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PRESIDENTIAL ADDRESS

FORENSIC PHYSICS

*President - Ran B. Singh**
SECTION OF PHYSICS

I am grateful to the Physics Community of the Indian Science Congress Association for electing me the sectional president for this session. Since I am fully conscious of my inadequacies, and the greatness of many stalwarts who presided over the physics section in the previous sessions of the Science Congress, I have continually wondered how the members of the sectional committee could have decided to give this great honour to a person from applied field. However, I never doubted your generosity and grace. I accept this honour with all humility and thank you very much.

The simplest and straightforward relation which I can derive amongst Science, Technology, and Industry is :

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Technology is application of science,

&

Industry is practice of technology.

In fact, technology is the totality of human knowledge used to provide things and means necessary for human sustenance and comfort. In view of this and the focal theme 'Science, Technology and Industrial Development in India' of the Indian Science Congress this year, out of the options which I could have had for the presidential address in the Physics Section, I found Forensic Physics to be more compatible with the focal theme.

If we define physics as the study of the properties of matter; that is the study how the matter behave under different circumstances, there are probably few fields in which the applications of physics are as varied as in the scientific investigation of crime. **Forensic Physics** can be defined, as the application of the methods and techniques of physics to produce evidence-objectives and circumstantial - for the judicial and social justice. Such evidences do not suffer from the various admitted weaknesses of personal testimony.

This application of science (technology) is an endeavour to solve crimes in society and reaffirm confidence in the social system for better living. Though, not in use in any industry, it has some indirect impact on the quality of many industrial products and thereby on the industrial developments. It plays important and significant role in protecting the interests of consumers of industrial products. For example, substandard building materials and other manufactured products, spurious products, imitations, et cetera are routinely examined in the forensic science laboratories.

The most important role of forensic science is to convert suspicion into reasonable certainty of either guilt or innocence. The applications of forensic physics, as all other branches of forensic science, may conveniently be divided into comparative and definitive (absolute) ones. There are instances when source correspon-

dence has to be established between the physical clue materials found at the scene of crime and those collected from the suspected person / tools / firearm / vehicles etc. The most important task in this context is, therefore, to discover whether or not the two samples are indistinguishable by all the tests that can be devised. Such applications fall under the category of comparative ones. The definitive examinations on the other hand are those in which the information sought rests on an accurate qualitative identification or quantitative analysis of questioned samples.

In a general report such as this one, it is not possible either to cover the whole range of subject or to give truly comprehensive or detailed account of any one part. Therefore, an effort has been made here to introduce the methods and techniques of Physics used in crime investigation and give a few examples of the possible applications.

Gross Macroscopic and General Studies

In some cases, a naked-eye examination is all that is needed to produce evidence of vital importance. If any thing gets broken or torn in committing a crime, and if one of the pieces is found at the scene of crime and the other can be linked with the suspect, the fitting together of the broken edges of these pieces may provide the most incontrovertible evidence to link criminal with the crime. The uniqueness of the randomly generated irregular contours of the broken edges can be inferred intuitively as well. However, Walls¹ has put forth a statistical concept of random breaking to prove the uniqueness of broken edges, while Thornton² has used computer generated fractal surfaces as models of evidence physical matches and has assessed the degree of uniqueness of the broken edges in terms of the complexity of the model surfaces. The complexity of the surface has been measured in terms of the time required for the calculation of the fractal surface parameters.

The mechanical fitting of randomly broken irregular edges of screw drivers, chisels, pliers, cast metal, door handles, wood,

plastics, fabrics, paper, adhesive tapes, idols, bamboo sticks etc. have provided valuable evidences in many cases. In a case of burglary, the recovered ornaments were found wrapped in a piece of *saree* and a torn *saree* was found in the burglarized premises. The irregular torn sides of the two pieces of the *saree* fitted exactly which established their source correspondence. The boarder design, weave pattern, and print of the pieces of *saree* were also found to match.

The radial and concentric cracks, crater shaped hole on the broken glass, and characteristics rib marks and hackle marks on the edges of the glass pieces yield very valuable information about the type of projectiles, nature of breaking force, and direction of applied force etc used for breaking the glass. The mechanism of glass fracture has been discussed by Thornton and Cashman³ in detail. The technique of physical comparison of fragments of glass by characteristics of their edges or cross section is well established but one runs into difficulty when faced with glass fragments, the edges of which can not be fitted. Von Bremen⁴ has described the technique for the matching of noncontiguous glass fragment by invisible heterogeneities within them. Ream or card are glassy inclusions whose physical and chemical properties differ from those of the surrounding glass. The demonstration of rim and card is accomplished by means of shadowgraph. These are produced by point source that cast a shadow of the sample on photographic film. Glass fragments can be related by their heterogeneous inclusions, even when they are separated by several centimeters.

In many cases invisible information is made visible with gamma rays, X-rays, ultraviolet and infrared radiations ; and filtered visible light with the help of special arrangements, equipments, and techniques. The interaction of electromagnetic radiation with matter results into its reflection, scattering, selective / differential absorption, transmission, and photoluminescence caused by it. These phenomena, though simple in nature, are extremely useful for preliminary interrogation of samples and provide, at times, conclusive results. Sometimes, it is required to extract relevant information

obscured in multicolored surface, for example the cancellation date on postage stamps. In such cases the observation / photography through suitable filters provides proper contrast by suppressing or highlighting some of the colors. In cases of obliterated writings, the infrared reflection photography is of much help. There are a number of inks and dyes which are transparent to infrared while others are opaque to it. If the obliterating ink / dye transmits infrared and the host ink / dye is infrared reflecting, the infrared photography will reveal the hidden writings. Similarly, two objects looking similar in colour in visible light may have widely different reflectivity to be photographed in varying shades in ultra violet radiation. For example, white pigments titanium oxide and zinc oxide photograph white and black respectively, in ultra violet radiation because titanium oxide is a good uv reflector and zinc oxide is a poor uv reflector. The selective transmission / reflection of ultra violet, visible, and infrared radiations by different materials are thus very helpful in the preliminary examination of forensic samples for decipherment and comparison.

The X-rays, hard and soft, have been in use for the internal interrogation of objects opaque to the other radiations, since their discovery. The forensic scientists use soft X-rays for the examination of clothes and fabrics, paper, powder patterns around bullet holes, documents, leather, jewelry, art, currency notes etc. and hard X-rays for the examination of suspicious packages, structural defects, counterfeit coins, dead bodies, guns etc. The hard X-rays are used for electronography also. In this technique, metallic elements are made to produce a recordable emission when irradiated with a high kilovolt monochromatic X-ray beam. All metallic elements have different emission points. In the case of lead the ejection point is 90 KV. The electronography has advantageous applications in developing fingerprint on skin and multicolored back ground, indented writings, non destructive differentiation of inorganic pigments in paintings etc. The gamma rays from radioactive sources like cobalt-60 have also been used for shadowgraphy, electronography, and autoradiography.

Cason⁵ has suggested the use of neutron radiography in forensic science. The absorption of neutron is a combination of production event (absorption) and neutron scatter. Both processes remove neutrons from the incident neutron beam and hence contribute to absorption. The high scatter of neutrons by light elements seems to be particularly advantageous for discrimination between several materials which have similar X-ray absorption coefficients. Californium-252 has been found to be a suitable source for neutron radioagraphy.

