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Application News

No. SCA-110-102

Spectroscopy - FTIR

Recycling of Fishing nets and other maritime lines FTIR-ATR analysis of net material from various Source in combination with EDX analysis

Introduction

Maritime waste is not only the actual discussed micro particles. Maritime waste can be larger fragments, pieces, lines, ropes or nets from the economical side – the fishing.
Nets like fish net, trawl net or aquaculture nets are in the water as well as fishing lines. Historically such fishing tools were made from natural things but nowadays these are prepared from polymers. Their possible characteristics allows diverse variations of net and line products confected to its need. Such variation is found as waste in the maritime areas like the water, at beach and partly in the recycling. Old nets are wasted and collected. The intension is to produce new nets from it.

Figure 1: Examble of fishing equipment

Such nets and lines were in contact with salt or sweet water, in contact with the fishing materials like fish (protein, fish fat), algae (protein, cellulose), and stone (particles in water, beach, at bottom of the sea or moved over heavy stones). UV light exposure from sun shine plays also a role. Some of the net material is with protection layer as the nets for the aquaculture could be. As heavy element copper (Cu) plays an important role for fish farms. The copper has an antimicrobial effect. Such should keep bacteria, fungi, viruses, etc. Away from the fish farming. As well as it has some anti-fouling characteristic. Net are painted or treated with copper alloy for protection. [1]
This application note shows examples collected from the beach and pieces from industrial net recycling. Beaches were in south of Europe Mallorca at “Platja de Muro”, in north-west Texel at “Paal 9” and the industrial net material for recycling from south east of Europe. Copper alloys and Copper salts are used.

Copper and its role in Aquatic and marine needs

Figure 2: typical view of an aquatic fish farm

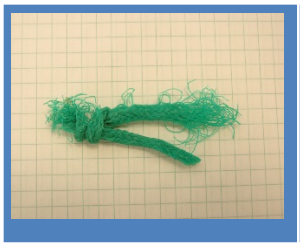
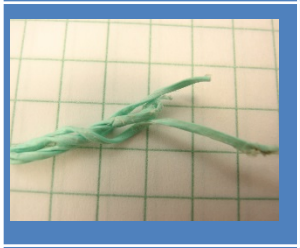
As mentioned in literature the fishes like tilapia or cat fish are reacting on copper. It was found that 58mg per L (Tilapia) and 70mg per liter (Catfish) of copper sulfate can cause effects to the fishes. However to high and longtime exposure of the fish can cause a hurt to gill, liver, kidneys and the nervous system. [2]
As part of anti-fouling paint copper plays a major role. In history it replaced the tri-butyl tin based color (anti fouling paint for ships), which was toxic. Some activities are starting to avoid copper as part of paint in the marine environment.

- **Aspect of recycling**

Recycling of fish nets and nets from fish farms should be checked very seriously on content of copper or other not healthy substances. During the recycling process such anti-fouling substance will be diluted by polymer. Perhaps a new created net has the anti-fouling already integrated. No need of additional need can be the advantage.

- **Sample preparation and spectral analysis with FTIR technic**

These samples were not special prepared. The net material was analyzed as it appeared. Partly the single fibers, bulk or group of fibers were checked. The sample – group of fibers or single fiber- was simply placed on the diamond window of approx. 2mm size. The anvil from the accessory was drilled down to press the fiber or group of fibers against the diamond window.

	
IR: Polyethylen mainly / R: plastic / fish-net / O: beach (Platja de Muro, Mallorca)	IR: Polyethylen mainly / R: plastic, fish-net / O: beach (Platja de Muro, Mallorca)
	
IR: Polyethylen,Polypropylene mixture / R: plastic, fish-net / O: beach (Platja de Muro, Mallorca)	IR: Polyethylen, Calcium Carbonate, Silicate / R: plastic, fish-net / O: beach (Platja de Muro, Mallorca)

