For illustrating the obtained ¹H NMR spectra, data were imported into the NMR software program MestReNova (v14.2.0), whereas the qNMR spectra for quantification were imported into the NMR software program TopSpin from Bruker (Version 4.1.3.). For all qNMR data a phase correction and baseline correction were performed manually. All data had a line broadening of 0.1 Hz. For each polymer type, a consistent ppm range was manually integrated in all samples. The integration of the signal areas correlates to the proton atoms and consequently to the concentration of the analyte in the solution. For quantitative assessment, special attention must be taken when integrating the signal regions of interest. To reduce potential measurement or integration errors, the internal standard method was utilized for all quantitative determinations [33]. The proton signal of DMSO_2 functioned as internal standard in all polymer samples. In order to use DMSO_2 as internal standard, it must be ensured that the same concentration is added to each polymer sample and that the concentration is chosen to be in the same intensity range as the deuterated solvents. The concentration of polymers in their corresponding solvents was calculated as follows:

$$C_u = C_r \frac{A_u n_r}{A_r n_u} \quad (1)$$

A_r : integral of the proton of the internal standard with known concentration

A_u : integral of the proton of the polymer sample with unknown concentration

C_r : concentration of the internal standard with known concentration

C_u : concentration of the polymer sample with unknown concentration

n_r : number of atoms of the proton of the internal standard with known concentration

n_u : number of atoms of the proton of the polymer sample with unknown concentration

Calculations and statistical analyses

For the first method, all data were analysed using RStudio (Version 4.1.3). The measured concentration of each polymer type (calculated by Eq. 1) was plotted against the nominal concentration. ANOVA (analysis of variances) was used to calculate variability within the regression models and for significance tests. Therefore, the significance level was set to $p < 0.05$ and F-statistic tests were analysed. Additionally, the confidence interval was set to 0.95. The linearity was established by determining the slope, intercept, and the coefficient of determination (R^2). Moreover, the precision of each polymer concentration level in the dilution series and the mean absolute percentage error (MAPE) of the dilution series compared to the nominal values were calculated for each polymer type (Eq. 2).

$$MAPE [\%] = \left(\left(\frac{1}{n} \right) \sum_{t=1}^n \left| \frac{A_t - M_t}{A_t} \right| \right) * 100 \quad (2)$$

n : polymer sample size

A_t : nominal concentration of the polymer sample

M_t : measured concentration of the polymer sample

For the second method, we used the signal-to-noise ratio (SNR). The limit of detection (LOD) defined as a SNR of 2:1 or 3:1 and limit of quantification (LOQ) defined as a SNR of 10:1, as previously determined [43, 44].

Prevention of contamination and quality control

To prevent the samples from being contaminated with microplastic from airborne particles, glassware and other plastic free equipment underwent a thorough washing process using water, acetone, and distilled water. Glass flasks were dried for 24 h at 60 °C before use and properly sealed with a lid or aluminium foil after cooling off. NMR tubes were dried for 30 min at 60 °C or overnight at room

temperature in a closed laboratory oven. Furthermore, precautions were taken to ensure that lab coats made of pure cotton were worn and closed during sample handling to prevent contamination by clothing polymer fibers. In addition, gloves were worn and changed regularly to prevent cross contamination. All procedures possible were performed under a fume hood. The work surface under the fume hood was cleaned with 95% ethanol and dried with nonabrasive tissues before and after the use and between polymer types [45, 46]. Moreover, the sample tubes were immediately sealed during the dissolution to avoid evaporation of the volatile solvents. As procedural blanks, ^1H NMR and qNMR spectra of pure CDCl_3 and THF-d_8 from bottles and ampules without polymer added, who were also exposed to the fume hood in the same manner as the diluted samples, were acquired.

Results and discussion

Sample preparation and investigation of suitable deuterated solvents

Not all polymers will dissolve in the same solvent. Several suitable solvents were tested, and six polymer types and two solvents were chosen for further method comparison. These were PS, PVC and PU which are among the most abundant polymers produced today (23.2% of the global plastic production [1]). Polyisoprene-cis (PI – “natural rubber”) and polybutadiene-cis (PB – “synthetic rubber”) that are mainly used for tire, footwear and latex production due to their highly elastic properties were chosen to represent rubber. Recently, PI and PB have gained increased attention and interest because of new studies on their presence in environmental samples, as well as their behaviour in the environment and possible harmful effects [47, 48]. PLA is a bioplastic that originated from renewable biomass sources. Due to its similar characteristics as the most abundant plastics PP, PE, and PS [49, 50], PLA has gained more attention in the last few years [51]. However, PP and PE are the most abundant polymers [39–41], but due to their low solubility under normal laboratory conditions, they were not used in this study. Hence, using qNMR for quantification of PE and PP will need further studies.

Conducting quantitative analysis by using NMR spectroscopy, a complete dissolution of the polymer in a deuterated solvent that meets specific criteria is necessary. These requirements include selecting a deuterated solvent whose chemical shift signal differs significantly from those of the polymer to allow for the effective utilization of proton signals as internal standards, and thus, facilitate accurate quantification. In addition, it is vital to ensure that the polymers are fully solubilized rather than simply “swollen”, as this renders measurement unfeasible [52]. We used deuterated chloroform (CDCl_3) and deuterated

tetrahydrofuran (THF-d_8) as solvents [34, 36, 38, 53–55]. Deuterated chloroform was found to be a suitable solvent for PS, PB, PI and PLA with its proton signal at 7.26 ppm. The more expensive deuterated tetrahydrofuran with its proton signals at 3.58 ppm and 1.73 ppm was also a suitable solvent for PVC, PU and again PS. The dilution series of PS were only performed with CDCl_3 to reduce costs.