The Betagraphy⁶ has also been used, in addition to soft X-ray and transmitted light, for the detection of alterations in documents. Carbon-14 in thin sheets of organic polymers (Methyl C-14 Methacrylate / Butyl C-14 Methacrylate) is used as flat source, producing beta particles of slight energy. The questioned document is placed between the source and the photographic film to get the betagraph. The technique can be used to study the distribution of fibers in papers,⁷ reproduction of water marks, thinning down of the texture of paper in the case of mechanical erasures, and additions with inks more or less composed of heavy pigments. Radioactive ³⁵Sulfur dioxide gas may be used to develop unintended handwriting impressions in underlying layers of papers. The uptake of sulfur dioxide is greater for surfaces which have been damaged, for instance by pressure, than for the unchanged surrounding area. An autoradiography of the ³⁵-sulfur dioxide exposed paper sheet reveals a positive image of characters written on the preceding sheet .

Amongst other method of developing indented impressions, the electrostatic imaging technique is quite popular. In this method the document is used as dielectric element in a capacitive arrangements. The electrostatic image of the variations in capacitance resulting from indentations in the document is converted into visible images with the help of electrophotographic developers. Behmen and Nelson⁸ have shown that for indented writing best result is obtained by first developing them by electrostatic method and then enhancing the lift using a high pass sharpening filters by digital image processing methods.

Tang⁹ has developed a computer aided system for the discrimination of seals by digital image processing. The system is non-destructive, fast, and offers good accuracy. It can compare the geometry and the intensity variations, while the conventional method is limited to the geometry match.

There are many substances which absorb radiation of one wave length and in its place emit radiation of another wavelength. This phenomena is known as, in general, photoluminescence. Phosphorescence and fluorescence are special cases of photoluminescence. Phosphorescent radiation continues after exciting cause has been removed and fluorescent radiation stops when exciting cause is removed. The ultraviolet radiation causes thousands of substances to emit characteristic fluorescence. Most of these are in the visible region. Some of the substances have invisible uv fluorescence¹⁰ also. The uv fluorescence is extensively used for the examination of a variety of samples like biological stains, glass, gem, finger nails, teeth, polish, cosmetics, dyes, pigments, minerals, paper, ink, chemical erasures, secret writings, wax seals, counterfeit tickets, and coupons etc. Similarly visible luminescence (commonly referred to as infrared luminescence) where exciting radiation is in the visible region and luminescence is in the infrared region, is used for the examination of inks, obliterations, alterations, overwritings, and erasures. Hardecastle and Hall¹¹ have shown that the luminescence of ink in infrared may be considerably enhanced by cooling to liquid nitrogen temperature. Sensi and Cantu¹² have observed that the examiners should use extreme caution in using these methods because contamination of writings with various substances like perspiration, milk, water, acetic acid, and other solutions found in household may alter the fluorescent character of inks, leading to wrong conclusions. Today, many video spectroscanner systems are available to facilitate the recording and observation of photoluminescence, which are difficult to record otherwise.

Microscopic Studies

The traditional picture of a forensic scientist is a man with a lens, the microscope is its further extension. In fact, many methods in forensic investigations rely heavily upon microscopy as a medium for identification and comparison of physical clue materials. All types of optical microscopes are needed for some purpose or the other in the routine laboratory examinations. Low power microscopes for determination of certain physical constants (melting points and refractive indices etc), and examination of fingerprints, hand writing, metal filing, tears or incisions, paper, paint chips, labels, erasures, cloth pattern etc ; high power microscopes for fibers, plant materials, spermátózoa and other microorganisms etc ; fluorescence microscopes for dyed textile fibers, fluorescent particles, diatoms etc ; polarizing microscope for fibers, minerals, soils, rocks etc ; comparison microscopes for comparison of tool marks, fired cartridge cases, rifling marks on bullets etc. Microprocessors and various digital image processing systems have added new dimensions in the utility of microscopes as diagnostic and analytical tools. The microscopic images can be stored, retrieved, added, subtracted, superimposed, enhanced, and compared in juxtaposition, as and when desired, for deriving required information.

Scanning electron microscopy (SEM) of opaque specimen permits a much better resolution and depth of field than optical microscopy. Spacious specimen chambers are also available now with SEM to accommodate larger samples and special stages. The SEM have been used for the morphological study of a variety of samples of forensic interest¹³. For example : cystolithic hairs of the upper epidermis of a *cannabis sativa* leaf¹⁴, paint chips, fine structure and ultra fine structure of hair, counterfeit dots on coins, firing pin impressions, identification of burnt matches, foreign material on bullets, transfer of PVC plastisol in collision between vehicles, identification of chironomide larvae, microstructure of bones, dried blood, comparison of splinters of wood, and gunshot residue etc.

In the examination of questioned documents some times it becomes very important to know the sequence of crossed lines which decide the relative age (before and after) of the lines. The enormous depth of field available with the SEM makes it possible to see the deposits of a second writing instrument on a first and the details of the fine structure. It has been observed that this method yields very good results in most of the heterogeneous crossings. The homogeneous intersection of lines made with liquid inks are not always revealed successfully. Waeschle¹⁵ and others suggested to cut the crossing zone from the document and mount them on the stage of a SEM after suitably coating with metal layer to make them conductive. The cutting of the disputed intersection damage the document, which is not desirable. Singh et al¹⁶ used improvised document holder to mount the folded document. The portion with the relevant crossed lines in the documents is kept on the top and the crossing zones are exposed by cutting suitable windows in the cover. In this manner only crossing zones are coated and rest of the document remains in its original form. In a case, the body of a hand written deed was erased chemically after execution, and fresh matter was written in its place. A few strokes of the new writings crossed the preexisting signature, at places. The knowledge of the sequence of the strokes at the crossings was most important in this case. This could be determined by examining the crossings under scanning electron microscope. The document mount, described above, was used to place the deed in the specimen chamber of the microscope. It was clearly observed that the strokes of the signature were below the strokes of the writings at the crossings. It may be mentioned here that the coating obliterates the sample, making it impossible to examine the crossed lines again with the other methods. Singh et al¹⁷ used anode spacers for observing the crossed lines without coating. This method can be used for quick observation by the operator examining the crossing zone.

Singh and Aggarwal¹⁸ made a detailed study of the cut end of the wires using SEM and have shown that matching of extrusion marks, correspondence of breakage at the edges of the cut ends,

and correspondence between the fine structure on the opposite surfaces revealed by SEM can be used to investigate source correspondence between questioned and known cut pieces of wires. Sehgal et al¹⁹ examined topography of cut ends of wires in detail using SEM. They have observed that SEM would be of much help in the examination of tool marks caused by extremely sharp blades of cutting tools. Ueyama and Ishiyama²⁰ have studied the morphologies of blasting caps, and the fragment associated with their detonation by scanning electron microscope and optical microscope. They have demonstrated that the characteristic 'dimple' patterns and 'knife-edge' patterns present in the morphology of fragments indicate their close connection with explosive devices.

The diagnosis of drowning is one of the most difficult task in the investigations, the diatoms test provides supportive evidence of drowning specially in putrefied bodies where no other tests are possible. Pachar and Cameron²¹ have described a simple and rapid method of processing organs and water samples, and have used SEM for identification and classification of diatoms. They have demonstrated scanning electron microscopy to be the most effective technique for photographic record and taxonomic analysis of diatoms.

