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Application News

No. A586

Spectrophotometric Analysis

Toward Recycling of Marine Debris
- Analysis of Microplastics Using FTIR and EDX -

In addition to microplastics (very small plastic particles) drifting in seawater, marine debris also includes relatively large pieces of plastic generated by the breakup of plastic products by ultra violet radiation and other external factors, and small pieces of fishing gear like the fishing line shown in Fig. 1.

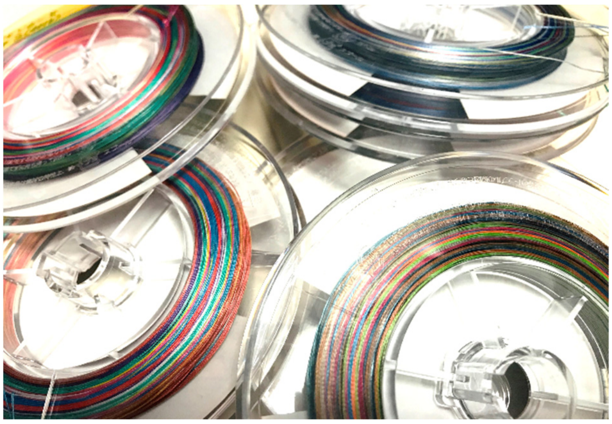


Fig. 1 Example of Fishing Gear

Fishing nets, trawling nets, fishing lines, etc., were formerly made from natural materials, but now they are usually made of synthetic resin. This is because it is easier to give functionality to synthetic resin. On the other hand, when such materials are not properly managed or disposed of, they become marine debris and are a factor in environmental destruction. Therefore, it is hoped that this kind of marine debris will be collected and reused as a raw material for new fishing gear.

The causes of deterioration and breakup of fishing nets are contact with fish, algae, and stones in the sea and on beaches, as well as ultraviolet radiation from the sun. An example of a way to prevent this kind of naturally occurring damage and continue using fishing nets over a long period of time is to give the surface of fishing nets used for aquaculture a protective coating of copper as shown in Fig. 2 [1].

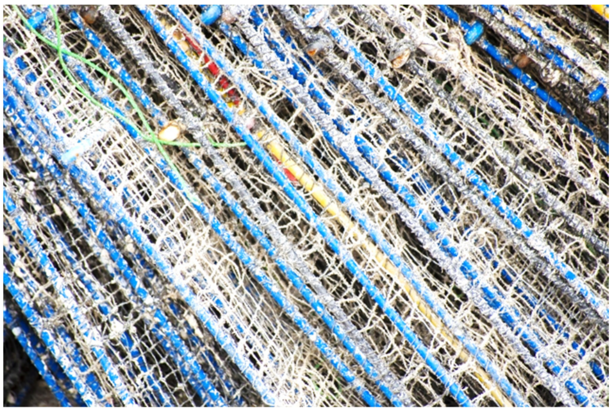


Fig. 2 Fishing Net Used for Aquaculture

The heavy element copper (Cu) used for the protective coating has an antibacterial effect and not only protects against bacteria and viruses but also has the function of preventing fouling, so it plays an important role on fishing nets. Copper not only maintains the strength of the fishing nets, but also gives excellent functionality. However, in recent years it has been reported that it might have a negative impact on fish and the marine environment, and its use has been a concern.

This article introduces an example of analysis using FTIR and EDX on actual fishing nets collected on the Playa de Muro beach on the Spanish island of Majorca and the Paal 9 beach on the island of Texel in the Netherlands, and on fishing nets obtained from a recycling plant.

R Fuji, E Marion

Effects of Copper on Fish

In the past, paints in which toxic tributyltin was used (anti-fouling paints for ships) was used as a protective coating on fishing nets, but copper came to be used from the standpoint of environmental protection. However, in recent years adverse effects of copper on fish have also been reported, and Marina Nikolaou et al. report in their literature that the effects are manifested at 58 mg of copper sulfate per liter in the case of tilapia (freshwater fish from the family Cichlidae in the order Perciformes), and 70 mg per liter in the case of catfish. It is suggested that exposure of fish to high concentrations of copper sulfate over a long period of time may lead to damage to the gills, liver, kidneys and nervous system [2].