Contamination control

As procedural blanks, samples of each solvent were taken from ampules and glass bottles and run without the addition of a polymer. The ^1H NMR spectra showed that both solvents from both sources contained, besides the water (H_2O) signals at 1.56 ppm in CDCl_3 and 2.50 ppm in THF-d_8 , several other contaminations especially in the lower ppm range [56]. These impurities were considered while observing possible signal overlays. Since all handlings were performed under a fume hood, external contaminations have been considered. As the procedural blanks were exposed to the fume hood, any contamination that might have entered the sample in the fume hood, was either not dissolvable in the corresponding solvent or too little to detect with the qNMR.

Qualitative analysis by ^1H -NMR

The standard ^1H NMR spectra of PS, PLA, PI and PB in CDCl_3 are presented in Fig. 1, and the ^1H NMR spectra of PU and PVC in THF-d_8 are shown in Fig. 2. A dissolution of the polymer particles was performed before conducting the measurements. The ^1H NMR spectrum of PS showed two signal ranges from 7.20 to 6.20 ppm and 2.30 to 1.10 ppm (Fig. 1A). The first range was assigned to the protons of the aromatic ring (H_a , H_b), and the second range to the protons of the CH_2 -group (H_c) and CH -group (H_d) [57]. PLA (Fig. 1B) was assigned to two proton signals. The first signal in the range of 5.20 to 5.12 ppm (H_a) was assigned to the protons of the CH -group and the second signal in the range of 1.61 to 1.56 ppm (H_b) to the protons of the CH_3 -group [38]. Two signals of PB were found (Fig. 1C). The signal at 5.38 ppm (H_a) corresponded to the protons of the two CH -groups along the double bond and 2.09 ppm (H_b) was assigned to the protons of the two CH_2 -groups [38]. PI was assigned to three signals (Fig. 1D). The signal at 5.12 ppm (H_a) corresponded to the protons of the CH -group along the double bond, whereas the signal at 2.04 ppm (H_b) represented the protons of the two CH_2 -groups and the protons of the CH_3 -group were shown in the signal at 1.68 ppm (H_c) [58].

The ^1H NMR spectrum of PVC showed two signal ranges from 4.70 to 4.25 ppm and 2.44 to 2.00 ppm (Fig. 2A). Both signal ranges were assigned to a CH -group (H_a , H_b) [34]. PU showed six signals (Fig. 2B). The proton