A detailed microscopic study of the separated edges of cuts and tears on clothing have been made by Monhan and Hardy²². They have suggested guide lines for the interpretation of the damage. Stowell and Card²³ have used SEM to identify cuts and tears in nylon fabrics on the basis of features on the fiber ends. The margins of incised wound in human skin have been studied by Luna et al²⁴ using SEM to assess its diagnostic ability in such cases. It was not found very useful in identifying a weapon, however, the determination of entrance margin in incised wound could be done better.

Different methods using various components of fingerprint material have been devised and tested, and at the same time search is on for efficient and better procedures to develop and record

fingerprints. Garner et al²⁵, and Sethi et al²⁶ have made efforts to detect and photograph latent fingerprints on non porous smooth surface using SEM. The fingerprints could be recorded without any treatment (application of powders etc). The results were independent of the background colors. Ulmanski et al²⁷ made a SEM study on fingerprints taken with dental impression materials and a replica tape. The SEM records of fingerprints are very encouraging and may be used to study the population and distribution of pores in the ridges.

Laser applications

Lasers have proved to be most important research tool in the field of science and technology. They have been used to solve many scientific, technological, industrial, military, medical, and other problems. In forensic field, lasers have been used for zonal application of photons to analyze elemental composition of minute samples ; fluorescence of fingerprints, chemical erasures, chemical and biological stains etc ; recording of corneal turbidity for determination of time lapsed after death, particle size distribution analysis, time lapse photography, Raman Laser Probe, crime scene investigations etc. The possible laser applications for the detection of indentations in documents, recording of footprints on rugs, comparison of fingerprints, crime scene photography, stress and fatigues in metals, and recording of striations for contour analysis have also been explored.

The pulsed lasers can provide enormous power densities for a brief instant. In a focal small point, the pulsed power densities can exceed a million watts per square centimeter. If the substance absorbing light is reasonably opaque, all the energy is delivered to a very small volume so that the rate of rise of temperature may be as much as 10^{10} degrees per second or more. The heating is so rapid that it is only superficial. The great rapidity of the selective heating ensures that the surface layer is evaporated completely and not just its more volatile components. The vapor can be excited by a spark or can glow brightly enough by itself so that its spectrum can be

observed ^d spectrochemical analysis performed. By control of the focus, it is possible to restrict the depth of pits to permit analysis of surface films^{28,29}. The laser probe excitation³⁰ has been used to study elemental composition of paint layers^{31,32}, gunshot residues^{32,33}, ink on documents³⁴, metallic fragments, body fluid stains³³, gold plating³⁵ etc. In a case, one coin was found to be genuine but there were some coatings / stains on it. The surface coatings were analysed using high power laser source to vaporize it, and it was found to contain lead, tin, and antimony. This information was consistent with the suspicion that the coin had been used to make mould for counterfeiting.

Lasers have been used extensively for the detection of latent fingerprints by inherent fingerprint luminescence and with the use of fluorescent dusting powders^d and other chemicals. Palmer sweat contains a variety of components like salts, amino acids, lipids, proteins, and vitamins etc. Some of these compounds such as riboflavin and pyridoxin show inherent fluorescence. In fingerprint deposits such compounds are present rather in small quantities and hence they do not show^w appreciable luminescence with weak source of excitation. Dalrymple et al³⁶ studied the excitation-emission spectra of fingerprint material and observed that the absorption band responsible for the yellow green fingerprint luminescence and the 514.5 nm argon laser line are almost ideally matched. They demonstrated the use of cw argon ion laser by detecting fingerprint on paper, knife blades, cups, glass bottle, paper towel^f, living skin etc.

The inherent fingerprint luminescence was found to be of limited use since background luminescence from surfaces holding fingerprint often dominate the inherent fingerprint luminescence. In order to overcome such problems a number of procedures³⁶⁻⁴¹ were soon explored. These include dusting fingerprint with fluorescent or phosphorescent powder, staining with fluorescent dyes, treatment with certain chemicals, and vapor deposition of fluorescent compounds, which react with fingerprint residue to form luminescent products.

It was observed that in some cases the conventional method using ninhydrin was better than laser methods for detecting latent fingerprints. The ninhydrin treated fingerprint did not show significant fluorescent under argon ion laser but the continuous wave dye (Rhodamine 6G) laser tuned to about 580 nm yielded clearly observable redfluorescence of such prints⁴². The treatment of fingerprints with a combination of ninhydrin and trypsin as well as ninhydrin followed by treatment with zinc chloride were also experimented⁴³. It was found that the ninhydrin-zinc chloride procedure gave good results. However, a very pronounced enhancement in detectability of reasonably fresh latent fingerprint was observed when the ninhydrin method was combined with enzyme treatment⁴⁴. Chemical developments with dansyl chloride and vapor staining with 9-methyl anthracene was found to be suitable for the detection of the fingerprints on substrate like card board, wood, leather, some metals, and plastics⁴⁵. The copper vapor laser, frequency doubled Nd : YAG laser, and several ninhydrin analogues⁴⁶⁻⁴⁹ have also been used for the detection of the latent fingerprints. The latent fingerprints treated with ninhydrin/zinc chloride were found to be unsuitable for the doubled frequency Nd : YAG laser. Cheng⁵⁰ observed that Nd : YAG laser was suitable for the visible bloody fingerprint treated with ninhydrin / zinc chloride.

Warrener et al⁵¹ found that strongly luminescent fingerprint can be produced on paper by initial treatment of latent fingerprint with the chemical reagent NBD chloride (4-chloro-7-nitrobenzo furozan) followed by the excitation with 150 Watt Xenon arc lamp filtered to transmit light in the 475 nm spectral region. This method was found to be more sensitive than ninhydrin for moderately old fingerprints⁵².

A number of body fluid stains fluoresce under ultra violet and laser light sources, which are valuable tools in the screening of crime samples for body secretion stains. Auvdel⁵³ evaluated the argon ion laser and a high intensity quartz arc tube for their detection limit for biological stains. The serial dilutions made from se-

men, saliva, and sweat specimens were used for the evaluations. Both the light sources were found to be comparable to each other. However, the high intensity quartz arc tube should be preferred if the cost, power consumption, lack of mobility, and replacement cost of plasma tube of the argon ion laser is taken into consideration.

Creer⁵⁴⁻⁵⁶ used argon ion laser and dye laser extensively for the examination of forensic samples and reported that fingerprints, shoeprints, erased writings, difference in inks, transfer of ink to other surfaces, effect of correcting fluids, stains on clothings, fire-arm residues, difference in paints, fibers, and interference patterns in glass, among other things, have all been either detected or enhanced by the use of lasers as a source when conventional technique have failed. A computer controlled scanner for laser enhanced photography has also been developed⁵⁷. It provides for variable speed, step size, and angle of radiation and has proved to be very effective method of controlling the movement of laser beam during photography. It is particularly useful when the angle of lighting is critical or when very long exposures are required.

