

Handheld Portable FTIR Spectroscopy for the Triage of Micro and Meso Sized Plastics in the Marine Environment Incorporating an Accelerated Weathering Study and an Aging Estimation

Debris in the marine environment can be either natural, such as floating vegetation or volcanic ash deposits, or man-made. The man-made human sources cover the whole gamut of material types, from sewage, glass, mineral, fabric and, of increasing concern, plastic or polymeric. Virtually all plastics absorb IR in a highly selective manner, making their IR spectra a useful qualitative diagnostic. The triage of the visible micro (~1mm-5mm), meso, macro or mega particles with portable and handheld FTIR enables rapid determination of the material on-site, and reduces time wasted on non-polymers on-site or at site. Four most prevalent commodity neustonic plastic types, and their FTIR spectral changes correlated with accelerated weathering, were successfully examined chronologically, detailing significant differences in aging profiles and chemical changes. Subsequently, a small spectroscopically identifiable degraded piece of plastic found in Greenland was correlated to the appropriate aging profile. Finally, a targeted methodology for quantification of sub-millimeter microplastic in dried estuarine sediment was evaluated to ascertain its potential limit of detection.

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Within a few decades of mass production of plastics in the early 1970s, and were largely inconspicuous. In the intervening years to the present, plastic pollution in the marine and coastal environment has

received tremendous amount of media, public, and scientific attention involving multiple scientific disciplines. To date, there are several excellent reviews covering the physical impact (1), plastic generation and potential impacts (2), identification and quantification (3), sources, distribution, and fate (4), and mitigation measures (5), as well as reviews of multiple studies (3,6). In all reviews, the actual particles that were further graded by a diagnostic qualitative instrumental technique were limited to a quotient of the full number of suspected particles. The lack of standard practices related to the quantification of plastics in the environment is a current subject that is well covered in the aforementioned reviews.

Primary sorting after sieving begins with visual sorting and separation and classified by their physical type (fragment, film, foam, pellet, and fiber) and their geometric aspects (including chips, spherical, round, and cylindrical). Where available, secondary qualification via instrumental identification of the micro and meso plastics involve a wide range of differing instrumentation with Fourier-transform infrared spectroscopy (FTIR) spectroscopy, by far, being the most popular technique (3,6). Where secondary confirmation by instrumental means is not used, then the categorization is purely visual and physical.

The four most commonly found polymers in a study of 68 white papers (3) were found to be HDPE (high density polyethylene), LDPE (low density polyethylene), PP (polypropylene), and PS (polystyrene); consequently these were chosen for an in-depth aging study to ascertain the accelerated

aging profile with time, using a hand-held portable FTIR to enable triage of samples in situ. Aging studies of HDPE (7), LDPE (8) and LLDPE (7) grades of polyethylene, polypropylene (9,10), and polystyrene (11) have been conducted in depth. These concentrate on either physical or chemical changes induced by UV radiation and other possible degradative pathways (12,13). UV radiation and the availability of oxygen are the most important factors that initiate and propagate polymer degradation (12,13).

The occurrence of microplastics in the environment is far-reaching covering oceans (14), rivers (15,16), bays (17), estuaries (18), lagoons (19), fauna and marine organisms (1,4,6,20), coastlines (21), and even activated sludges used in waste water treatment plants (22), as well as a variety of freshwater systems (23). The prevalence of anthropogenic sourced plastics litter is an increasing environmental concern with the potential to affect man's pelagic food sources in both salt and fresh water environments. Moreover, the extent of the degradation of specific polymers can lead to increasingly poor FTIR identification.