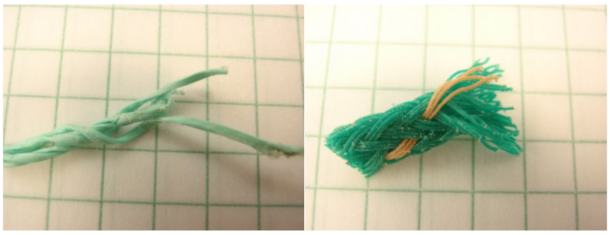
Challenges in Recycling

When recycling the fishing nets used in fishing grounds, the materials of the fishing nets and the copper and other toxic substances used for protection have to be strictly managed, requiring measurement using analytical instruments suited to the purpose.

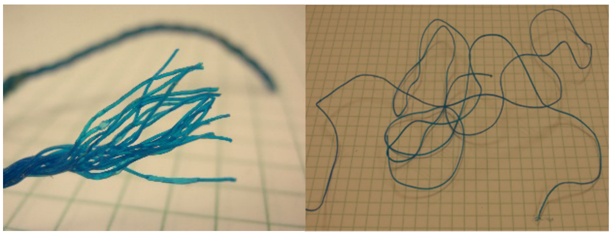
FTIR can determine the materials of the filaments used in fishing nets and fishing lines, while EDX facilitates the elemental analysis of copper, etc., used in protective coatings, so they can be utilized in the management of recycled materials.

Measurement Samples

The measurement samples are single filaments such as a fishing line, and nets in which the filaments are bundled. Figs. 3 (a) to (d) show the fishing nets and fishing lines collected at Majorca island in Spain and Texel island in the Netherlands. Figs. 4 (a) to (d) show fishing nets obtained at a recycling plant.

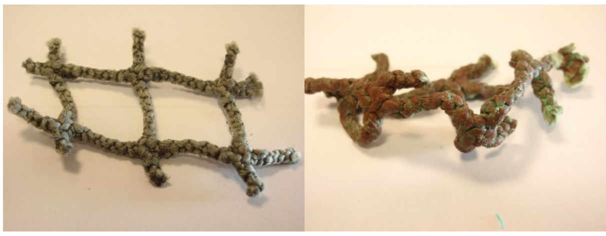


(a) Collected at Playa de Muro, Majorca   (b) Collected at Playa de Muro, Majorca

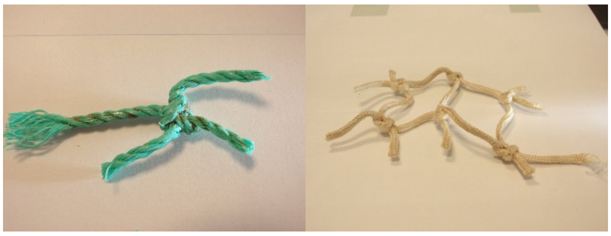


(c) Collected at Playa de Muro, Majorca   (d) Collected at Paal 9, Texel

Fig. 3 (a) to (d) Fishing Nets and Fishing Lines Collected on Beaches



(a)   (b)



(c)   (d)

Fig. 4 (a) to (d) Fishing Nets obtained at a Recycling Plant

Instruments Used and Measurement Conditions

Analysis was performed using a system comprised of an IRTracer™-100 Fourier transform infrared spectrophotometer connected to a Quest single-reflection ATR accessory, and an EDX-8000 energy dispersive X-ray fluorescence spectrometer. Figs. 5 and 6 show the appearance of each instrument and Tables 1 and 2 list the measurement conditions. The measurement samples shown in Figs. 3 and 4 were analyzed without undergoing any processing or special pretreatment.

