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Application News

No.A517

Spectrophotometric Analysis

Analysis of Discoloration and Coloration Using FTIR and EDX

With just minor discoloration which is now a sufficient reason for complaint, it is no easy task for manufacturers to investigate root cause of discoloration from a wide range of possibilities and pinpoint the correct one.
When the quantity of material causing discoloration or coloration is small, extraction is normally performed before analysis. In this article, using the merits of Fourier transform infrared spectrophotometer (FTIR) and energy-dispersive X-ray fluorescence spectrometer (EDX), we identified discoloration materials and coloring compounds by direct sample measurement without pretreatment. Focusing on an analysis of color, this article describes some example analyses that explore causes of discoloration and coloration from organic and inorganic compounds, using an analytical approach that combines FTIR and EDX.

Analysis of Discolored Paper Using FTIR

Using FTIR, normal paper and discolored paper were analyzed, the results were compared, and the cause of discoloration was explored. Fig. 1 shows images of the paper samples, and Table 1 shows the FTIR analytical conditions used.

(1) Samples
Normal paper and discolored paper

Fig. 1 Normal Paper (left) and Discolored Paper (right)

(2) Analysis
Approach: Single reflection ATR

Table 1 FTIR Analytical Conditions

Instruments	: IRTracer-100, MIRacle 10 (Diamond prism)
Resolution	: 4.0 cm^{-1}
Accumulation	: 40
Apodization	: Happ-Genzel
Detector	: DLATGS

(3) Results
Analysis: Calculation of difference spectrum using data computing function

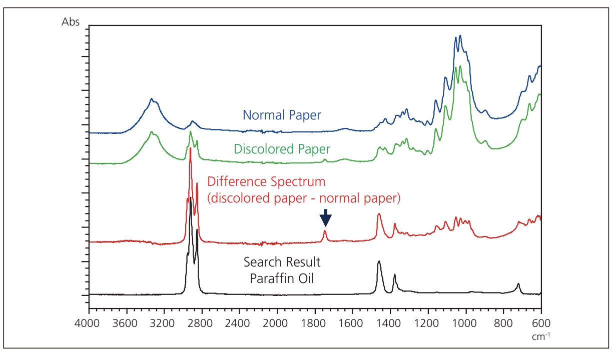


Fig. 2 Infrared Spectra and Search Result

Fig. 2 shows the infrared spectra and difference spectrum (discolored paper - normal paper) for normal paper and discolored paper, and a search result for the difference spectrum. Although paraffin oil was found after performing a spectrum search, paraffin is normally colorless at room temperature. The discoloration is therefore assumed to be a paraffin oil (e.g., machine oil) containing a discoloration-causing additive that adhered to the paper.
The peak at around 1750 cm^{-1} (C=O bond) in the difference spectrum identified by the arrow in Fig. 2 is presumed to be derived from the additive in the paraffin oil.
Because the discolored paper spectrum is dominated by the base paper material, it is difficult to ascertain differences with the normal paper spectrum. Calculating a difference spectrum shows these differences clearly, and simplifies identification of discoloration.

Analysis of Discolored Resin Product Using EDX

Using EDX, measurements were taken from a normal area and discolored area of a resin product, the results compared, and the cause of discoloration explored. Fig. 3 shows images of the samples, and Table 2 shows the EDX analytical conditions used.

(1) Samples
Resin product with discolored area

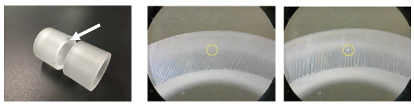


Fig. 3 Resin Product (left), Normal Area (center) and Discolored Area (right)

(2) Analysis
Approach: $_{6}C$-$_{92}U$ qualitative/quantitative analysis

Table 2 EDX Analytical Conditions

Instrument	: EDX-8000
X-ray Tube	: Rh target
Voltage / Current	: 50 kV (Al-U) / Auto
Atmosphere	: Vacuum
Measurement Diameter	: 1 mm ϕ
Integration Time	: 100 sec

(3) Results
Analysis: Calculation of difference profile using blank-corrected function
Detected elements: $_{13}Al$ (99.8 %), $_{26}Fe$ (0.2 %)

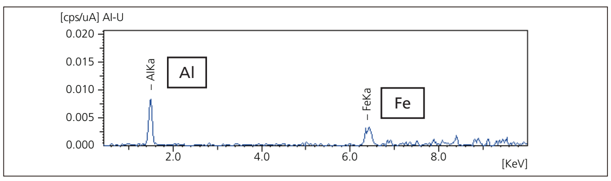


Fig. 4 Blank-Corrected Qualitative Profile

Fig. 4 shows the blank-corrected qualitative profile obtained by subtracting the profile of the normal area of resin from the profile of the discolored area. $_{13}Al$ and $_{26}Fe$ were only detected from the discolored area, with quantitative results showing the discolored area is 99.8 % $_{13}Al$ and 0.2 % $_{26}Fe$. Based on these results, the discoloration is assumed to be a fragment of aluminum alloy, and could be from a cutting edge that adhered to the product during the cutting process.

Analysis of Coloration Using FTIR and EDX

FTIR and EDX were used to take measurements from white resin and green resin, and identify the coloring compounds in each resin. Fig. 5 shows images of the samples, Table 3-1 shows FTIR analytical conditions, and Table 3-2 shows EDX analytical conditions.