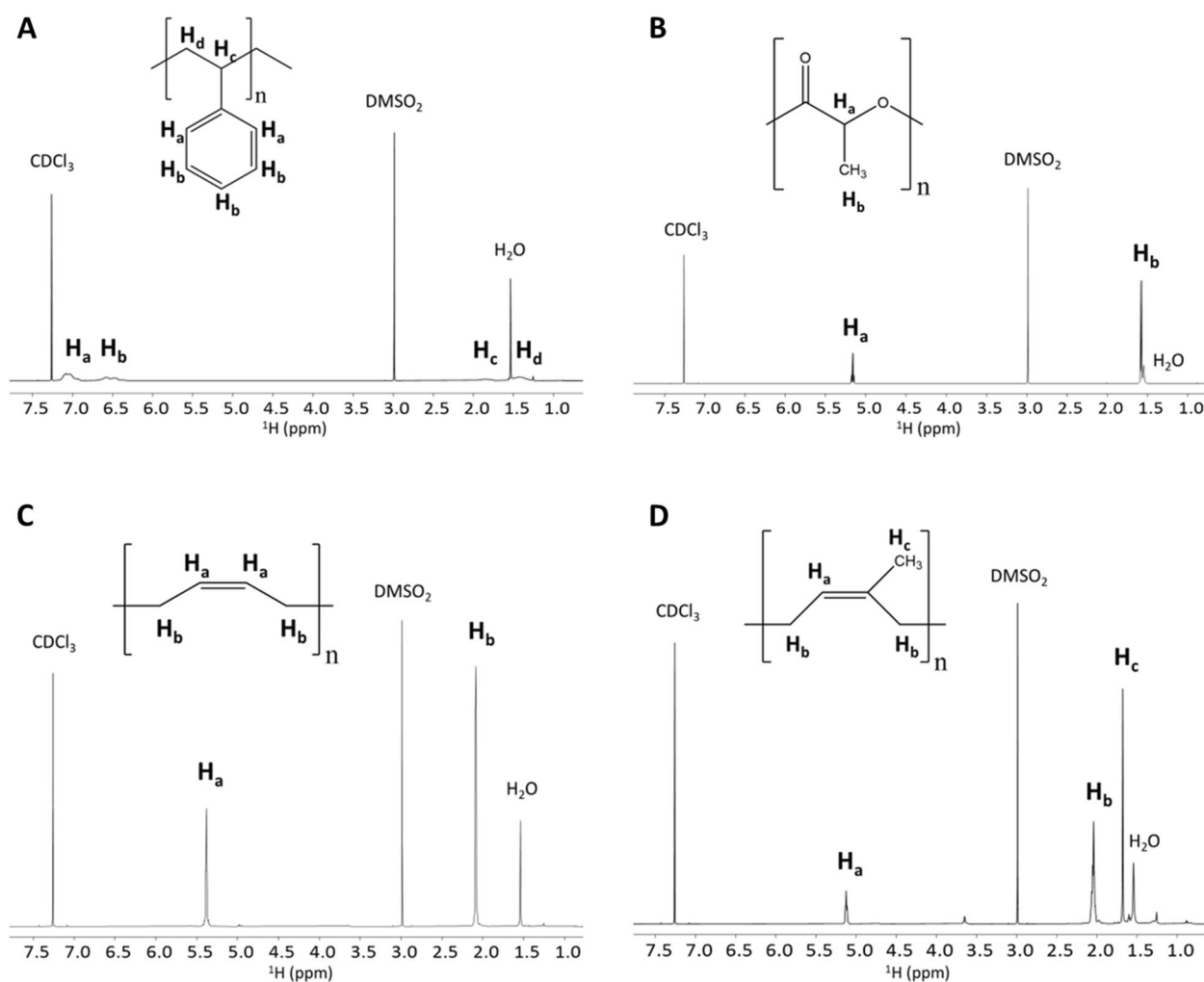


Fig. 1 ^1H NMR spectrum and structural formula of (A) polystyrene (PS), (B) polylactic acid (PLA), (C) polybutadiene-cis (PB) and (D) polyisoprene-cis (PI) in CDCl_3 with a nominal concentration of 1 mg mL^{-1} and DMSO_2 as internal standard. The spectra were acquired on a 600 MHz instrument

signals of doublets in the range of 8.67 to 8.47 ppm (H_a , H_c), 7.07 to 6.98 ppm (H_c) and 4.15 to 4.95 ppm (H_f) were assigned to the protons of the NH-group, the aromatic rings and a CH_2 -group, respectively. A proton signal was found in the range of 7.43 to 7.29 ppm (H_b) and belongs to the protons of the aromatic rings. The proton signal at 3.82 ppm (H_d) was assigned to the CH_2 -group between the aromatic rings and the proton signal at 3.36 ppm (H_g) belongs to a CH_2 -group [59].

Calculations and statistical analyses

To validate the suitability of NMR spectroscopy in quantitative analysis of polymer concentrations, the measured concentration limits according to Eq. 1 and parameters such as MAPE, accuracy and linearity were determined (method 1). For comparison with the concentration in method 1, the LOD and LOQ were calculated based on the SNR (method 2).

Method 1

In method 1, linear regressions were used to determine the linearity between nominal concentrations and measured concentrations based on the integrated signals for the dilution series for each polymer (Figs. 3, 4 and 5). The nominal concentration of each polymer in the corresponding solvent was plotted against the measured concentration in microgram per millilitre (see Eq. 1), along with upper and lower confidence limits of 0.95 and coefficient of determination (R^2) for each regression line. The method can be considered linear with a R^2 of >0.99 [60]. Data points that reduced R^2 values of the regression lines were omitted. This was most often the case for the low concentrations of each polymer type which then affected the lowest concentration that could be considered accurately quantified (see Supplementary Material). The chosen proton signal regions of the polymer types of PS, PB, PI, PLA and PU showed $R^2 > 0.9914$. Only PVC had

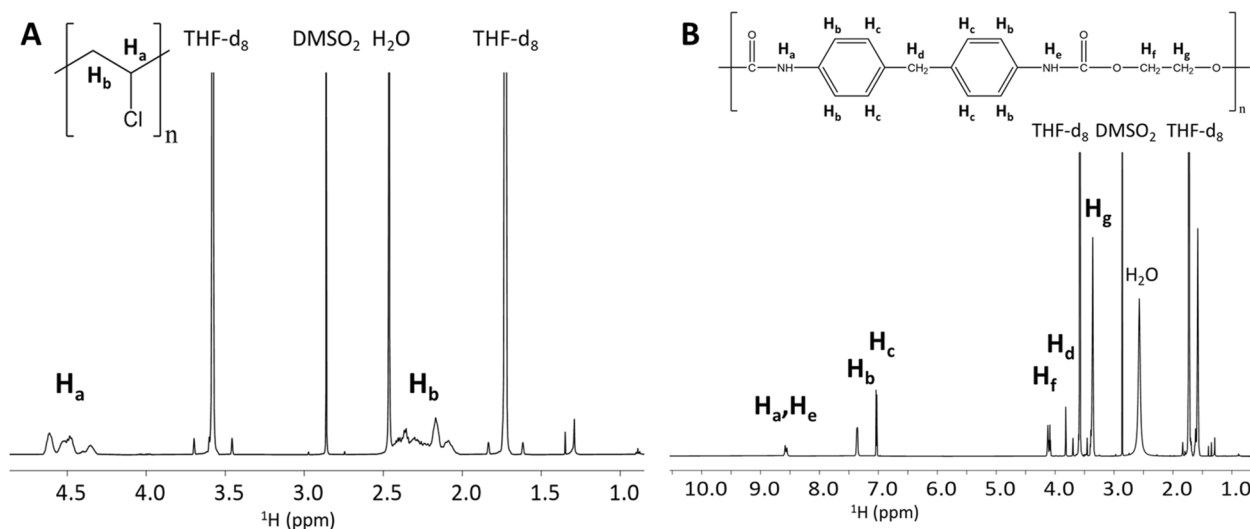


Fig. 2 ^1H NMR spectrum and structural formula of (A) polyvinyl chloride (PVC) and (B) polyurethane (PU) in THF- d_8 with a nominal concentration of 1 mg mL^{-1} and DMSO₂ as internal standard. The spectra were acquired on a 600 MHz instrument

a slightly lower R^2 of 0.9879. The application of MAPE (mean absolute percentage error) as a loss function for regression analysis is viable from both practical and theoretical perspectives, as it can be demonstrated that an optimal model exists and the empirical risk minimization is consistent [61]. The MAPE was also used in utilizing the robustness of a regression model and as regression quality measure [62]. The MAPE values of the different polymer types ranged between 1.35% and 17.17%. Additionally, ANOVA showed a significance level of $p < 0.05$ and a large F-statistic value for the statistical analysis of each polymer type which concluded a significant relationship between the measured concentration limits and the nominal concentrations.