A number of workers⁵⁸⁻⁶¹ have used different lasers to study the fluorescence of ink strokes for differentiation of inks with varying degrees of success. Von Bremen⁶² used an argon ion laser and a dye laser excited by it for locating luminescing inclusions and fibers in paper matches. The size, color, and intensity of luminescence varied from match to match and provided a good parameter for their discrimination. It was observed that the argon laser produced more luminescing inclusions whereas the dye lasers excited more fibers. A technique of utilizing time-lapse photography in conjunction with fiber optic and helium neon light source for recording the striae appearing along the edges of single counterfeit currency note have been described by Cain⁶³. Papers cut by the same hydraulic or manual paper cutting blade exhibit consistent striae details in relative position and depth perspectives. Thornton and Cashman⁶⁴ used laser beam interferometry for the reconstruction of fractured glass. An organ ion laser was used to produce reflection interograms from

glass pieces. The Fizeau ^{fringes} ~~lines~~ observed in the reflection images are, in essence, microtopographical contour maps in the up and down directions. The interference patterns shown by different pieces of glass are unique and the application of Fizeau fringes to the reconstruction of fractured glass is easily achieved. The technique is not suitable for disannealed or tempered glass. Raman laser microprobe is another powerful technique which can be suitably used for the examination of micron sized samples. This can greatly aid authentication of historic art objects with no major damage to them. Guineau⁶⁵ used this method with argon laser source to identify inorganic pigment used in ancient manuscripts.

Double exposure hologram interferometry provides a means of detecting very small disturbances. Instead of a single exposure the plate is exposed in two steps and when the developed plate is viewed the observer sees two images. If the object does not change in any way between the exposures the two images are identical and superimposed but if slight change in shape or position has taken place then the two images interfere and the regions of disturbance are delineated by interference fringes. This technique⁶⁶ has been suggested for deciphering indented impressions in paper. A special document holder has been described to produce the required change in the depth of impression, between the exposures. The holographic method has been suggested to record hard-to-see foot prints on carpets⁶⁷ also. The minute movement of carpet fiber returning to their positions after the compression are recorded on the holographic plate as a series of contours outlining the footprint. The rate ^{of} fiber movement can also be measured by the double exposures to estimate approximately, the time when the impression was made. Holography can be used to speed up fingerprint identification⁶⁸ also; since a hologram is made by two interfering light sources either source can be used to reconstruct the other. Fingerprints on micro films can be used as the scene to illuminate the hologram of the suspect's fingerprint. If any of the known fingerprint correspond with the unknown one a bright spot of light would be seen on the output screen. The holographic methods described above have not

been put to use for obvious reason of the lack of development of suitable equipments which can be operated simply in a routine manner. However, when such equipments are available, the proposed methods could solve many problems which are very difficult otherwise.

The cornea gradually turns opaque after death. This is one of the important indications for estimating the time of death. A laser apparatus⁶⁹ has been developed to have an objective estimate of the corneal turbidity so that the time of death can be predicted more accurately. Wanogho et al⁷⁰ have used laser diffraction technique for particle size distribution analysis, of sub-63 μm fraction obtained by wet sieving of soil samples. The results obtained suggest that a combination of organic matter, and laser diffraction analysis could be usefully employed to be routine analysis of soils in forensic work.

Peterson⁷¹ has described a method for examining the contour of striated tool marks. Laser light is focused on tools striation moving at a constant rate. Due to irregularities in the tool mark surface, the incident light is reflected at various angles and intensities. The different levels of light thus obtained are recorded using photo detector system. The graphical representations of the reflected light may be used to compare tool marks.

Portable laser sources have been developed to facilitate their use at the scenes of crime for locating latent fingerprints, hairs, fibers, body fluid stains, gunshot residues and other physical clue materials.

Trace Element Analysis

The physical evidence can be examined with regard to both their class characteristics and their individual characteristics. The class characteristics served to categorize the evidence. Although the class characteristics are useful, the greatest value of physical evidence lies in its ability to individualize. The more individual characteristics an item has the smaller the probability is that it can

occur twice in the same form. The inevitable trace impurities present in the material provide usable class and individual characteristics for forensic comparison in many cases.

The major (10-100 percent) as well as minor (0.1-10 percent) constituents of natural and manufactured products are controlled precisely, in general, by the nature or the manufacturer, but the trace impurities (1-100 ppm) make their ways into these products uncontrollably in the process. In forensic context, very significant trace impurity can also be present owing to contact transfers. The trace elements are analyzed to get information regarding the presence and level of a specific element or a group of elements in a sample depending upon the specific goal of the analysis. The population and levels of trace elements in the samples are studied to profile the material for its individual characteristics and establishment of source correspondence between two or more specimens.

The characterization of a substance by means of its inevitable trace impurities to establish as firmly as possible the probability that two or more specimens of a given type being compared do or do not have a common origin is known as trace element characterization. The population of trace elements in a given type of sample is explored and their quantitative variation within and between the samples of the same type is studied to evaluate the discriminating power of the various trace impurities present in the sample. This provides background data for characterization of the substance being investigated. This technique is used for different kinds of forensic problems. For example, determination of source correspondence between the pieces of transmission wires seized from the culprits and the pieces taken from the poles in the wire theft cases. The techniques of atomic emission spectroscopy, atomic absorption spectroscopy, energy dispersive X-ray analysis, neutron activation analysis, and other methods are used for trace element characterization.

The atomic emission spectrography has been used traditionally in most of the moderately equipped forensic science laborato-

ries for the analysis of trace elements and it still serves its purposes. In many cases very small quantity of samples are received for analysis and one has to be very careful in handling them. The microbrush abrasion technique may be used to recover trace materials for spectrographic analysis. A small sample could also be compressed in the tip of a graphite pellet and burnt in the arc or the carrier distillation method can be used for better sensitivity. The spectrongraphic method has been used for the analysis of paints, metallic trace transfers, glass, wires, soil, fillers in papers and plastics, poisonous metals in toxicological analysis, minerals, and numerous other materials. These analyses are always qualitative or at least semiquantitative, since the condition and variety of samples to be examined makes the normal quantitative method impossible. However, if two samples analyzed under identical conditions yield identical spectra, that is a *prima facie* evidence that they are identical in composition, even though one can not quote a percentage figure for any of the constituents. Emission spectrography is one of the oldest techniques in forensic science and has been used in innumerable cases for qualitative analysis. Methods for quantitative spectrongraphic analysis have also been developed for a few types of samples like glass, copper wires, aluminum wires etc.

Chan and Li⁷² used spectrographic method for comparison of single stranded copper wires in a telegraph wire theft case by quantitative estimation of seven elements : Sb, Pb, Fe, As, Mn, Sn, and Ni in parts per million level. The results were used to opine on the source correspondence of various samples in the case.

The trace element content of glass samples were measured using emission spectrongraphy by Andrasko and Maehly⁷³. The elemental ratios were calculated from the intensities of the elemental lines for semi quantitative analysis. No variation in chemical composition was detected within panes of sheet glass. The samples from different panes could be differentiated successfully. Blacklock et al⁷⁴ analyzed about two hundred glass samples and determined levels of Al, Ba, Ca, Fe, Mg, and Mn by emission spectrography. Six

standard glasses were prepared with varying concentrations of chosen elements and were used for quantitation of the element present in each sample. They have demonstrated that this method could provide useful information for the classification of glass samples into container, sheet, and tableware categories. The discrimination between a large number of samples could also be achieved. It was further observed that calcium with its high degree of correlation with refractive index is of no value for either classification or discrimination.