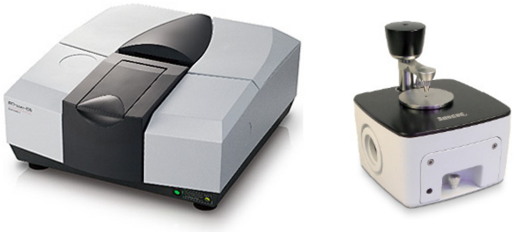


Fig. 5 IRTracer™-100 (Left), Quest (Right)

Fig. 6 EDX-8000

Table 1 FTIR Measurement Conditions

Instrument	: IRTracer-100 Quest (Diamond prism)
Resolution	: 4 cm^{-1}
Accumulation	: 45
Apodization function	: Happ-Genzel
Detector	: DLATGS

Table 2 EDX Measurement Conditions

Instrument	: EDX-8000
X-Ray tube target	: Rh
Voltage / current	: 50 kV (Al-U) / Auto 15 kV (C-Sc) / Auto
Atmosphere	: Vacuum
Analysis diameter	: 3 mmφ
Filter	: None
Integration time	: 50 seconds

The ATR method of FTIR stands for Attenuated Total Reflection. By measuring all of the light reflected by the sample surface, the absorption spectrum of the sample surface can be obtained. The penetration depth of the light is several µm. Fig. 7 shows measurement in progress.

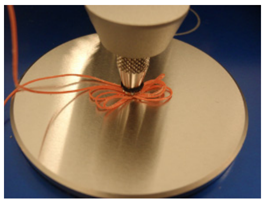


Fig. 7 ATR Measurement in Progress

Fluorescent X-ray spectroscopy is a technique for analyzing the composition of a sample by irradiating it with X-rays and measuring the X-ray fluorescence generated from the elements contained in it. A 3 mmφ collimator (irradiation diameter) was selected in accordance with the size of the sample. The measurement atmosphere was made a vacuum.

Results of Measurement Using FTIR and EDX

Figs. 8 and 9 show the FTIR and EDX measurement results.