Method 2

The determination of LOD and LOQ is based on the SNR, whereas a SNR of 3:1 or 2:1 is considered to be the LOD and a SNR of 10:1 as LOQ [43, 44]. Therefore, the SNR of all polymer concentration levels were established and LOD and LOQ compared with the results from method 1.

Detection limit by qNMR quantification

The measurement and evaluation of spectra in quantitative NMR spectroscopy require a different set of considerations compared to those utilized in qualitative NMR spectroscopy [32, 33]. However, the importance of precision and accuracy must be emphasized when using phase correction, baseline correction, and integration for polymers in different concentration levels. The quantification of each polymer type at different nominal concentrations

was done by using the signal intensities specific for that polymer and the internal standard DMSO₂ according to Eq. 1. Due to overlaps and impurities in some polymer signals, only specific protons were used to quantify the polymer concentration.

The linear regression of PS- H_a, H_b in CDCl_3 and PVC- H_a in THF- d_8 with concentration ranges of 0–100 $\mu\text{g mL}^{-1}$ and PLA- H_a in CDCl_3 with a concentration range of 0–10 $\mu\text{g mL}^{-1}$, including their corresponding R^2 are given in Fig. 3.

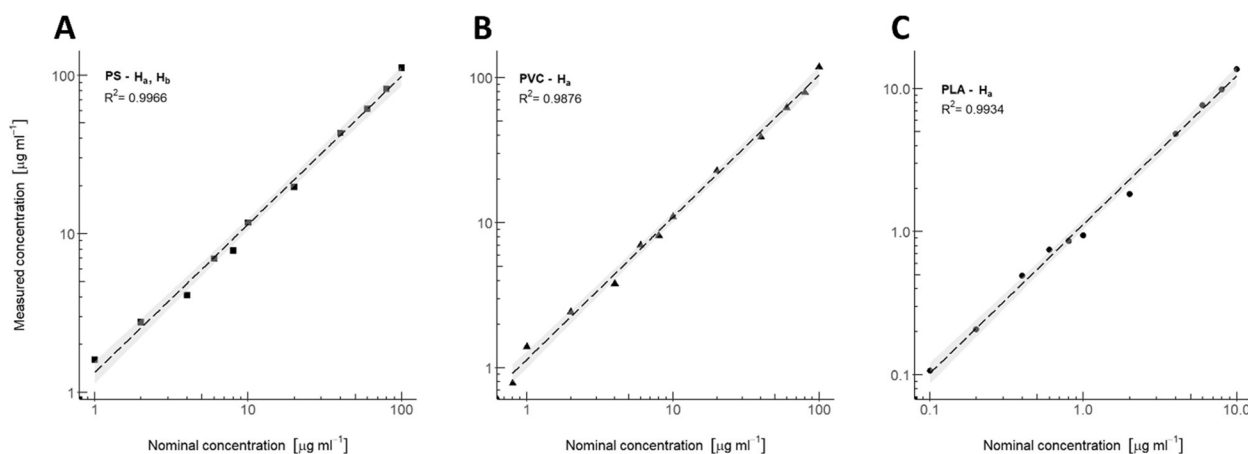
Polystyrene

Results for PS- H_a, H_b using method 1 showed a concentration limit of 4 $\mu\text{g mL}^{-1}$ with an R^2 of 0.9966 (Table 1). Based on method 2, the LOQ was $> 10\ \mu\text{g mL}^{-1}$ and the LOD was 2 $\mu\text{g mL}^{-1}$. The proton NMR spectrum of pure CDCl_3 observed the solvents ^{13}C -satellites at 7.43 ppm and 7.08 ppm [63]. The right satellite of CDCl_3 collided with the PS region of the aromatic ring. However, at higher concentrations the overlap of the signals will not be evident, but it will be present at lower concentrations which will lead to higher SNR in the different concentration levels of PS. Therefore, the SNR of PS was determined by choosing the best suitable PS signal without the ^{13}C satellite of CDCl_3 to determine the corresponding LOD and LOQ values.