(1) Samples
White resin and green resin

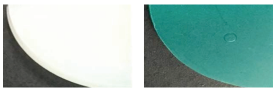


Fig. 5 White Resin (left) and Green Resin (right)

(2) Analysis
Approach (FTIR): Single reflection ATR
Approach (EDX): $_{6}$C-$_{92}$U qualitative/quantitative analysis

table 3-1 FTIR Analytical Conditions

Instruments	: IRTracer-100, MIRacle 10 (Diamond prism)
Resolution	: 4.0 cm^{-1}
Accumulation	: 40
Apodization	: Happ-Genzel
Detector	: DLATGS

Table 3-2 EDX Analytical Conditions

Instrument	: EDX-8000
X-ray Tube	: Rh target
Voltage / Current	: 15 kV (C-Sc, S-K)
	: 50 kV (Ti-U, Zn-As, Pb) / Auto
Atmosphere	: Vacuum
Measurement Diameter	: 10 mm ϕ
Integration Time	: 60 sec

(3) Results of FTIR Qualitative Analysis

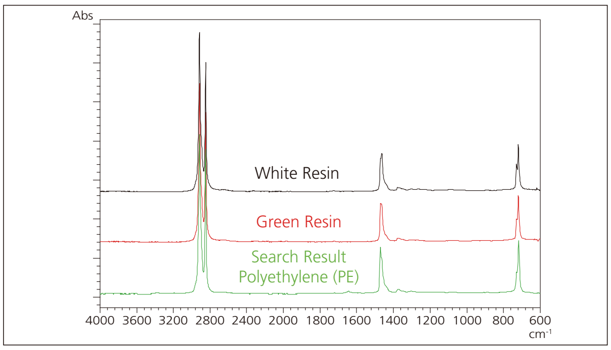


Fig. 6 Infrared Spectra and Search Result

Fig. 6 shows infrared spectra for white resin and green resin and a spectrum search result. The results showed that polyethylene is the resin component present in both the white resin and green resin. It is presumed that no coloring component was detected because only a very small quantity is present in each sample.

(4) Results of EDX Qualitative/Qualitative Analysis

Table 4 Quantitative Results

Units: % -: Undetected

	Cl	Si	P	Al	S	Cu	C_2H_4
White	–	0.010	0.007	0.007	0.003	–	99.97
Green	0.030	0.012	0.007	0.006	0.003	0.002	99.94

Note: Polyethylene (C_2H_4) was set as the balance.[1]

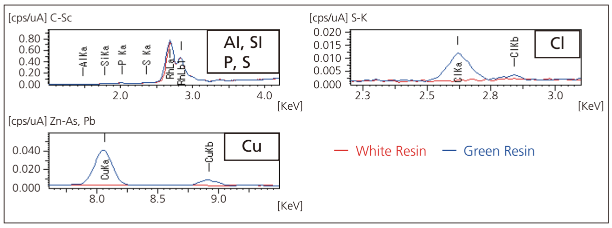


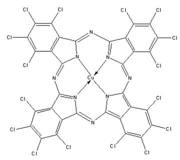
Fig. 7 Qualitative Profiles

Table 4 shows the quantitative results and Fig. 7 shows the qualitative profiles. $_{13}$Al, $_{14}$Si, $_{15}$P, and $_{16}$S were detected in both the white resin and green resin, and $_{17}$Cl and $_{29}$Cu were only detected in the green resin. FTIR analysis showed the resins are polyethylene, which is normally transparent, so detected elements are expected to contribute to resin coloration.

First, because $_{14}$Si, $_{15}$P, $_{13}$Al, and $_{16}$S were detected in both resin samples, these elements are presumed to be derived from additives used to improve resin functionality, and not from compounds used to impart color. The filler aluminum silicate (kaolin, $Al_2Si_2O_5(OH)_4$) is a likely additive that contains $_{13}$Al and $_{14}$Si. $_{15}$P and $_{16}$S are often found in oxidation inhibitors.

As for $_{17}$Cl and $_{29}$Cu only found in the green resin, green pigments that contain these elements include the organic pigment phthalocyanine green ($C_{32}Cl_{16}CuN_8$), and the inorganic pigment atacamite ($Cu_2(OH)_3Cl$). Ferrous pigments, cadmium pigments, and chrome pigments are also used to impart green coloration, but these materials do not match the elements and composition detected in the sample. EDX qualitative results of 0.03 % $_{17}$Cl and 0.002 % $_{29}$Cu show a higher $_{17}$Cl content than $_{29}$Cu. Phthalocyanine green is probably the best match when the composition of candidate pigments and qualitative results obtained by EDX analysis are compared.

Based on the above findings, the white color in the white resin was assumed to be derived from an additive, and the green color in the green resin from phthalocyanine green. Fig. 8 shows the structure of phthalocyanine green for reference.



Reference: Chemical Risk Information Platform (CHRIP), National Institute of Technology and Evaluation

Fig. 8 Phthalocyanine Green

Conclusion

Causes of discoloration can be quickly identified with FTIR when discoloration is caused by an organic material, and with EDX when discoloration is caused by an inorganic material. When analyzing a colored material, FTIR was effective in determining its main constituents, and EDX was effective in identifying the pigment.

Combining FTIR and EDX provides a non-destructive and speedy analysis that is effective in the investigation of discoloration and coloration.

References
1) Shimadzu Application News No. X255

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