Singh et al⁷⁵ used emission spectrographic technique for characterization of aluminum wires. Levels of B, Cr, Cu, Fe, Pb, Mg, Mn, Ni, Ti, and V were determined in eleven wires from different sources. The concentration of trace elements along the length of a hundred meter wire was found to be uniform. The intercomparisons of different possible pairs formed from the samples revealed significant differences between the wires. It was found that Ni, Cr, B, Mn, and Fe had better discrimination power for intercomparisons of aluminium wires.

The development of plasma sources for the excitation of emission spectra renewed the interest of analysts in the atomic emission spectroscopy and the Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) has been used by a number of workers for trace element determinations, and characterization of samples.

Carpenter and Till⁷⁶ used ICP-AES for quantitative determination of Zn, Pb, Ni, Mn, Fe, Sn, Cu, and Al in thirty seven samples of brass. The pattern recognition techniques of hierarchic clustering and non linear mapping were applied to the data for the classification of the brass samples. Koons et al⁷⁷ determined the barium concentration in gunshot residue (GSR) collection swabs. They have observed that ICP-AES is superior to atomic absorption spectrophotometric technique for barium determinations in GSR swab extracts. The ICP-AES technique was used for the determination of the concentration of Al, Ba, Ca, Fe, Mg, Mn, Na, Sr, and Ti in 184 colorless container and sheet glasses by Koons and co-

workers⁷⁸. They were able to classify 180 of the 184 samples using pattern recognition technique. Good discrimination among sources of glass within a class was also achieved. Hickman analyzed 1350 glass samples of various types by ICP-AES and determined the levels of Mn, Fe, Mg, Al, Sr, and Ba. The multivariant statistical techniques were used to classify the samples. Singh and co-workers⁷⁹⁻⁸⁰ have used ICP-AES for quantitative analysis of ^{the} levels of inorganic poisons in visceral tissues. The methods for the determination of copper⁷⁹ and arsenic⁸⁰ in body tissues namely stomach, liver, kidney etc. have ^{been} developed and used for the analysis of case exhibits.

An analytical procedure using Atomic-Absorption Spectroscopy (AAS) was developed by Hughes et al⁸¹ for the determination of Manganese and magnesium in glass fragments of approximately 1 mg. The levels of concentration of these elements in glass were found to be very useful for classification and discrimination. In a case, a man claimed that he had been hit over the head with a milk bottle. Pieces of glass found in his scalp were analyzed by AAS and compared with the glass from broken bottle found at the scene. The elemental analysis showed that not only did the suspect and control glass have the same magnesium and manganese concentrations but also that magnesium concentration was typical of a container glass. Koons et al⁸² have developed methods for accurate determination of antimony and lead concentrations on cotton tipped swab used for gunshot residue collection, using flameless ASS ; the ICP-AES technique was used for the determination of barium by them. A procedure of preparing spiked standard swabs, their storage and use has also been discussed. Singh et al⁸³ analyzed many samples of different types of copper wire for Sb, Cd, Mn, Ni, and Zn by ASS and concluded that Sb and Zn are more useful in discriminating the samples.

The Spark Source Mass Spectrometer (SSMS) was used for the analysis of small glass fragment encountered in forensic applications by German and Scaplehorn⁸⁴. Fifteen elements were found

to occur most frequently at levels greater than 1 ppm in the glass samples. The results proved that the technique has suitable precision to show that the concentration of trace elements varied significantly between the modern production glasses. This method was used to analyze⁸⁵ many glass samples indistinguishable on the basis of refractive index and density. The data was statistically analyzed and it was found that the method provided an increased discrimination in the glass samples. Butterworth et al⁸⁶ analyzed trace elements present in vehicle headlamp and auxiliary lamp glass using SSMS. It was observed that a pattern of trace element levels exists within the glasses of different manufacturers such that it is possible to identify their glasses, although there are sufficient differences that enable glass of similar physical properties to be separated. A comparative study of trace elements in window glasses was conducted by Haney⁸⁷ using isotope dilution SSMS. This method yields accurate, and absolute elemental concentration without the use of standards. It was found that potassium, strontium, Zirconium, and barium were distributed uniformly over the window panes. The SSMS was used for the analysis of the high purity copper wires taken from the electrical cables by Locke et al⁸⁸. The characteristic elements were in the concentration range of 0.1 to 35 ppm with Ag, Fe, Pb, and Zn being most prominent. The elements Mn, Ni, As, Sc, Sb, and Bi were also frequently detectable. The experimental and sample variation within and between various electrical conductors were studied and a good discrimination was achieved between the samples by this technique.

Caldwell⁸⁹ analyzed PVC coated copper cable in a theft case by neutron activation analysis (NAA) technique. The cable consisted of nineteen strands of copper wire twined together. Only four trace elements Ag, Au, Co, and Sb were present in both the control and the suspected stolen samples. The average of several determination of both the samples were compared. Thirty nine samples recovered from a junk dealer and twenty nine samples taken from the ends of the wires left on the poles were examined by Weaver and Bowman⁹⁰ using NAA, in a copper wire theft case. On the

basis of the results obtained, the salvage yard wires could be linked with some of the wires from the pole. Chan⁹¹ also used NAA for the analysis of copper wires. In the case of multi-stranded cable only the central strand of the cables were analyzed and compared. These studies were based on the assumption that trace element concentration was uniform along the length of the wires.

Singh and Singh⁹² made a detailed systematic study to verify the above assumption. The elements determined were Ag, Au, Se, and Sb. The variation of trace element concentrations along the length of a wire and between the wires from known different sources were studied and the usefulness of the NAA technique in the comparison of copper wires was demonstrated. They also analyzed three different nineteen-stranded cables⁹¹. Each strand of the cable was analyzed separately. It was observed that the levels of trace elements in various strands of a cable varied significantly. The average of the quantities of trace elements in all the strands of a cable was also calculated and compared. Two of the three cables were found to be indistinguishable on the basis of the above average values. Thus, neither the analysis of all the strands together nor that of only one strand, as adopted by the earlier workers, was found adequate. The analysis and comparison of all the corresponding strands was recommended for a conclusive opinion in the cases of multi-stranded cables.

Chattopadhyay and Singh⁹⁴ analyzed aluminium wires by NAA technique and determined concentration of nine elements Mn, Cu, Ga, La, Sm, Cr, Fe, Hf, and Sc. The variation within and between the aluminium wires were studied. The results revealed that these elements were uniformly distributed along the length of a long wire. The method was found quite useful for characterization of aluminium wires.

Schlesinger and Settle⁹⁵ conducted a large scale study of papers by NAA technique. Thirteen elements Ti, Al, Ca, Mn, Na, Cl, Ta, Zn, Sb, Cr, Sc, Au and La were detected in 129 samples drawn from nine manufactures and analyzed by them. The positive source

identification based on trace element profile, establishment of a common source of two or more paper samples, and allied problems have been discussed. Blanchard and Harrison⁹⁶ analyzed twelve different clays used as a pigment fillers in papers. It was observed that clays vary substantially in their trace element profile and provide a database for the identification of unknown filled papers. The nine elements chosen for the study were Al, Sc, Th, Co, Cr, Ce, Sm, Eu, and La. Successful identification of unknown clay filled sheets indicates that analysis of fine papers by NAA utilizing trace element profile and concentration ratios is a viable instrumental technique which can provide useful supportive evidence. The NAA technique was used for the analysis of glass⁹⁷ samples also. In a case of theft of silverware, minute fragments of glass recovered from the under side of the shoe of the suspect, were found to be consistent with the glass from the broken window with respect to their density and refractive index. The elemental analysis of the samples was taken up to fix the source correspondence and levels of some eighteen elements were determined and compared on the basis of which it was concluded that glass from the shoe and the control sample came from the same batch of manufactured glass.