In this proof of concept study, our main aim was dedicated to assess the benefits and extent of UV initiated aging for each polymer, and the use or prevalence of these selected polymer types; to equivalently age floating micro and meso plastics at sea, in rivers, on beaches, sediments, and other marine environments in situ. Since these polymers are highly likely to be prevalent in any significant localized concentration (such as oceanic gyres and other deposition sites), useful information can be gleaned

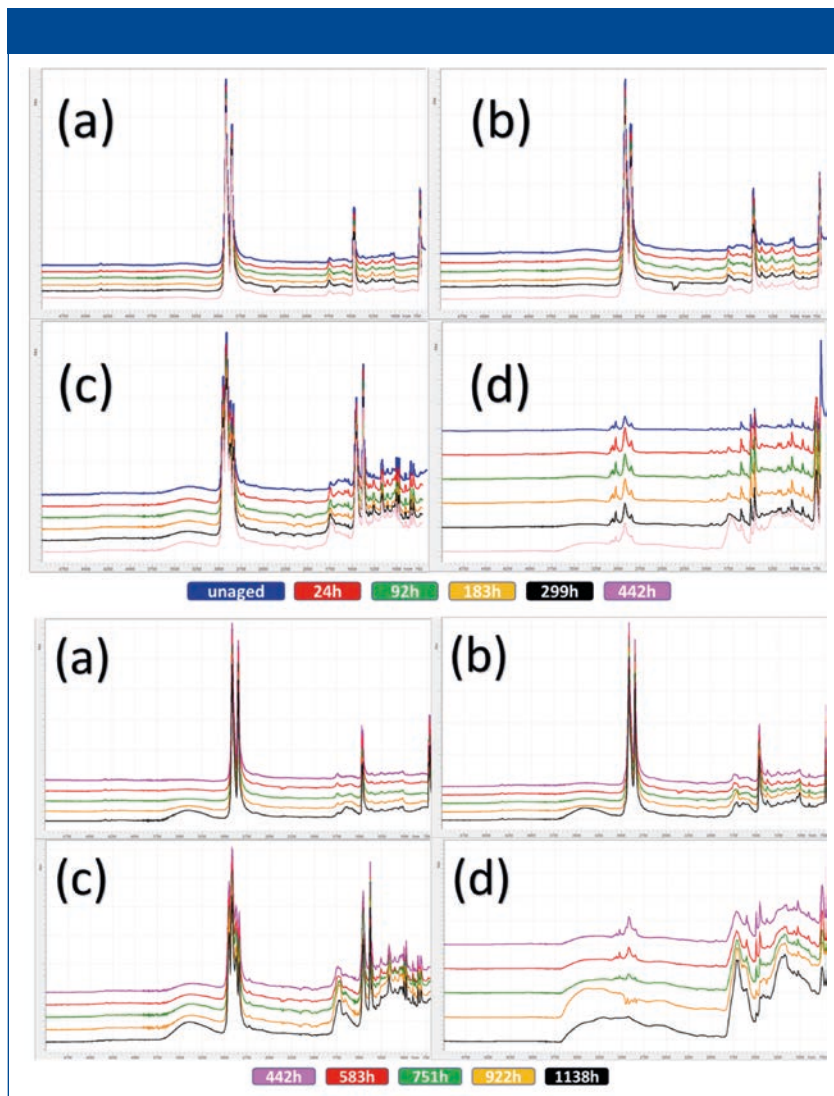


Figure 1: Normalized (top set) and averaged (bottom set) of ATR spectra for (a) high density polyethylene (HDPE), (b) LDPE (low density polyethylene), (c) (polypropylene) PP and (d) (polystyrene) PS. Spectra stacked and color coded for clarity.

from their individual aged states and their population variance. Consideration of the cross-correlated (all four types of polymer) quantification of the residence time of HDPE/LDPE/PP/PS will collectively act as inter-population verification.