Peez et al. [35] and Peez & Imhof [34], both determined LOQ and LOD for PS which was much higher than the LOQ and LOD of PS within this study. Papini et al. [37] reported a quantification in multiphasic matrices of marine sediments with $\sim 27 \pm 16\ \mu\text{g L}^{-1}$ of PS and detected a LOQ of 1.4 μg and LOD of 0.6 μg based on

Table 1 Quantification limits of the different polymer types by method 1 and method 2. The measured concentration limits [$\mu\text{g mL}^{-1}$], the accuracy [%], the MAPE per polymer type [%] (method 1) and the determination of limit (LOD) and quantification (LOQ) [$\mu\text{g mL}^{-1}$] (method 2) are given

Polymer type and proton signal	Method 1			Method 2	
	Measured concentration limit [$\mu\text{g mL}^{-1}$]	Accuracy [%]	MAPE [%]	LOD [$\mu\text{g mL}^{-1}$]	LOQ [$\mu\text{g mL}^{-1}$]
PS - H _a , H _b	4	102.7	14.72	2	> 10
PB - H _a	0.8	98.7	10.58	0.2	1
PB - H _b	0.4	100.5	12.03	0.04	0.4–0.6
PI - H _a	2	102.3	8.11	0.8	2
PI - H _b	0.6	99.5	9.09	<0.01	0.8–1
PLA - H _a	0.2	103.5	17.17	0.6	>2
PVC - H _a	8	101.9	6.35	1	>10
PU - H _a , H _e	4	100.5	5.39	6	>10
PU - H _b	2	103.6	6.64	2	>10
PU - H _c	1	101.0	1.35	1	6

**Fig. 3** Linear Regression for (A) PS-H_a, H_b in CDCl₃ and (B) PVC-H_a in THF-d₈ with concentration ranges of 0–100 $\mu\text{g mL}^{-1}$ and (C) PLA-H_a in CDCl₃ with a concentration range of 0–10 $\mu\text{g mL}^{-1}$. All polymer types include an internal standard of DMSO₂ and are represented with a confidence interval (0.95). The nominal concentration is plotted against the measured concentration (calculated by Eq. 1)

the proton region of two protons of the aromatic ring by using NMR measurements. In comparison, Peetz et al. [35] reported a LOQ of 77 $\mu\text{g mL}^{-1}$ and LOD of 19 $\mu\text{g mL}^{-1}$ for PS in a concentration range of 30–930 $\mu\text{g mL}^{-1}$ based on DIN32645. In their follow-up study in 2020, they referred to the same PS values from 2019 and stated a LOQ of 92 $\mu\text{g mL}^{-1}$ and LOD of 28 $\mu\text{g mL}^{-1}$ based on the SNR, anyhow this means a LOQ of above 77 $\mu\text{g mL}^{-1}$. In addition, Peetz et al. [35] determined a possible overlap of the signals of CDCl₃ and the aromatic ring of PS in case to use the solvent for quantitative analysis. Compared to this study's observation, there is an overlap which was considered during the determination of LOD and LOQ based on the SNR. In contrast, the PyGC/MS

method demonstrated a LOD of less than 1 μg for PS particles, as determined by SNR [31].

Polyvinyl chloride

The observed concentration limit using method 1 for PVC-H_a was 8 $\mu\text{g mL}^{-1}$ with R² of 0.9876 (Table 1). Method 2 on the other hand gave a higher LOQ > 10 $\mu\text{g mL}^{-1}$ and a LOD of 1 $\mu\text{g mL}^{-1}$. In previous studies, Peetz and Imhof [34] determined a LOQ of 281 $\mu\text{g mL}^{-1}$ and a LOD of 84 $\mu\text{g mL}^{-1}$ for PVC in a concentration range of 0.28–1.40 mg mL⁻¹ based on the SNR [43]. In comparison, the PyGC/MS method showed a LOD of < 2.7 μg for PVC particles, based on the SNR [31].

Polylactic acid

For PLA-H_a the concentration limit using method 1 was 0.2 $\mu\text{g mL}^{-1}$ with R^2 of 0.9934 (Table 1), while method 2 gave a tenfold higher LOQ of $>2 \mu\text{g mL}^{-1}$ and a LOD of 0.6 $\mu\text{g mL}^{-1}$. Although PLA is an environmental relevant polymer, it has not been quantified with qNMR so far, and therefore, there are some difficulties in comparing this study's findings to previous studies. However, its increasing attention due to the enormous use in packaging, PLA needs to be quantified fast and accurate.

Polybutadiene and polyisoprene - rubbers

The two rubber types of polybutadiene-cis (PB) and polyisoprene-cis (PI) with two of their proton signals each and their corresponding R^2 are shown in Fig. 4. Both polymer types were dissolved in CDCl_3 . The linear regression is shown in a concentration range of 0–10 $\mu\text{g mL}^{-1}$ for each polymer signal. The concentration limit using method 1

for PB-H_a was 0.8 $\mu\text{g mL}^{-1}$ with R^2 of 0.9950 (Table 1). For method 2 the LOQ was similar, with an LOQ of 1 $\mu\text{g mL}^{-1}$ and LOD of 0.2 $\mu\text{g mL}^{-1}$. The second signal, PB-H_b, had its concentration limit using method 1 at 0.4 $\mu\text{g mL}^{-1}$ with R^2 of 0.9957 (Table 1), while method 2 gave a similar LOQ of 0.4–0.6 $\mu\text{g mL}^{-1}$ and a LOD of 0.04 $\mu\text{g mL}^{-1}$. Similarly, the concentration limit of PI-H_a using method 1 was 2 $\mu\text{g mL}^{-1}$ with R^2 of 0.9975 (Table 1), which was close to the result using method 2, with a LOQ of 2 $\mu\text{g mL}^{-1}$ and a LOD of 0.8 $\mu\text{g mL}^{-1}$. For the second signal of PI, the results were also similar where the concentration limit of PI-H_b using method 1 was 0.6 $\mu\text{g mL}^{-1}$ with R^2 of 0.9938 (Table 1) and for method 2, the LOQ was 0.8–1 $\mu\text{g mL}^{-1}$ and LOD was below 0.01 $\mu\text{g mL}^{-1}$.

