NUCLEAR ANALYTICAL TECHNIQUES:
AN AID TO CRIME INVESTIGATION

M. Sudersanan
Head, Analytical Chemistry Division

T. Mukherjee
Associate Director, Chemistry Group

N. Chattopadhyay and A. K. Basu
NAA Unit of CFSL (Hyderabad) at ACD, BARC

C.N. Bhattacharyya
Director, CFSL, Hyderabad

and

M.S. Rao
Director-cum-Chief Forensic Scientist, Directorate of Forensic Science, Ministry of Home Affairs, New Delhi

Introduction

Forensic science is oriented towards the examination of specimens, collected from a scene of crime in order to establish the link between a criminal and a crime.

Analytical Chemistry provides a scientific basis to aid crime investigation. This is on account of the availability of a number of sensitive and selective analytical techniques capable of analysing wide varieties of evidentiary materials like complex synthetic or natural organic products. The power of analytical techniques has also been enhanced substantially by a judicious hyphenation of techniques to accomplish sufficient sensitivity and selectivity to deal with minute evident specimens. One example is the use of HPLC for selective separation, followed by AAS or ICPAES for the final determination. This procedure has the advantage of combining the advantages of both the techniques and at the same time removing some sources of interference. Forensic scientists have been one of the major beneficiaries of recent advances and rapid strides in analytical instrumentation. Use of nuclear analytical techniques in the form of neutron activation analysis (NAA) has greatly benefited forensic science. This technique is particularly useful in cases where the low level of elements have to be determined accurately. Realising the importance of nuclear techniques for forensic applications, a collaborative programme was started over thirty years ago between BARC (DAE) and Ministry of Home Affairs, Government of India. As a part of this programme, a small group of Central Forensic Science Laboratory started functioning at Analytical Chemistry Division so that both the infrastructural facilities as well as scientific guidance on nuclear techniques was readily available. This interaction has grown over the years into a healthy collaborative programme between Analytical Chemistry Division, BARC and CFSL, Hyderabad. The close interaction has led to the effective investigation of various problems of forensic interest by using both nuclear and non-nuclear techniques using judicious combination of analytical tools. The interaction has also resulted in the formulation of joint collaborative proposals for the solution of burdening forensic problems of national importance.

Activation analysis consists of irradiation of a test sample material by an intense beam of neutrons from a nuclear research reactor. The nuclear reactors APSARA, CIRUS and DHRUVA at BARC can provide a neutron flux in the range of
$10^{12}$ to $10^{14}$ neutrons per cm$^2$ per second depending on the type of reactor. The induced radioactivity produced is measured by using suitable detectors for beta or gamma radiation. The measurement of gamma radiation is conveniently carried out by using multichannel analysers. NaI(Tl) or HPGe detectors are employed for the determination of energy and number of gamma rays, which characterise the elements with respect to their identity and concentration. This is possible because each of the gamma rays emitted is characteristic of the daughter isotope, which in turn is characteristic of the parent nuclide. The elemental composition and concentrations are computed from such measurements. The high sensitivity, permitting analysis of very small samples, versatility in providing simultaneous multielement analysis and freedom from reagent blank are the positive points of this analytical technique. The freedom from blank is a major advantage compared to other trace analytical methods where the sample blank controls the detection limit. Moreover, since in the case of instrumental neutron activation analysis, no chemical processing is needed either before or after irradiation of the sample, the chances of contamination and blank are less. Moreover, as the sample is not destroyed except for the production of induced radioactivity, the method can be considered to be a non-destructive method. This feature makes INAA a valuable technique for forensic investigation.