Results and Discussion

Handheld FTIR-ATR Aging Study Analysis

FTIR is a well-documented technique for the identification of polymers. Since polymers degrade from the outside in, attenuated total reflectance (ATR) is

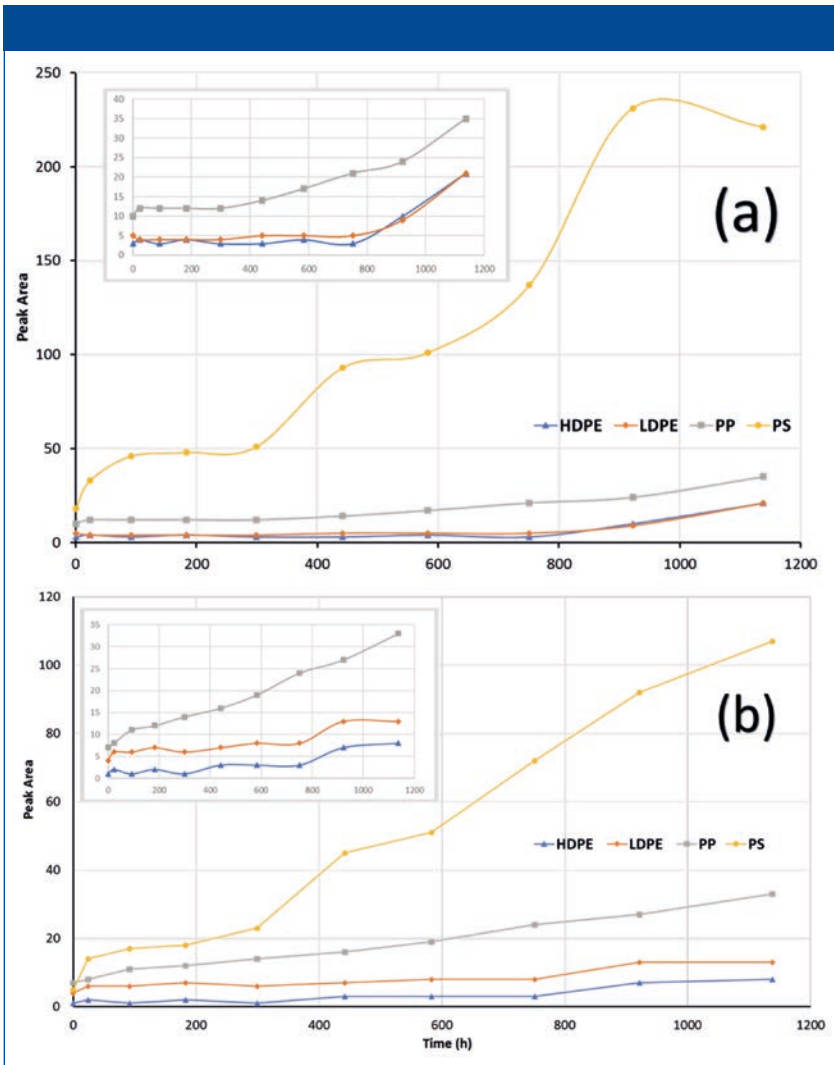


Figure 2: Peak area analysis of zone (a) 3750-3000 cm^{-1} for HDPE, LDPE and PP; 3750-2200 cm^{-1} PS, and (b) 1850-1500 cm^{-1} for HDPE, LDPE, PP and PS. Increase in signal signifies greater absorbance in that region.

particularly suited to the surface chemical changes. These environmentally induced chemical changes precede physical changes, and could be used as markers. The UV induced changes for HDPE, LDPE, PP and PS are shown in Figure 1. The spectra have been split into two aging segments, and stacked

for clarity. The unaged HDPE and LDPE can be discriminated from the fine details in the methyl group symmetric deformation vibrational mode centered around 1369 cm^{-1} , where the LDPE with the higher degree of branching contains a higher density of this functionality. For the accelerated aging