However, as qNMR has not been used to quantify these two types of rubber thus far, there are challenges in comparing the findings of this study to previous research. Nonetheless, due to their widespread use in tire

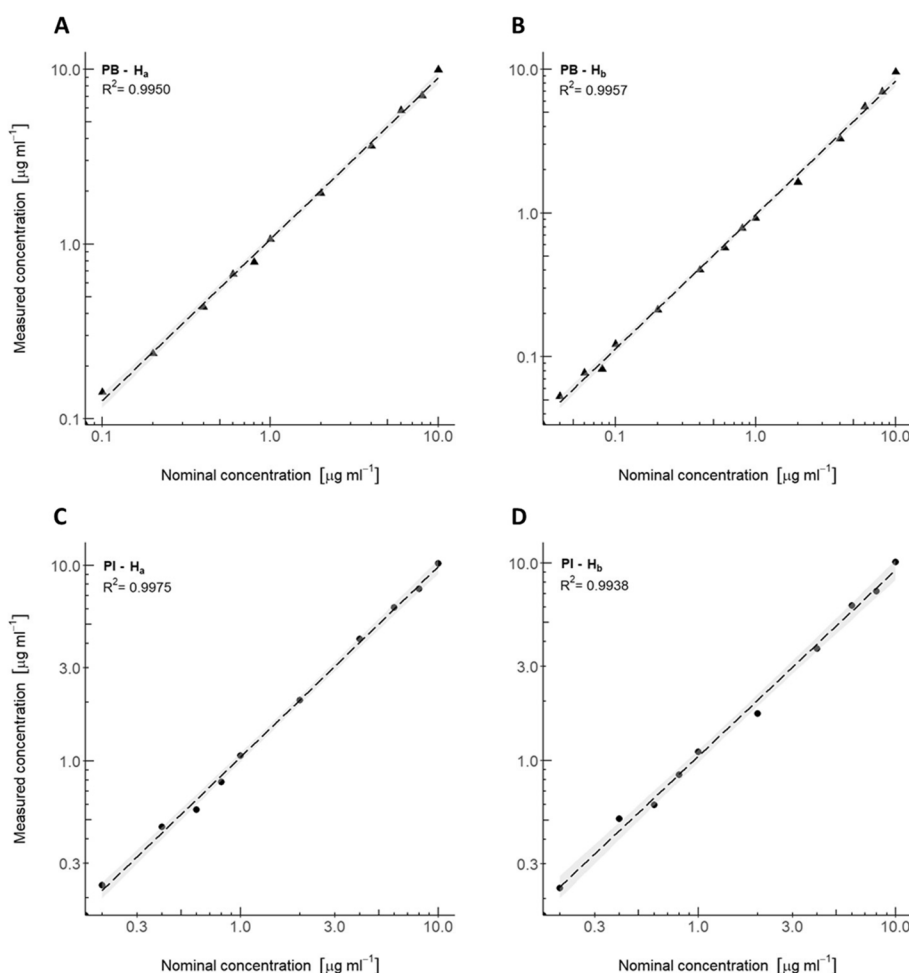


Fig. 4 Linear Regression for (A) PB-H_a, (B) PB-H_b, (C) PI-H_a and (D) PI-H_b in CDCl_3 with concentration ranges of 0–10 $\mu\text{g mL}^{-1}$. All microplastic types include an internal standard of DMSO_2 and are represented with a confidence interval (0.95). Plotted is the nominal concentration against the measured concentration (calculated by Eq. 1)

production [47], it is essential to quickly and accurately quantify PB and PI as they continue to attract increasing attention.

Polyurethane

The linear regression of the three signals of PU in THF- d_8 with concentration ranges of 0–10 $\mu\text{g mL}^{-1}$ and their corresponding R^2 are given in Fig. 5. The concentration limit using method 1 of PU- H_a, H_e was 4 $\mu\text{g mL}^{-1}$ with R^2 of 0.9914 (Table 1). Method 2 gave a higher LOQ of >10 $\mu\text{g mL}^{-1}$ and LOD of 6 $\mu\text{g mL}^{-1}$. The second signal, PU- H_b , had its concentration limit using method 1 of 2 $\mu\text{g mL}^{-1}$ with R^2 of 0.9987 (Table 1), while method 2 gave a five-fold higher LOQ of >10 $\mu\text{g mL}^{-1}$ and a LOD of 2 $\mu\text{g mL}^{-1}$. The concentration limit of the third signal, PU- H_c , using method 1 was 1 $\mu\text{g mL}^{-1}$ with R^2 of 0.9992 (Table 1), while method 2 gave a sixfold higher LOQ of 6 $\mu\text{g mL}^{-1}$ and a LOD of 1 $\mu\text{g mL}^{-1}$. PU is one of the most prevalent polymers due to its widespread use [64]. To date, qNMR has not been used for its quantification. Therefore, comparing the results of this study with previous research poses certain difficulties. Nonetheless, fast and accurate quantification of PU could offer an advantage for future studies.