Krishnan⁹⁸ has described in detail the methods of collecting GSR from hands of a suspect and has used NAA for the detection of Sb and Ba and AAS for lead. A very interesting case involving gunshot wounds in which the firing distance and firing angle were determined using NAA technique has been described by Capannesi et al.⁹⁹. The Sb pattern around the bullet entrance hole on the garment of the victim was determined to evaluate the distance and the angle of firing. Hair is one of the most extensively studied material by NAA technique and the results have been presented in the proceedings of many conferences, and publications in scientific journals¹⁰⁰⁻¹⁰³. Even the hair from the head of Napoleon was subjected to activation analysis for the determination of arsenic. Once it was thought that NAA techniques could provide such data on hair that it would be possible to individualize persons on its basis. However, amongst other problems of trace analysis, the natural products have their own limitations.

The X-rays methods of elemental analysis have also been used extensively for identification and characterization of forensic samples. Thirty single layered household paints sample, ten from each of the three colours red, green, and white were analyzed by Howden et al¹⁰⁴ using Energy Dispersive X-ray (EDX) Fluorescence Spectrometry. The reproducibility of X-ray fluorescence spectra was investigated. In cases where the spectra was qualitatively similar the spectra were further examined by determining the elemental peak area ratios. Discrimination of all the paints within the red and green color groups was achieved. The white paint flakes were discriminated into nine groups. The EDX spectrometry was used to analyzed 1974 automotive paints also, and its ability to discriminate among similarly colored samples was demonstrated¹⁰⁵. Reeve et al¹⁰⁶ analyzed 81 glass samples using EDX for the elements Ca, Mn, Fe, Cu, Zn, As, Rb, Sr, and Zr. The net counts of the elements were ratioed to the Ca net count in each sample. The consistency of the elemental composition across a pane of window glass was demonstrated. The EDX was used for the examination of glass samples by Andrasko and Maehly¹⁰⁷ also. Harada¹⁰⁸ analyzed nine types of black inks using X-ray micro analysis technique and demonstrated that all the inks could be identified on the basis of traces of characteristics metallic elements. It is expected that this method should give good results in the case of computer ribbon ink also. Polk et al¹⁰⁹ applied the technique of micro probe analysis to the characterization of plain paper, and Totty et al¹¹⁰ analyzed coated papers used in photocopying processes. Their work demonstrated the usefulness of the method in the examination of papers. Cain et al¹¹¹ studied major mineral constituents Fe, Ti, Al, Ca, K, Si, Mg, and P of pencil lead using wave length dispersive X-ray fluorescence spectrometric technique. Comparisons of selective elemental ratio of various clay material permit identification among the different lead products.

Winstanley¹¹¹ used simulated stomach contents matrix to determine the lower level detection for the sixteen metals using EDX technique. All of the metals could be detected at the levels which

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might be expected for the acute fatal doses. However, where small doses are administered over a prolonged period this method may not be sufficiently sensitive. The above method was applied to a case of fatal poisoning by the ingestion of mercuric chloride. In this case mercury was also detected and determined at highly significant level in blood and liver as well. Colored and opaque polyethylene bags can not be examined and compared by infrared spectroscopy owing to their strong pigment absorption superimposed on the polyethylene spectrum. Colored polyethylene bags are manufactured by blending small quantity of pigments with polyethylene. Nir-EI¹¹³ studied elemental profile of colored polyethylene bags using X-ray fluorescence spectroscopy. Homogeneity in single bags and reproducibility of bags in a batch were ascertained.

Scanning electron microscopy combined with Energy dispersive X-ray analysis (SEM-EDX) has been used very extensively as a technique for elemental analysis of a variety of forensic samples including gun shot residues (GSR)¹¹⁴⁻¹¹⁷. When a fire arm is discharged, very small (micron sized) particles of the various components of ammunition are formed under high temperature and pressure. These particles deposit on the shooters hand and other surfaces in the immediate vicinity. Basu¹¹⁸ has studied the GSR formation in detail. These particles have a characteristic structure and are formed by rapid cooling from ~~are~~ extreme temperature and high pressure. The primer vapor constituents lead, antimony, and barium may condense uniformly and concurrently or irregularly and discontinuously or as a layer of lead around a nucleus of barium and antimony.

SEM-EDX technique has been used by many workers for the identification of the bullet holes and shooters¹¹⁹⁻¹²¹. Booker et al¹¹⁴ analyzed a set of priming mixtures and found that they have widely varying barium and antimony compositions. Therefore, one should be very cautious using predetermined threshold levels of barium and antimony to identify the presence of GSR. The main disadvantage to GSR analysis utilizing SEM-EDX technique is the exces-

sive operator time required for the search and identification. In view of this automated particle recognition and characterization programs¹¹⁵⁻¹¹⁷ for unattended GSR search and identification have been developed. The system allow for automatic matrix search, particle sizing, chemical typing and spectral acquisition with subsequent storage of data to disk for later review and verification. Varetto¹²² has suggested an effective method of removing organic materials from adhesive tapes, employed for collecting particles on the hands, using plasma ashing. The method ~~of~~ does not alter the morphology or composition of GSR.

The particles of foreign material embedded in or adherent to bullets provide critical information in the reconstruction of a crime scene. Di. Mio et al¹²³ have used SEM-EDX technique in two cases to identify mineral fragments and bone fragments, respectively and have demonstrated the usefulness of the technique. The proton induced X-ray emission (PIXE) analysis was used by Fischbeck¹²⁴ to verify the presence of lead in the finger bone of a murder victim. The bone was scanned with a 1.5 MeV proton beam, PIXE analysis showed that lead was present only in the vicinity of the fragment previously detected in the radiographs. The ease of sample preparation and the capability to analyze large objects nondestructively make PIXE an attractive alternative to other trace element analysis methods, if an accelerator facility is available. Hellmiss et al¹²⁵ has used Augar Electron Spectroscopy for the analysis of GSR particles. It is a surface sensitive technique and offers the feasibility of detecting many other useful elements than Sb, Ba and Pb in GSR.

Ultraviolet, Visible and Infrared Spectroscopy

Absorption spectrometry covers a group of methods which are very useful for the identification and determination of a wide variety of compounds. This technique is indispensable to any adequately equipped forensic science laboratory. These methods investigate the properties of substances to absorb ultraviolet, visible, and infrared radiations.

The ultra violet-visible spectrophotometry is used routinely in the forensic science laboratories for classification and provisional identification of various chemical compounds. There are many substances which show a change in the ultra violet absorption curve with change in pH and provide another parameter for their identification and comparison. The availability of uv-vis spectrophotometer with derivative accessory and microprocessor has made this technique more useful and it can be used for identification and differentiation of compound with very similar uv-vis spectra. The conversion of first order spectrum into a derivative spectrum has the effect of transforming shoulders and inflections points into new peaks, which provide more points of comparison*for visual comparison of a known sample with that of questioned sample.