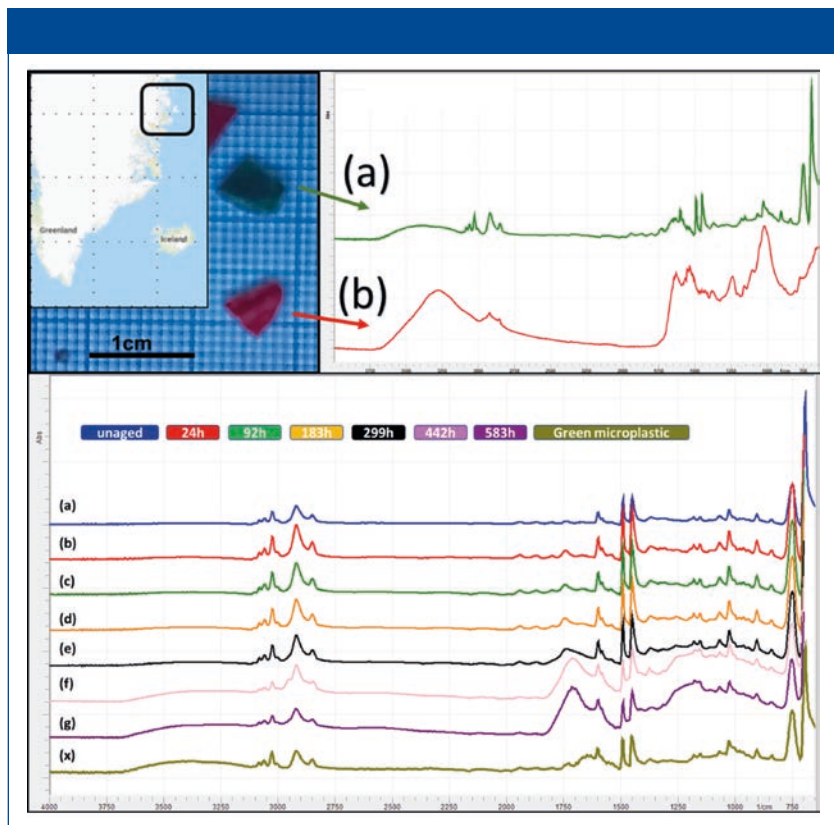


Figure 3: Top unidentified microplastic from Greenland (a) ATR spectra of green microplastic sample, and (b) ATR spectra of red microplastic sample. The bottom set represents accelerated UV aged PS sample 0h-583h plus green microplastic.

0h-442h sector (Figure 1, top), both HDPE and LDPE show only slight to no changes, whereas the changes for PP are mild, and the changes for PS are especially evident in the carbonyl region at the latter analysis interval (442h), where significant carboxylic acid and alcohol formation becomes evident. For the second sector (aging time 442h-1138h), the HDPE only just begins to show changes toward the end of the aging experiment. LDPE changes are a little more severe, likely due to the higher degree of branching and, therefore,

greater concentration of more reactive methyl groups. The even higher methyl concentration of PP results in discernible aging even earlier than LDPE around the 183h mark. HDPE, LDPE and PP share the same -C-C- backbone, and are fully saturated polymers; this affords them excellent UV resistance. Although PS also has the -C-C- backbone it also has an aromatic ring on every other carbon atom, causing PS to have the least UV resistance of the common neustonic polymers studied. Changes are apparent from early on and continue

Table I: Peak area analysis of the ATR spectra for HDPE, LDPE, PP and PS for the chronological set of UV treatment times. Grey=high wavenumber, Blue=Carbonyl and related spectral regions.

Time (h)	HDPE		LDPE		PP		PS	
0	3	1	5	4	10	7	18	5
24	4	2	4	6	12	8	33	14
92	3	1	4	6	12	11	46	17
183	4	2	4	7	12	12	48	18
299	3	1	4	6	12	14	51	23
442	3	3	5	7	14	16	93	45
583	4	3	5	8	17	19	101	51
751	3	3	5	8	21	24	137	72
922	10	7	9	13	24	27	231	92
1138	21	8	21	13	35	33	221	107
x (green aged PS microplastic)							60	20

to increase in severity, until, at 1138h, the spectra is unrecognizable from the starting material; by this point the PS is in a very advanced state of oxidation.