**Role of Analytical Techniques for Forensic Applications**

Analytical techniques covering both nuclear and non-nuclear methods have a very extensive application in forensic science. Forensic case exhibit samples are of varied nature covering both materials of biological and non-biological origin. Since some of the techniques are applicable only for organic or inorganic materials, the selection of a proper analytical technique is essential for successful analysis. Moreover, there may be effects due to matrix elements in some of the techniques. The use of appropriate method along with selective separation processes provides the best option for many challenging analytical tasks. The proper choice of sample treatment and analysis techniques helps in the generation of reliable analytical data for proper interpretation of results, which is an essential part in reconstructing the scene of crime. The major areas where Analytical Chemistry Division is actively interacting with NAA unit of CFSL pertains to forensic ballistics involving investigation of shoot outs. The use of NAA and other complementary techniques help in answering certain questions like the identification of the firearms, the range of firing, an opinion about entry and exit hole, etc. Quantitative determination of a known group of specific elements is of paramount importance in many forensic investigations. Gunshot Residues (GSR) / Firearm Discharge Residues (FDR) and matching of bullet specimens are examples where the use of nuclear and allied analytical techniques are extremely useful. A forensic scientist comes across problems where he has helped in ascertaining whether a suspect has fired / handled a firearm. Gases and discharge residues consisting of sub-microscopic particles originating from primer, propellant and projectile leave the muzzle during a shoot out incident. The space between the front of the cylinder and rear end of the barrels in a revolver allows firearm discharge residues (FDR) to escape out as leakage residues to be deposited on the hands of a shooter. In addition, due to any defect in manufacture of weapons, residue can be expected to be deposited in different parts of body of a shooter. Analysis of such residues helps in providing a clear answer to various forensic questions.

Thus, there is a scope for detection, identification and characterization of FDR particles with an ultimate aim to identify shooter by applying a suitable analytical method. The analytical method chosen should be capable of providing elemental abundance information with
respect to elements like Pb, Sb, Sn, Cu, Ba, Hg, Zn and Zr (rarely) originating from primer, propellant and projectiles. It is imperative that method of detection and quantification should be not only specific and selective but sensitive, reliable and accurate. In view of a small quantity of sample available, techniques with simultaneous multielemental capability of determination is desirable. This is because the amount of sample available is often very less and sometimes may be contaminated with extraneous materials like cloth, parts of skin, etc. The use of neutron activation analysis satisfies many of these requirements and has been employed extensively. However, since some elements like lead, zinc and nickel are more sensitive by other techniques like AAS or ICPAES, they are employed for the purpose. The use of ICPAES has the advantage that the sample consumption is less as this technique has almost simultaneous multielement capacity and a large linear dynamic range so that the calibration curve is linear over a wide concentration range. This helps in avoiding dilution of the sample as in the case of AAS. The use of ICPMS is also advantageous for this reason. Additionally, information on various elements including their isotopic composition can be obtained by this technique. It is needless to stress that this provides additional clues in source correspondence. The availability of nuclear and non-nuclear analytical techniques at Analytical Chemistry Division is a boon to forensic analytical scientists.

Analytical chemistry plays a vital role in establishing the source correspondence to decide on commonness or origin via recourse to suitable standard procedures, which can provide validated multielement data. An example is the use of analytical techniques to characterise acetic anhydride, which is sometimes employed for the illegal manufacture of heroin. The use of titration procedure for bulk characterization of the acetic anhydride or the use of HPLC / GC for organic elemental content alone may not help unless techniques for trace element determination of metals are also employed. The trace element profile can show some variation depending on the nature of catalyst employed, the containers used or the effect of the environment. Analysis of acetic anhydride by NAA and techniques like AAS provide some valuable information in differentiating various makes of acetic anhydride from different manufacturers. This type of analysis will definitely be facilitated by the use of techniques like ICPMS, NAA and GC / MS or LC / MS. Another area where NAA unit of CFSL at ACD has contributed is in the area of characterization of opium for source correspondence. The use of NAA brought out some characteristic feature, which could not be obtained by HPLC analysis alone. Moreover, the use of appropriate techniques like pattern recognition is also valuable in this respect. The use of modern sensitive analytical techniques has an edge over other techniques, as conventional analytical methods may not provide the desired sensitivity and resolution.

The four thrust areas of application of NAA and allied methods to analytical techniques in forensic science are categorised with objective necessities in Table 1.

Apart from this, analysis also provides solutions in situations like (a) customs related typical white-collar crimes, (b) suspected electrocution cases, (c) establishing authenticity of documents / antiques, (d) relative age of ink, and (e) signature analysis of C, N, O for explosive detection, etc.