The absorption spectra in the infrared are much more characteristic than uv-vis ones. Identification of very small amounts of organic compounds can be achieved by infrared absorption spectroscopy. A infrared spectrum may be divided into two parts ; the region of group frequency from 4000 cm^{-1} to 1350 cm^{-1} , and the fingerprint region from 1350 cm^{-1} to 650 cm^{-1} . In the region of group frequencies many spectra have some strong bands only, which correspond to stretching vibration of definite bonds. The frequency is quite independent of the effect of other parts of the molecules. In the fingerprint region, however, there are additional absorption bands due to molecule as a whole. An infrared spectrum rich in detail embodies so many structure parameters that two spectra identical in all features can have been obtained only for the same compound.

Microspectrophotometers were developed for recording absorption / reflectance spectra of micron sized samples and are quite useful. An objective study of the spectra over the entire useful spectral regions can be done for microscopic samples.

The dispersive infrared photometers are relatively slow and less sensitive, also the transmission method of recording IR absorption spectra is not suitable for the recording of infrared spectra of many substances. With the development of interferometric

(Fourier Transform) infrared spectrophotometers, the above limitations of the conventional infrared spectroscopy could be overcome to a very great extent. This technique has greater energy throughput, higher resolution, and better wave length calibration, higher signal to noise ratio as compared with the conventional technique. Hundreds of scans can be run and added together in just a few minutes. In forensic context, the increase in sensitivity made possible by interferometric technique lead to newer applications like recording of reflectance spectra, development of quantitation methods, and use of microspectrophotometers etc.

Microspectrophotometry has been used for identification and characterization of various types of samples¹²⁶⁻¹²⁸ like paints, fibers, rodenticides etc. A rapid method for preparing and mounting paint fragments for visible microspectrophotometry and FTIR microscopy was developed by Wilkinson et al¹²⁶. In both the cases spectra are obtained in transmission from the paint sections. Infrared spectra can be produced from the nanogram sized samples by this method. It was observed that the transmission measurement can provide more discrimination than those in reflectance. The use of ultraviolet, visible, and infrared spectroscopy for the examination of the base and dye composition of plastics of side light units of vehicles was explored by Krikwood and Isaacs¹²⁹. These methods have limited use in discriminating side light plastic fragments. Zeichner and Glattstein¹³⁰ studied visible transmitted spectra of inks and observed that transmission spectra of small samples of inked paper fibers smeared (crushed) on glass slides resemble spectra of smeared ink deposits and are more reproducible than spectra of inked fibers in mounting media.

A large numbers of fiber samples using microscopy and microspectrophotometry etc for dye batch variation were examined by Wiggins et al¹³¹. Degrees of variations were found. The results and their implications for the court going officers have also been discussed. It was demonstrated by Grieve¹³² that infrared spectrometry and microspectrophotometry of cosmetic and decorative

glitter particles are quite useful in their characterization. The necessary sample preparation for the infrared spectroscopy has also been discussed in detail. A method has been developed by Cousins et al.¹³³ for the prediction of pesticide type from the small samples found in case work, using a microspectrophotometer to obtain reflectance spectra of the dyes or pigments used in these products. These spectra are then compared with those obtained from known samples.

The infrared spectra of toners (ink) used in plain paper photocopying machine may be studied using small samples removed from the paper surface. Kemp and Totty¹³⁴ recorded and compared absorption bands of the toners from different sources. The method could discriminate between different sources of toners only with moderate success. Williams¹³⁵ analyzed the infrared group frequency in the spectra of toners to identify and characterize the major chemical compositions of toners. Smalldon¹³⁶ studied pyrolysis products of resinous material using infrared spectroscopy. The usefulness of the method in forensic examination was demonstrated with case examples. In a hit and run case¹³⁷ a piece of an automobile rubber bumper guard was found at the scene of crime. It was compared with the sample obtained from the front bumper guard from the suspected vehicle. The samples were examined by attenuated total reflectance spectroscopy using FTIR. The two samples had identical spectra indicating common source of their origin. Cleverly¹³⁸ studied the infrared spectra of low density polyethylene plastic bags. All the polyethylene have similar absorption bands between 4000 to 1800 cm^{-1} . Which are mostly due to C-H stretching modes and the remaining bands are over tones and combinations. The minor levels in the spectra of low density polyethylene in the region 1600-400 cm^{-1} show significant difference and are useful for their characterization. The frequencies, shapes, and relative intensities of infrared absorption bands are compared for matching and identification.

Zieba¹³⁹ studied the infrared spectra of oil samples extracted from textile and characterized them by the absorbance ratio of some

bands. The method enables the objective evaluation of the statistical significance of differences between the spectra. The rate of oil degradation in cars during their use was also studied by him¹⁴⁰ using IR spectroscopy. Significant changes in the intensity of some absorption bands were observed. These changes are due to the oxidation and degradation products of the oil components. A comparison of the absorbance of these bands make it possible to differentiate oil samples of different degrees of decompositions.

The Fourier transform infrared spectrophotometric (FTIR) analysis of five monomethylated fentanyl compounds, widely abused designer drugs, in vapor phase was done by Suzuki¹⁴¹. He found that infrared spectra alone was not enough for discrimination for isomers. However, the structural configuration of illicit street drugs are determined by FTIR, in general. Wielbo and Tebbett¹⁴² have used this technique for the determination of interference by common diluent and adulterants of these drugs and have shown that little or no interference is contributed by these excipient substances at greater than 20% drug concentration.

With the availability of rapid scanning FTIR spectrophotometer, it could be possible to perform routine diffuse reflectance measurements in the infrared region. Suzuki and co-workers¹⁴³⁻¹⁴⁷ have used diffused reflectance FTIR spectroscopy for the characterization of a variety of samples of forensic interest. This technique is very sensitive and require a minimal sample preparation. It has been used for analysis of various types of tablets, capsule contents, other powders, polymer foams, and metallic paints etc. Brenner¹⁴⁸ et al used the FTIR spectroscopy for differentiating between treated and untreated human hair. The treatments of an oxidative nature for example dyeing or coloring, bleaching, ⁿ ₂ titing permanent waving etc were considered. The presence of the 1044 cm^{-1} sulphonic acid absorption peak was shown to be a result of the oxidation of sulfur bonds in human hair. It was suggested that this peak may be used to differentiate between treated and untreated hair samples. Normal hair color, moisture and age of hair sample were found to have little or no effect.

X-Ray Diffraction

In many cases of identification and comparison of samples of forensic interest, the knowledge of the crystal structure and the nature of molecule is of critical importance. In such cases the X-ray diffraction technique provides a valuable supplement to spectrochemical methods of analysis. The X-ray diffraction techniques are very useful in the identification as well as comparison of forensic samples. As this method can be used only for crystalline materials, the non-crystalline impurities do not interfere with the identification. The method is non destructive allowing samples to be reexamined if the need arises, and has a wide range of applications. The XRD method is used for the identification of minerals, corrosion products, fillers in plastics and papers, clay fractions of soil, mortar, brick, dust, paint pigments, drugs and narcotics etc. The synthetic textile fibers also give characteristic diffraction patterns when slightly tensioned to orient their molecules. There are certain substances which exist in forms differing only in the atomic lattice, these can be identified only by XRD. For example, rutile and anatase are two forms of titanium dioxide, which is used as pigment in make-up creams, and paints. Recent advancements in computerization have made diffraction a more attractive technique because of the enhanced probability of identification of multi component mixtures. It may be advantageous to compile data file of forensically relevant substances for selective searches¹⁴⁹.