The main spectral regions of change for the HDPE, LDPE and PP samples are confined to hydroxylation and carbonyl species formation, and these have been documented in several studies (7–10, 12,13) as only occurring toward the closing stages of the aging study. The PS aging, on the other hand, is much more complex, with a wider variety of chemical changes. Figure 2a shows the FTIR peak area changes for the region from 3750-3,000 cm^{-1} for HDPE, LDPE and PP, and a wider region of 3750-2250 cm^{-1} for PS, whereas Figure 2b shows the peak area changes for region 1850-1500 cm^{-1} for all four targeted polymers. The increase in area is concomitant with increasing chemical changes due to UV induced oxidative and chemical degradation.

The spectra for both a green and a red piece of microplastic found on the northern coast of Greenland were measured by handheld FTIR-ATR. Spectrally, the green piece was visually identified as being a degraded piece of PS, and gave a correct polymer identification library hit quality index (HQI) value of 0.84. This can be further confirmed by comparison of the degraded plastic with the set of accelerated aging spectra for PS and is shown in Figure 3. Unfortunately, the red piece of microplastic gave a best incorrect match as wood with a HQI of 0.72. A speculative guess would be that the red microplastic may be an aged polyacetal.

To estimate the equivalent accelerated age of the green microplastic, the two zones used in Figure 2 peak area protocol were applied and then compared to the peak area value table for PS as shown in Table I, which includes the peak area values for all four neustonic polymers. The accelerated age is estimated to be equivalent to approxi-

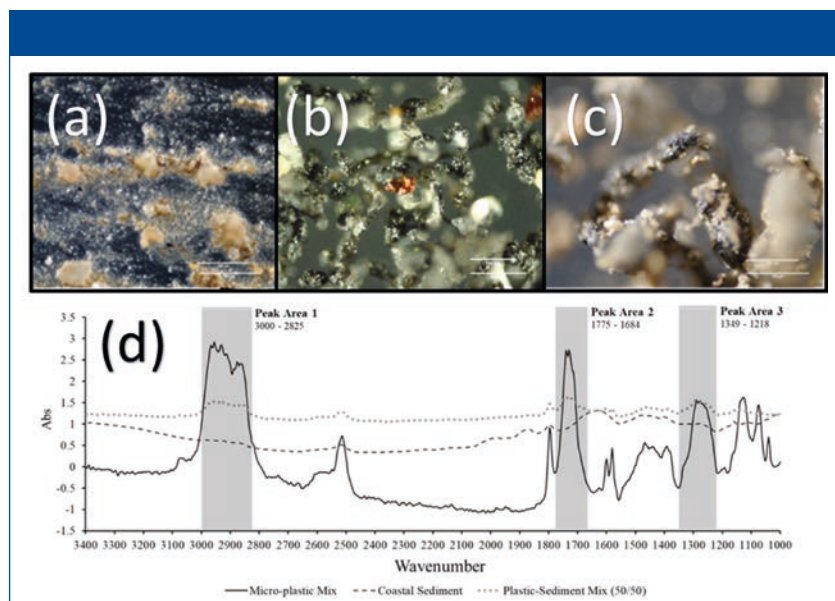


Figure 4: Optical micrographs of (a) estuarine sediment, (b) routed engineering plastic, and (c) 50:50 mixture. White scale bars are 150 μ m and 180 μ m, respectively in each picture; (d) represents handheld diffuse spectra of samples a, b and c.