Analysis of hair also has acquired significance as potential evidence specimen. A large number of elements are found in human hairs and a majority of them arise due to an accumulation of products of sweat. Some elements like Na, P, K, S, As, Cd, Hg or Pb are important in hair analysis. In some cases, correlations have been obtained in the trace element profile. For
example, copper is low in gray hairs of an old man but is high in black hair. Zinc is low in dwarf and blond hair and in the hair of pregnant woman but is high in ill-nourished children. Such correlations are also of significance in forensic investigations. NAA was used at ACD for this purpose. However, one should exercise adequate care in the sample preparation as the hair may contain extraneous materials like traces of selenium from a shampoo or mercury from a medicated soap. The optimised IAEA washing procedure is adopted to avoid the loss of metal ions. The use of this analysis has advantage in distinguishing cases of chronic and acute poisoning.

**Development (Methodologies)**

A selected list of development procedures (methodologies) towards successful utilisation of the technique or combination approach as per demand is depicted in Table 2.
Table 2: Trace element patterns in the form of parameters (information) established and utilised for different types of forensic exhibit samples

<table>
<thead>
<tr>
<th>Type of exhibit</th>
<th>Trace elements</th>
<th>Method(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wearing apparels, wood, plastic, card-board, paper, skin, glass, leather, metal piece, etc.</td>
<td>Ba, Cu, Sb (Hg), Pb, Ni, Zn, and (Sn)</td>
<td>RNAA / DPASV / AAS or ICPAES RNAA with β measurements for Sn</td>
</tr>
<tr>
<td>Transmission copper wire.</td>
<td>Ag, Au, Sb and Se (Discriminating)</td>
<td>INAA after long irradiation in CIRUS / DHRUVA reactors</td>
</tr>
<tr>
<td>Transmission aluminium wire</td>
<td>Mn, Cr, Hf, Sc and Fe (Discriminating)</td>
<td>INAA in 2 batches of irradiation, i.e., short (APSARA) for Mn and long (CIRUS / DHRUVA) for Cr, Hf, Sc and Fe</td>
</tr>
<tr>
<td>Glass</td>
<td>Eu, Ce, Co, Fe, Th, Sb and Se</td>
<td>INAA</td>
</tr>
<tr>
<td>Cannabis</td>
<td>Mn, Cu, K, Cl, Br, Fe, Sc, Hf and Zn</td>
<td>INAA (combination of short and intermediate duration of irradiations)</td>
</tr>
<tr>
<td>Animal Hair</td>
<td>Mn, Cl, Na, K, Cu, Br, Au and Zn</td>
<td>INAA (combination of short and intermediate duration of irradiations)</td>
</tr>
<tr>
<td>Ornamental Gold</td>
<td>Ag, Cu, Zn, As, Pb, Cd ad Bi</td>
<td>CNAA / DPASV / DPP</td>
</tr>
<tr>
<td>Water</td>
<td>As with relative ratio of As (III) and As (V)</td>
<td>Ion exchange method of differential separation or treatment with ferrous Sulphide, followed by NAA by precipitating ‘As’ as Sulphide in the presence of mgs of inactive carrier.</td>
</tr>
</tbody>
</table>

Perspective

One of the important aspects in forensic analysis is in maintaining the integrity of the sample and avoiding all sources of uncertainties. This makes it essential to control the blank. The use of clean room facilities is important in this respect since the laboratory air or atmosphere as well as the chemicals used contribute substantially to the blank. Another area, which requires attention, is in the evaluation of uncertainties in analytical data. This is generally carried out by multiple analysis of the same sample but is not possible due to the limited availability of the sample. It is, therefore, essential to evaluate the uncertainties through statistical techniques. Increasing application of computer - based data evaluation can certainly help in this respect.

In conclusion, it can be said that a synergistic combination of sensitive methods like AAS, ICPAES, ICPMS, Glow discharge mass spectrometry, GCMS, LCMS, NAA, electroanalytical methods and other sophisticated analytical techniques alongwith separation methods like ion exchange, solvent extraction and chromatographic techniques can lead to specific and sensitive procedures as the aid towards establishing the truth in the criminal justice system. Proper appreciation of the need for validation of the analytical methodology is no doubt important to generate data of known quality. This is very crucial in the final interpretation of the data to arrive at definitive inferences to convict the real guilty and more importantly in the acquittal of the innocent. Thus, analytical techniques do play a pivotal role in the criminal justice delivery system, which has a true social impact.