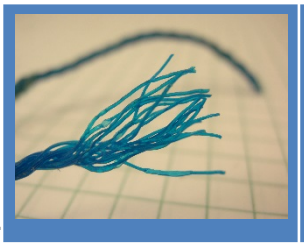
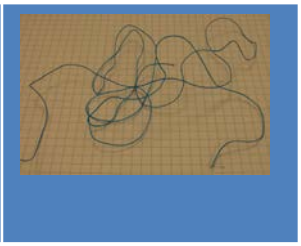
	
IR: Polythylen / R: plastic, fish-net / O: beach (Platja de Muro, Mallorca)	IR: Polyethylen / R: plastic Fish line/ O: beach (Texel, Paal 9)

Table 1a-f: Lines and net collected at a beach from Mallorca Island (Spain)

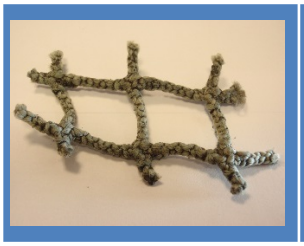
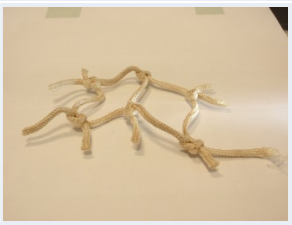
	
Tab. 2 a: IR: Nylon and acetate / R: Cu treated fish-net / O: fish farm	Tab. 2b: IR: Pe and protein / R: Cu treated fish-net / O: fish farm
	
Tab. 2c: IR: Polyethylen mainly / R: Cu treated fish-net / O: fish farm	Tab. 2d: IR: Polyamide, acrylate mixture / R: Cu treated fish-net / O: fish farm

Table 2a-d: Net material for the recycling, the material was collected from fish farms, place of origin unknown

Table 1 shows 6 samples which are 5 lines and 1 net collected from a beach in Mallorca. Table 2 shows 4 examples from a polymer recycling plant. The source of samples is unknown. It should be used for recycling.

- **ATR-Technic**

With the ATR technique the infrared beam can

penetrate into the sample surface. Such penetration depth is depending on the incident angle of the beam and the refractive index of the crystal in use as well as from the analytical wavelength. In principal a penetration of 2µm at 1000cm^{-1} and approx. 1.0µm at 2000cm^{-1} is to be expect for the diamond crystal when the organic material has theoretical a refractive index of 1.5.

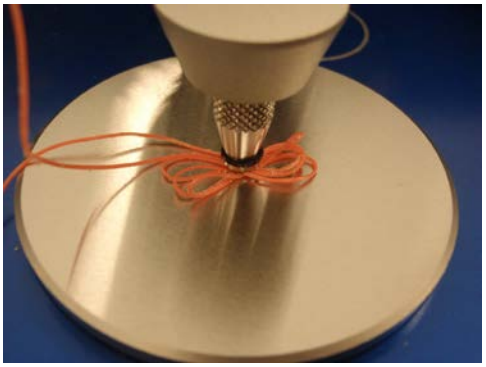


Fig. 3: Quest™ diamond ATR, orange line folded and pressed with anvil to the diamond window (line is from beach Texel Paal 9, material is polyethylene and silicate (sand))

- **Sample preparation and X-ray analysis with EDX-8000**

In addition to FTIR-ATR analysis EDX measurements have been done. The EDX (energy dispersive X-Ray fluorescence spectrometer) is a technique which allows to obtain the elemental composition of the sample in the ppm to percentage level without the need of sample preparation. Standards for calibrating the instrument are useful to increase accuracy of measurement results, but are not mandatory. The analysis is non-destructive, making the technique very useful for screening of unknown samples.

With a collimator (standard accesssory) the measurement range was narrowed down to 3mm. With a camera (standard accessory) the exact position of the sample within the sample chamber was confirmed. For the measurements a simple standardless FP parameter method was used. A calibration of the instrument was not needed. Vacuum condition (optional accessory for measurement of light elements) had been used. Sample 2a contained 15% and sample 2b 8% copper, the others contained in average <0.03%.