Uncertainty and accuracy in polymer quantification using qNMR

In total, previous research on quantifying and determining LOD and LOQ of different polymer types have been done with different methods. Peez et al. [35] calculated the LOD and LOQ according to the German standard DIN32465, Peez and Imhof [34] estimated the limits according to the SNR by Shrivastava and Gupta [43] and Papini et al. [37] used the SNR based on LOD being

2:1 and LOQ being 5:1 and having the SNR dependent on the MP concentration. In addition, Papini et al. [37] acquired their data with a line broadening of 5 Hz which makes it difficult to directly compare the LOD and LOQ of this study with a line broadening of 0.1 Hz. Data that is acquired with a higher line broadening improves the SNR but is insufficient for quantification. Moreover, the dependence on the MP concentration indicates the assumption of a stable SNR.

In fact, using the SNR comes with a higher uncertainty. The quantitative imprecision of qNMR is documented to be less than 2.0%, which is an acceptable threshold for precise and accurate quantification [32, 65]. The quantification with LOQ with a SNR of 10:1 would have approximately a 5% standard deviation. The validation protocol by Malz and Jancke [65], which is based on the test of robustness, linearity, accuracy, selectivity and specificity of qNMR measurements, revealed that with a 95% confidence interval, the uncertainty of the qNMR measurements is 1.5%.

Recent research used a calibration curve to estimate the concentration [34–37]. The calibration curve method in qNMR involves preparing standard solutions with known concentrations of the analyte, recording instrument response, and plotting signal intensity against nominal analyte concentration. An equation for the calibration curve is developed by linear regression and used to compute unknown solution concentrations. This technique is useful for quantitative estimation of small molecules or simple mixtures [32]. However, there are challenges associated with using the calibration curve method in qNMR. These include time-consuming establishment of standard curves, require larger sample volumes, and difficulties in maintaining consistent experimental parameters.

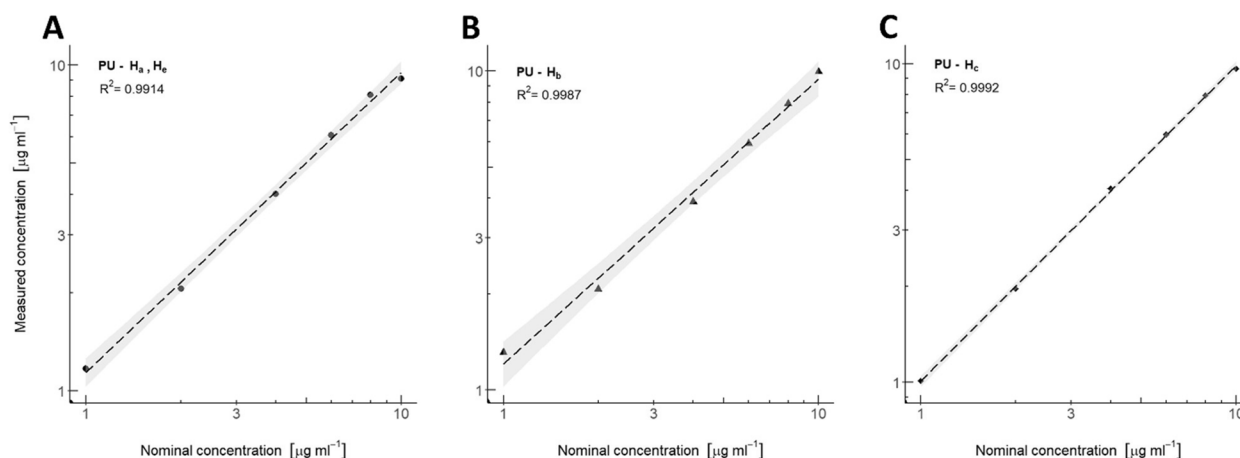


Fig. 5 Linear Regression for (A) PU- H_a, H_e , (B) PU- H_b and (C) PU- H_c in THF- d_8 with concentration ranges of 0–10 $\mu\text{g mL}^{-1}$. All microplastic types include an internal standard of DMSO_2 and are represented with a confidence interval (0.95). Plotted is the nominal concentration against the measured concentration (calculated by Eq. 1)

Especially for expected low concentration, such as in the case of MPs in environmental samples and different organic matrices, the use of the calibration curve is not suitable [33].

Method 2 vs. method 1

In general, quantitative analysis using qNMR relies on the proportional correlation between the integrated signal area and the quantity of resonant nuclei [32, 33, 66]. Founded on this, by including an internal standard with a known concentration and considering the number of protons of the specific region of interest, the measured concentration limits of each polymer types based on Eq. 1 are more accurate than the LOQ based on the SNR. In summary, the concentration limits for quantification of the six polymer types are in the range of 0.2–8 $\mu\text{g mL}^{-1}$ using method 1. Method 1 consistently shows lower concentration limits than method 2 for all polymers except for the second signal of polybutadiene-cis (PB-H_b) and the first signal of polyisoprene-cis (PI-H_a). The difference can be as much as tenfold higher for method 2 than method 1. Moreover, the concentration limits using method 1 are supported by accuracy and MAPE results. Most LOQ values are either close to the measured concentration limits of the different polymer types or way above it which is also due to the restricted dilution series and therefore, missing concentration levels. Using the SNR shows that the LOQ for most polymer types are not as precise as the measured concentration limits.

Sample processing and limitations of NMR

Overall, for qNMR to be effectively applied, it is essential for the detection and quantification limits to align with environmentally significant concentrations. This study shows that qNMR proves to be an effective instrument for quantitative analyses down to 0.2 $\mu\text{g mL}^{-1}$ for a selection of environmentally relevant polymers. While these concentration limits may render qNMR unsuitable for monitoring very low concentrations in small samples, it may be viable for monitoring environmental samples like sediments and soil with high concentrations or plenty of available sample material such as water. Water samples with large volumes can easily be concentrated by filtration and sediment samples where volumes over 1 kg can be used for extraction by density separation using the Munich Plastic Sediment Separator (MPSS) [67, 68].

