Forensic Differentiation of paper by X-ray diffraction and infrared Spectroscopy

Background:

The aim of this article was to investigate the value and reliability of a differentiation procedure of similar paper samples on the basis of X-Ray Differentiation data and its discriminating power. The background information provided in the article is sufficient in order to understand the results and the discussion regarding the results. The article discusses why X-Ray Diffraction is a valuable technique for studying papersamples. It also talks about the properties of paper. The article explains previous techniques that have been proposed to carry out this type of investigation and why they were insufficient for the purpose of discriminating between various sheets of white office paper.

There were a couple of terms that I was unfamiliar with. One is the method of pyrolysis gas chromatography. I researched the method of pyrolysis gas chromatography and found that it is an indirect method in which the substance of study is characteristics of gas chromatography of the volatile products of its pyrolysis. With this method, conclusions can be made about the structure and composition of the initial polymer system. I was also unfamiliar with the details of crystallinity. The article stated, crystallinity refers to the degree of structural order. I researched crystallinity further in order to completely understand how it was being utilized in this experiment. I found that, the degree of crystallinity has a big influence on hardness, density, transparency and diffusion. In a gas, the relative positions of the atoms or molecules are completely random. Amorphous materials, such as liquids and glasses, represent an intermediate
case, having order over short distances but not over longer distances. Many materials can be prepared in such a way as to produce a mixture of crystalline and amorphous regions. In such cases, crystallinity is generally specified as a percentage of the volume of the material that is crystalline. Even within materials that are completely crystalline, the degree of structural perfection can vary. Crystallinity can be measured using x-ray diffraction.

**Methodology:**

The methods used for this research were IR Spectroscopy and X-RAY Diffraction. IR spectroscopy equipped with an attenuated total reflectance sampling device can be used to characterize paper. This method is non-destructive and has small sampling depths. This method can differentiate a larger population of white sheets of office paper which are indistinguishable by visual examination. The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra.
The second method, X-Ray diffraction, is also valuable in paper discrimination. This method investigates both polymeric matrix and the inorganic formulation of paper. Cellulose is added with a number of different inorganic fillers. The quantity and nature of the fillers is characteristic of each manufacturer. The basic idea is that the waves from all parts of the object combine to form the intensity in any direction. The intensity will vary depending on how the waves end to reinforce or cancel. The dispersion of the waves is bigger for smaller objects than for large, and so the diffraction pattern is not just an enlarged copy of the object.

**Assumptions:**

There were many assumptions within this article. Most were regarding results obtained from the study. One result mentioned in the introduction was that all common photocopy paper weighed 80 g/m². The authors also assumed that a large population of white sheets of office paper could be differentiated due to the fact that all samples of a set of six paper varieties could be differentiated by diffuse reflectance and 67% of the possible pairs of a population of 8 types of paper could be discriminated by ATR. In the experimental section, the assumption was made that the variety of office paper was randomly selected from the shops in Italy and these samples were representative of all office paper. When selecting the region for the IR spectroscopy, they assumed that the samples would fall into the region of 4000 to 650 cm⁻¹. Also, due to the preliminary tests on selected samples showing an increasing number of sheets and of locations on the same sheet to more than five did not significantly increase the precision, they assumed the sampling scheme of 5 different locations for five different sheets for each ream would be sufficient. They also made the assumption that one replicate was sufficient due to repeatability of three measurements that obtained diffractograms were superimposable. Another assumption presented in this study was that the intensity of the peak in the paper spectrum was principally
ascrivable to CaCO$_3$ due to its molar absorptivity being much higher than that of the signals of cellulose in the same spectrum range. They also assumed that the Kaolin additive was no longer used at least in Italian and possibly the European market because no sample peak appeared for it during the experiment. Another assumption made by the authors is that manufacturing procedures that determine an uneven distribution of filler in the cellulose matrix is the reason for the differences between the two sides of the sample papers.

**Arguments:**

The arguments presented in this study can be understood by a non-expert in the field. The authors argue that the IR spec and X-Ray diffraction methods are the most suitable for their research. They did consider other techniques such as Ramen spectroscopy and pyrolysis gas chromatography. They explained that these methods were less viable because they require special apparatus and imply destructive tests. They also yield insignificant results due to the high standardization of the market and production procedures. They provide the example of all photocopy paper weighing the same. Another argument made by the authors was that the profile due to inorganic peaks allowed differentiating all the couples but one that had resulted indistinguishable by the degree of crystallinity. The production process of paper can produce an uneven distribution of the inorganic additives along the thickness off the sheet but not the plane of the paper. The authors argue that this procedure is useful for the identification of paper. They provided an example of how a blind test had been performed using the samples that had been previously analyzed during the experiment. They were analyzed by an operator that had not participated in their study. The results showed that there was agreement within the experimental error.
Conclusions:

All of the samples out of 19 white sheets of office paper which are indistinguishable by visible examination could be discriminated using the methods of X-Ray diffraction and IR spectroscopy. The results were achieved by a non-destructive technique. The IR spectroscopy and X-Ray diffraction methods allowed detection of the variations in the structure brought about by different processing parameters, manufacturing conditions and formulations of additives. The possibility to discriminate between sheets of paper is valuable in questioned documents examinations.