- **Conclusion**

The infrared spectroscopy is able to identify the major components in natural and complex sample material. The domain of infrared is the identification of substances from organic or inorganic characteristic. As inorganics have more unspecific signal groups the EDX is a good sister analysis for the elemental distribution.
Astonishing is that the beach material were mainly polyethylene or polypropylene related material. Both polymers are light materials and swimming in the upper water level. So, they will easily fall from the sea water onto a beach this with light or heavy swell. PE and PP are cheap polymers, most used. More detailed results are presented in table 3.

- **Instrumentation**

Shimadzu IRTracer-100 with LabSolutions IR software
Single reflection unit – Specac Quest™
Shimadzu Libraries
EDX-8000
EDXIR Contaminant Library

- **Literature**

[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

- **Acknowledgement:**

Co-operation partner was Albert van Oyen, Carat GmbH, Bocholt, Germany

- **Abbreviations: used in table 1and table 2:**

“IR: Polyethylen mainly / R: plastic / fish-net / O: beach (Platja de Muro, Mallorca)”

IR – infrared analysis and result of library search
R- X-ray fluorescence analysis and detected major components and elements
O – origin of sample

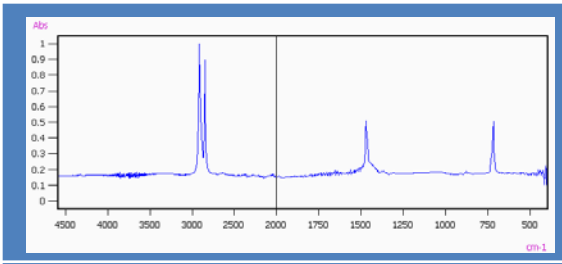
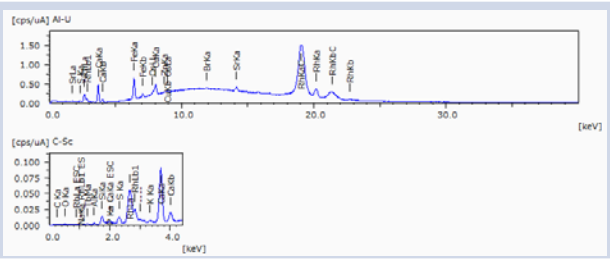
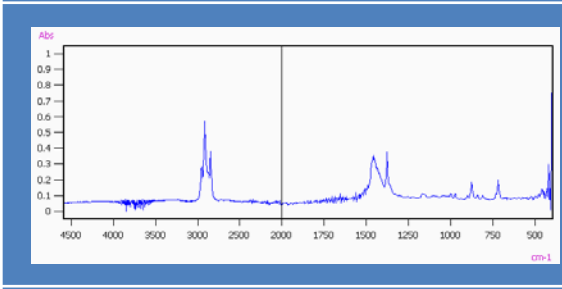
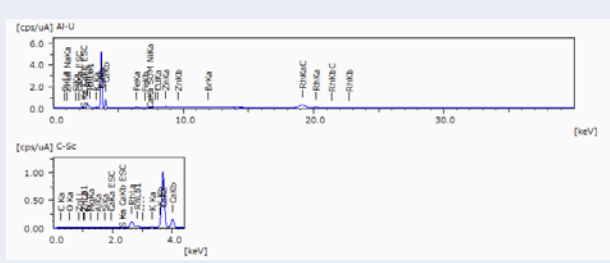
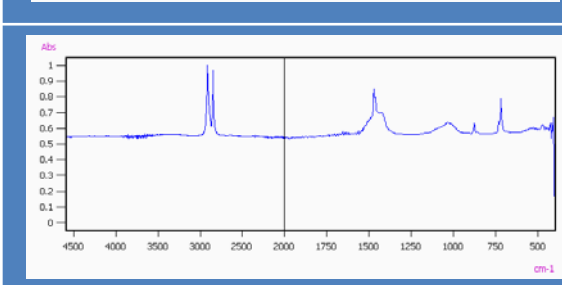
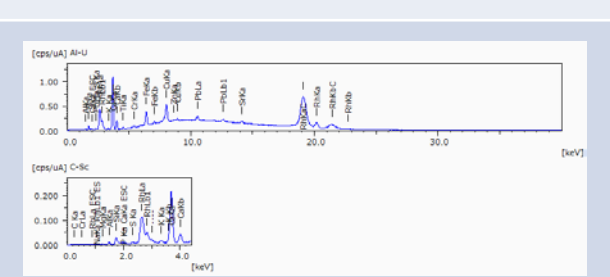
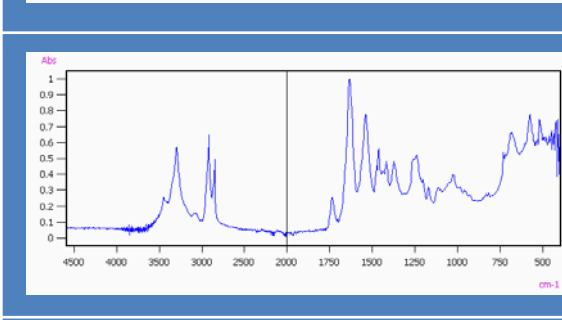
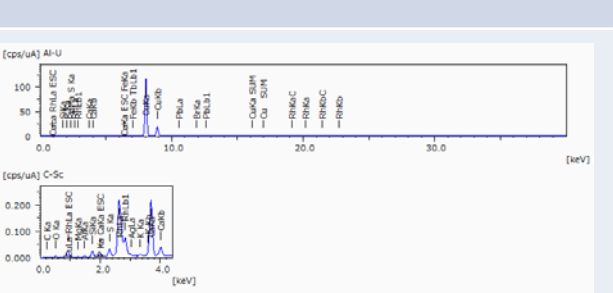
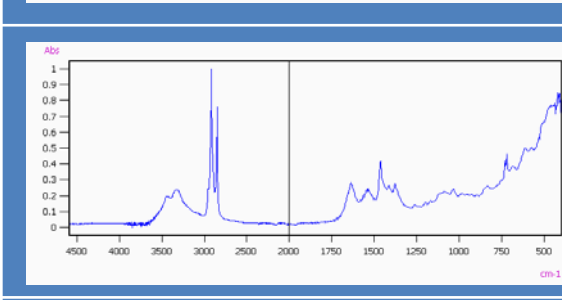
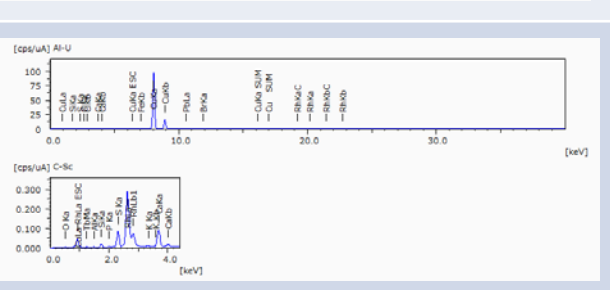
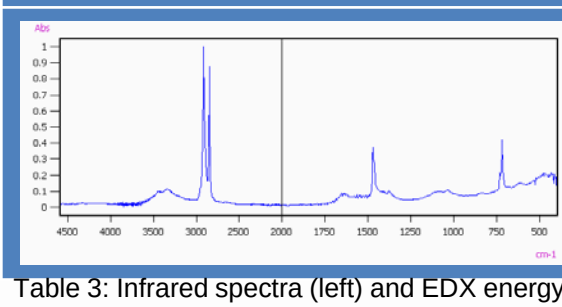
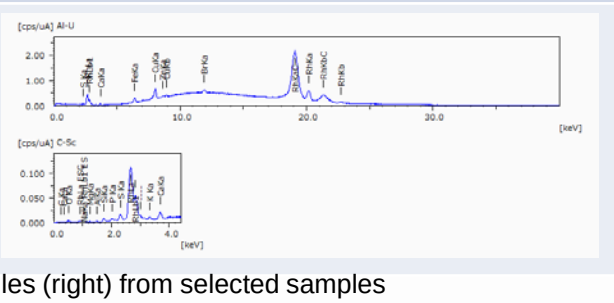
FTIR-ATR-Spectrum	EDX - Spectrum	Figure
		1a
		1c
		1d
		2a
		2b
		2c

Table 3: Infrared spectra (left) and EDX energyprofiles (right) from selected samples

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