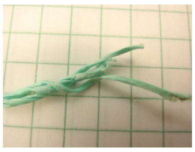
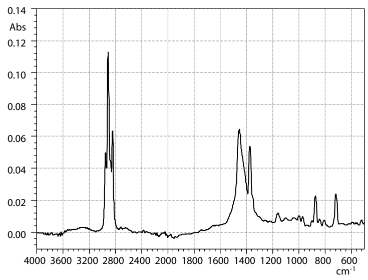
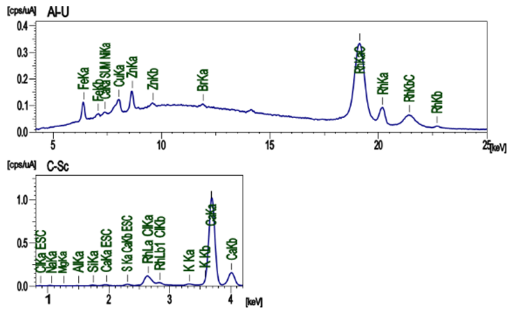
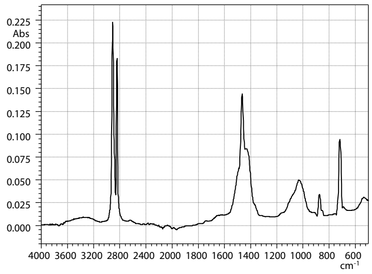
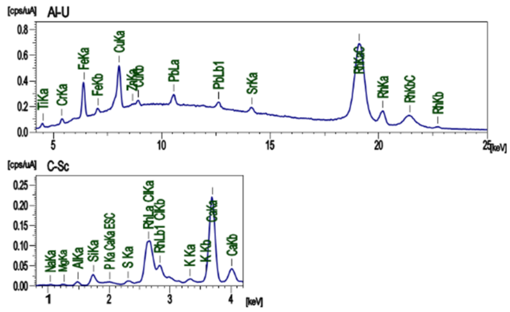
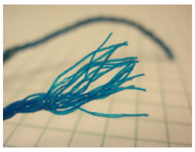
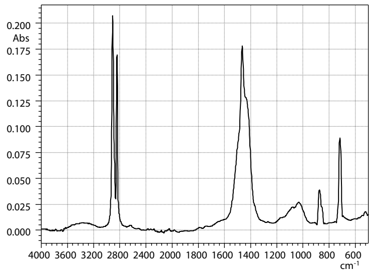
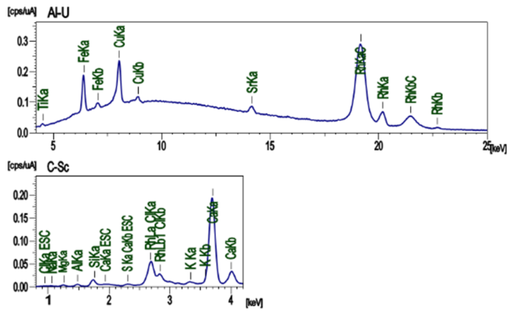
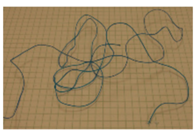
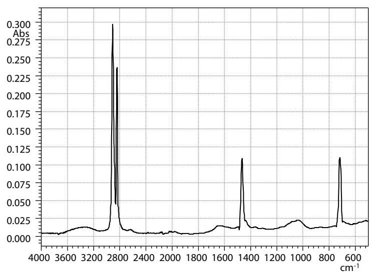
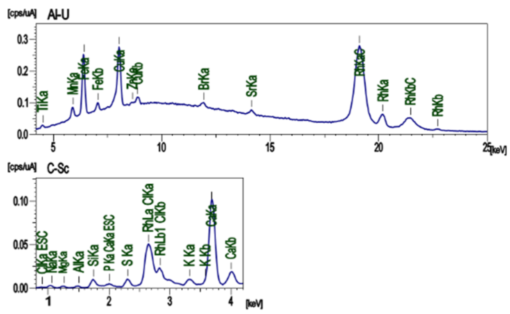
Figure	FTIR Measurement Results Infrared Spectrum	EDX Measurement Results Fluorescent X-ray Profile
3 (a) 	 Qualitative results: polyethylene, polypropylene	
3 (b) 	 Qualitative results: polyethylene, calcium carbonate, silicate	
3 (c) 	 Qualitative results: polyethylene, calcium carbonate, silicate	
3 (d) 	 Qualitative results: polyethylene	

Fig. 8 Measurement Results

The results of measurement using FTIR showed that, for the samples in Figs. 3 (a) to (d), polyethylene was the main component in many cases, and the other components were polypropylene and, as additives, calcium carbonate and silicate. From the results of qualitative quantitative analysis by EDX, it was found that the Cu content of the samples in Figs. 3 (a) to (d) was less than 0.03 wt%, and that they have no Cu protective coating.

On the other hand, it was found that various types of polymer including polyethylene, polypropylene and polyamides were used in the samples in Figs. 4 (a) to (d). In addition, the Cu content was estimated to be 15 wt% in the sample in Fig. 4 (a), and 8 wt% for that in Fig. 4 (b), which is more than others, so it could be inferred that was fishing net with a Cu protective coating.