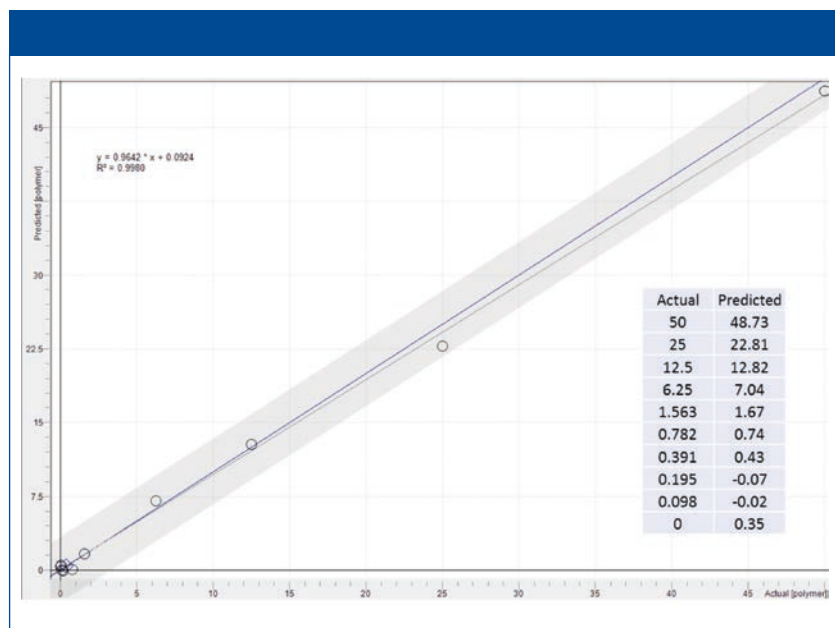


Figure 5: PLS1 model for the percent submillimeter polymer content in a dried sediment and the actual vs. predicted values.

mately 299h. The fact that the marine environment aged sample has an increased higher wavenumber changes is likely due to the salt water environment prior to beach deposition.

Both ATR and a dedicated diffuse interface were evaluated for a serial dilution factor of 2 for a dried estuarine sediment mixed with a formulated polymer blend; this was routed to achieve a particle size of less than 1mm. The sizes were subsequently confirmed by optical microscopy. ATR is highly surface sensitive, and therefore had a very high limit of detection for a sub-millimeter microplastic sediment mixture. This was attributed to textural effects limiting adequate contact for the sub-millimeter microplastic where the acicular shape limited the area of contact. Parts a, b and c of Figure 4 show optical images of the pure sediment, polymeric formulation, and then a 50:50 mix by weight. The sediment is not only highly carbonated, but also fairly humic, whereas the polymer contains a small fraction of inorganic additives. This is, in effect, the worst-case scenario. The corresponding spectra are shown in Figure 4d.

Where the ATR excels at polymer identification when the spectra and degradation state are available it is not ideal for thoroughly mixed bulk mixtures. Here the shallow depth of penetration for ATR is a hindrance rather than an advantage. Handheld Diffuse reflectance on the other hand has nearly two orders of magnitude greater penetration depth and is much more suited to well mixed powder-like materials

or ground or pulverized materials. The microplastic powder was serially diluted with a dilution factor of 2 to low ppm levels. Spectra were collected between each dilution and models were created as a proof of concept. The Beer-Lambert based LOD was determined to be ~6.25% whereas the MVA based PLS1 analysis was able to yield a LOD of around 0.4% for the microplastic using the same spectra, with a standard error of prediction (SEP) of 0.09%. Figure 5 shows the actual vs. predicted plot for the PLS1 model utilizing multiplicative scatter correction (MSC). Biological or environmental accumulation of polymeric sub millimeter microplastics or suspected sites can be triaged with targeted analysis.

Conclusion

Degradation of the four most prevalent polymers accelerated aging profiles have been investigated and examined by handheld FTIR-ATR. Where photo-initiated abiotic degradation dominates, these changes can be used for the semi-empirical quantification of the equivalent accelerated age of a real microplastic particle. This polystyrene microplastic example, collected on a beach in Greenland, a country with the lowest population density on the planet, was significantly aged. The accelerated UV aging directly confirms the spectroscopic chemical oxidative changes, and confirms the UV resistance order of HDPE>LDPE>PP>PS. The Library HQI results and the degradation profiles demonstrate the risk of over reliance on library searches alone, whereby polymers that age quickly

are increasingly difficult to identify. A serially diluted ground polymer that was then mixed with estuarine sediment was found to have a LOD of about 0.4% weight for weight. The aging profiles can be further enhanced by the introduction of other degradation factors and other commodity polymers.

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