However, before the method can be used for analysing environmental mixed samples, a solvent for common polymer types such as PP and PE must be developed further and a good strategy of how to treat one sample for different polymers since they require different solvents. Moreover, a diversity of organic compounds and different polymers present in environmental samples

may lead to overlapping signals, making spectral interpretation challenging. Therefore, like FTIR, PyGC/MS and Raman spectroscopy, thorough sample preparations such as extraction by density separation, filtration, and purification by oxidizing agents or enzymatic digestion may need to be performed. Hence, controlled studies comparing pristine polymer mixtures and realistic environmental samples containing aged or weathered polymers are necessary. However, with the low cost of NMR, method development may be faster and cheaper than the currently used methods.

Quantification and concentration estimates

MP concentrations in literature are typically expressed as particle numbers found in environmental samples, but only recently have started to report a mass concentration as well, based on an estimated third dimension of the particle [23]. However, there is also a need for accurate polymer concentrations in environmental samples in terms of mass [69] in order to perform risk assessment and classify contamination levels. Studies on MP in soil revealed MP concentrations of 4.5 mg kg^{-1} including the most common polymer types that have been analysed by time-consuming methods like light microscope, FTIR, PyGC/MS, and Raman [70, 71]. The number of replicates and the number of sampling sites is often limited by the cost of processing and analyses using FTIR. Despite the expensive and time-consuming methods, the results often show a large variance across laboratories, and there is an urgent need for ring tests and harmonized methods and reporting units [28, 72, 73] before the quantitative results of FTIR may be considered reliable. Using NMR, the low costs of analyses are of benefit. Although parallels may be considered technical replicates and subsamples from an inhomogeneous extract of MPs, the low cost and short time running the qNMR analyses allows for a higher degree of certainty than a single analysed subsample can provide.

This study, however, shows that qNMR can be a good supplement and a method for rapid and reliable quantification of MPs in the medium to high concentration ranges of selected polymers. Limitations to the quantification of the most common polymers PE and PP can be overcome by developing new methods for their complete dissolution.

The utility of new and old methods

A combination of qNMR and non-destructive spectroscopic technique, such as FTIR or Raman, enables the analysis of both the size distribution and concentration of polymers in single samples. Although visual cues to the source of microplastics can be desired sometimes, there are now a number of environmental matrices

where the occurrence of microplastics is expected, and where the particles are well known to be a range of different shapes and sizes, and where it has been known for some time that particles under 100 μm dominate [68, 74–76]. Since the presence of microplastics in the environment is no longer newsworthy, and the need for reliable monitoring-tools has been expressed for some time already. A rapid quantitative analysis that is sufficiently detailed to enable environmental classification of MP may be of higher interest than descriptions of the colour and shape of a small subsample of an inhomogeneous mixture. Further development of this method to quantify MPs in mixed environmental samples is therefore of the highest interest. Moreover, there are also relevant sample types, such as human tissue samples, where the need for detection of very low concentrations and knowledge of the particle size and shape is still of the essence and cannot be performed by qNMR. Such analyses must still be performed using FTIR or Raman.

Conclusion

In conclusion, this study demonstrates that qNMR spectroscopy provides a suitable way to quantify the concentration limits of polystyrene (PS), polyvinyl chloride (PVC), polyisoprene-cis (PI), polybutadiene-cis (PB), polylactic acid (PLA) and polyurethane (PU) in their corresponding solvents, in the range of 0.2–8 $\mu\text{g mL}^{-1}$. All concentration limits were measured by using an internal standard with a known concentration, which proved more accurate and sensitive than determining the limit of quantification based on the signal-to-noise ratio (SNR). qNMR represents a fast, accurate, reliable and size-independent analysis for qualitative and quantitative measurements of selected polymers.

Abbreviations

PS	Polystyrene
PI	Polyisoprene-cis
PB	Polybutadiene-cis
PLA	Polylactic acid
PVC	Polyvinyl chloride
PU	Polyurethane
PET	Polyester
PP	Polypropylene
LD/HD-PE	Polyethylene
MP	Microplastic
NP	Nanoplastic
SEM	Scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
PyGC/MS	Pyrolysis gas chromatography-mass spectrometry
TDS-GC-/MS	Thermal desorption gas chromatography-mass spectrometry
qNMR	Quantitative Nuclear Magnetic Resonance
LOQ	Limit of Quantification
LOD	Limit of Detection
CDCl_3	Deuterated chloroform
THF-d_8	Deuterated tetrahydrofuran
r.t.	Room temperature

DMSO_2	Dimethyl sulfone
$^1\text{H NMR}$	Proton nuclear magnetic resonance
SNR	Signal-to-noise ratio
MAPE	Mean absolute percentage error
MPSS	Munich Plastic Sediment Separator

Supplementary Information

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Supplementary Material 1.

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Authors' contributions

JS designed the study, acquired, and analysed the data; MH and JS contributed to validation of method and data; JS, MH, JU and WW contributed to the drafting and revising the study; WW contributed to funding acquisition and management.

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Availability of data and materials

No datasets were generated or analysed during the current study.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors have read and approved the manuscript and agree with its submission.

Competing interests

The authors declare no competing interests.

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