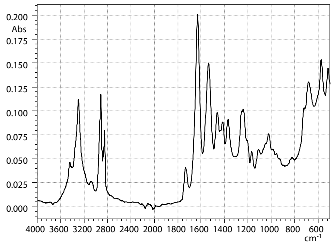
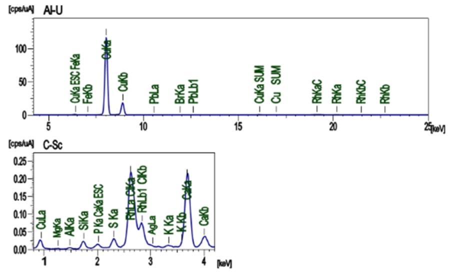
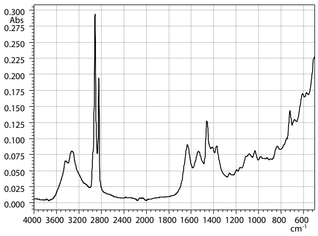
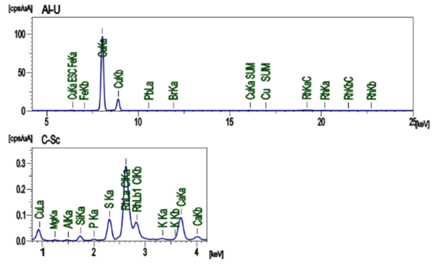
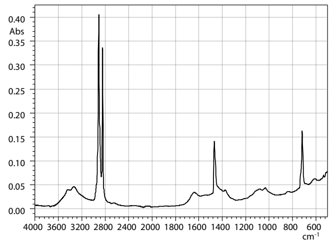
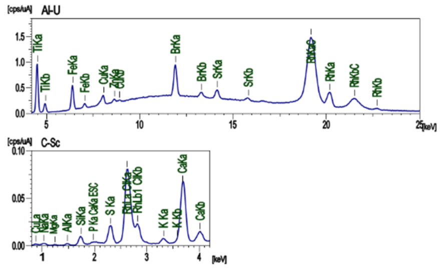
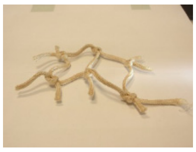
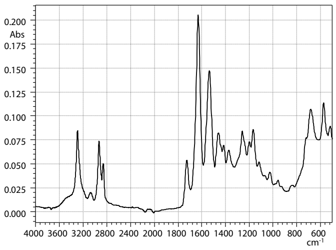
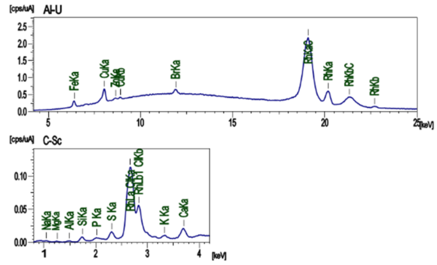
Figure	Infrared Spectrum	Fluorescent X-ray Profile
4 (a) 	 Qualitative results: polyamides, acetates	
4 (b) 	 Qualitative results: polyethylene, polypropylene, polyamides	
4 (c) 	 Qualitative results: polyethylene	
4 (d) 	 Qualitative results: polyamides	

Fig. 9 Measurement Results

Conclusion

In this article, we analyzed the marine debris (plastic fishing nets) collected on the beach and the fishing nets obtained at a recycling plant. The results showed that a lot of polyethylene, polypropylene, and polyamides were used as materials for fishing nets. These materials are lightweight and are likely to float in the sea, so they wash up on beaches and are easily collected as marine debris.

FTIR can qualitatively analyze organic matter and some inorganic matter, so it allows quick determination of the main components of fishing nets. Moreover, the element information obtained using EDX can reveal the characteristics of the fishing nets, such as the presence or absence of a protective coating, in more detail.

For analysis of marine debris such as microplastics, we recommend use of FTIR and EDX, which allows rapid measurement.

References

(1) "Biofouling in the Marine Aquaculture Industry, with Particular Reference to Finfish – Current Status and Future Challenges", Mark G. J. Hartl, Douglas Watson and John Davenport, Nov. 2006, Marine Estate Research Report, (AQU/06/03), The Crown Estate

(2) "Fish farming and anti-fouling paints: a potential source of Cu and Zn in farmed fish", Marina Nikolaou, Nikos Neofitou, Konstantinos Skordas, Ioanna Castritsi-Catharios, Lamprini Tziantziou, June 2014, Vol.5: 163-171, Aquaculture environment interactions

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