Canfield and De Forest¹⁵⁰ have described a method for analyzing and identifying a single crystal of explosive as small as 30 μm in diameter of an explosive residue. The method uses the Gandolfi X-ray diffraction camera to produce a detailed X-ray diffraction pattern of the small crystal which is directly comparable with the data obtained by the powder diffraction method. Samples of known explosive compounds and formulations were run on both the Debye-Scherrer and Gandolfi X-ray diffraction cameras. The information derived from a given explosive substance was essentially the same for either method, although the sample size necessary for the

Gandolfi camera is as much as three orders of magnitude smaller. The role of this technique in an over all scheme for explosive residue analysis has also been discussed. Tassa et al¹⁵¹ have used X-ray diffraction complemented by scanning electron microscopy and energy dispersive X-ray analysis for characterization of gunshot residues. The results have been used to elucidate the GSR forming process.

The identification and characterization of papers is often required in the forensic examination of questioned documents. Many methods depending upon physical properties and chemical composition of paper have been suggested as characterizing parameter, most of which are non specific or destructive or both. Foner and Adan¹⁵² investigated the X-ray diffraction technique for characterizing paper samples. The crystallinity of the cellulose constituent of paper is a function of raw material used and manufacturing processes. Hence to explore the utility of this parameter, the crystallinity index and crystallinity ratio for a variety of paper samples were studied and it was demonstrated that different papers have varying crystallinities and one can distinguish a high quality paper from a medium quality or a poor quality one. They also examined the mineralogy of the inorganic component of papers and have shown that very useful and informative data can be obtained by X-ray diffraction analysis of the minerals used in the manufacture of paper. This technique can be applied to the routine testing of stamps, currency notes, and security documents etc.

Diffraction data on some seventy one pigment have been obtained by Debye-Scherrer powder photography¹⁵³. The d-spacings of the three most intense diffraction lines of each pigments are listed in a form to allow identification using the Hanawalt search-and-match technique. The diffraction data acquired for pure pigments can be used to identify pigment in paints, if their concentration in the paint is sufficient for detection by XRD.

Lynch and Kerrigan¹⁵⁴ reported use of X-ray diffraction analysis in the identification of single fiber sample. In cases where the

fiber is small and the confirmation is required or when the microscopic features are obscured by wear or the presence of dyes, XRD analysis can be most helpful. The use of X-ray diffraction analysis in routine investigation into the illicit drugs have been demonstrated by Folen¹⁵⁵, and Barrick et al¹⁵⁶. The most useful aspect of XRD in drug area is the identification of the diluent used for providing bulks. Rendel and Connett¹⁵⁷ have detected the presence of glucose monohydrate / sodium chloride complex in a powdered mixture containing diacetylmorphine hydrochloride etc by XRD. In a case, two samples of mica were compared using XRD to determine their source correspondence by Sehgal and Garg¹⁵⁸.

Marumo et al¹⁵⁹ have used XRD technique, *inter alia*, other analytical methods for clay-mineralogical analysis of soil for estimation of sites. It has been suggested by Hashimoto et al¹⁶⁰ that X-ray diffraction line profile may also be studied to determine microcrystalline structure for the discrimination of ceramics. Adulteration in cement is not very uncommon, sometimes two or more adulterant are blended in such a way that values of the basic constituents remain within limit prescribed in the specifications and therefore the analysis of these constituents by conventional chemical methods may not always be of much help. In such cases the X-ray diffraction method is used to identify the adulterant. In one of such cases¹⁶¹ XRD analysis revealed presence of α -quartz, hematite, Ca(OH)_2 and CaCO_3 , confirming the presence of fuel ash and lime as adulterant. In a case of hit and run accident¹⁶² the grease deposits on the dead body were compared with the grease taken from the rear axle area of the suspected vehicle. These were found to be similar on the basis of spectroscopic and other examinations, but their source correspondence could not be ascertained. The hydrocarbons were extracted from the grease samples and the resultant insoluble fractions were examined using X-ray powder diffraction techniques. These fractions were, in fact, a composite sample of all the different soil samples which have adhered to the grease over a long period of time and thus formed a soil of unique composition. The components identified included quartz, feldspars, chlorite, mica,

goethite, haemaetite etc. All the components were found in relatively similar proportions. This could provide most significant evidence to link the particular vehicle with the crime.

With all the above positive factors it is indeed strange that XRD is not yet popular technique in forensic science laboratories in the country. In fact there is a dearth of equipments and trained manpower in this field in these laboratories. I hope this will attract the attention of the physics community here and we can expect collaborative work in this field and generate local database on different kinds of samples of forensic interest.

Photo Acoustic Spectroscopy, Electron Spin Resonance Etc.

Photo acoustic spectroscopy is a nondestructive technique suitable for small sized samples. It is also advantageous that no sample preparation is required and samples in the form of powders, gels, liquids, fibrous material etc can be studied. If electromagnetic radiations in ultraviolet, visible or infrared region is absorbed by the sample, provided the sample does not fluoresce or degrade photochemically, it reappears as heat at the surface of the sample and can cause a periodic pressure wave in the gas in a closed cell containing the sample. Singh et al ¹⁶³ employed the near infrared photoacoustic spectroscopy for the examination of the natural and synthetic fiber and have demonstrated the usefulness of this technique. It can be used for a wide variety of samples like paint, ink, fibers, fabrics, powders etc.

There are many difficult but very important problems in crime investigation which defy accurate determination. For example, if the time lapse after bleeding could be estimated from the dried blood stains, it would be of great help in many cases to fix the time of the commission of crime. It has been shown ¹⁶⁴ that the intensity of electron spin resonance signals of methemoglobins, non heme ions and organic radicals in dried human blood increases with the time. Thus, electron spin resonance studies of dried blood stains can provide an estimate of time lapse after bleeding.

The thermoluminescence methods can also be used for the comparison of forensic samples¹⁶⁵. If a material is exposed to natural or laboratory ionizing radiation at or below the temperature at which heating is started, the radiant energy displaces some electrons in the solid which are trapped in imperfections and vacancies in the crystal lattice. These trapped electrons escape with the emission of light when the temperature is raised to supply the kinetic energy required to get them out of the traps. The color or wave length distribution of the light may vary over the entire visible spectrum and appears at different temperatures depending on the basic crystal structure, presence of impurities or trace components, and the radiation, thermal and pressure histories of the materials. This can be very useful as discriminating method for differentiating between the samples of several types of material including glass, soils, safe insulation, salts, and other non-metallic solids.

Raman spectroscopy is complementary technique to infrared spectroscopy and has been used, though sparingly in forensic studies. The Fourier transform Raman technique is very powerful for detecting small differences in chemical structure, orientation and conformational isomerism and even the residual internal stresses of solid materials. The high reproducibility and wave number accuracy inherent in the fourier transform methodology make the detection of these differences with reliability a routine practice. This technique can be advantageously employed¹⁶⁶ for the examination of gemstones, antique inorganic paints, automotive paint coatings, papers, polymer lens materials etc.

It was my intention to focus attention of a large number of physicists to the possible applications of physics to detection, investigation, and solution of crime so that forensic scientists and law enforcement agencies may share the knowledge, facilities, and expertise available in the country. I hope my presentation was commensurate with my intentions.

I thank you again for the honor and for the patience you have shown in listening to me today.

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