

CHAPTER II

METHODS OF TRACE ANALYSIS.

2.1. PRINCIPLES AND METHODS OF TRACE ANALYSIS:

There are quite a number of techniques used to determine small quantities of materials present in plants with sufficient accuracy. Methods used for determination of macro-elements may not be sensitive enough for trace element determination. Trace elements in plants are usually determined in the plant ash, which is prepared generally by drying the materials at first and then incinerating the dried material at a high (about 450°C to 600°C) temperature in a furnace. In the process, Nitrogen, sulphur and similar substances largely or wholly pass off in gaseous form from the incinerator. In general, the quantities of trace elements present are so small that the ordinary methods of quantitative chemical analysis are quite useless for the purpose. The various methods employed for trace element analysis are briefly given below. 1-3

1. Spectrophotometry:

The absorption and subsequent re-emission of radiant energy in various regions of the electromagnetic spectrum forms the basis of the method of trace analysis called 'Absorptiometry'. When a beam of light is passed through a

transparent container filled with a liquid, the resultant loss of radiation is primarily accounted for the absorption of radiant energy by the liquid. The absorbed energy raises electrons of the molecules from their ground state to higher electronic states; the difference in intensity of the incident and the transmitted radiations is a measure of the concentration of the solution in the light path.

In Spectrophotometry, which is a branch of this method of analysis, a coherent monochromatic beam of light is passed through the absorbing medium. The radiant power of the beam will diminish in proportion to the number of absorbing molecules or ions in its path. Depending on the wave-lengths involved, the method is referred to as visible, ultra violet or infrared spectrophotometry.

2. Fluorimetry(Fluorometry):

When some substances in solution are irradiated by ultra-violet light, fluorescence is produced, i.e. a radiation which has wave-lengths characteristic of the light-absorbing molecules, is emitted, in addition to those of the incident beam. The process of observation and measurement of the fluorescence is known as Fluorimetry or Fluorometry. The fluorescence depends on the chemical properties of particular molecules and can be used to detect and measure quantitatively specific solutes in filtered homogeneous solutions. The sensitivity of this method is 10^2 to 10^4 times greater than

comparable absorptiometric methods.

3. Atomic absorption spectroscopy:

This method involves the study of the absorption spectrum produced by the radiations from an electric lamp, when a volatilized specimen is placed in its path. Vaporisation of the samples (atomization) can be done by using a flame (Flame atomic absorption spectrometry) or by electrical heating devices (Non-flame atomic absorption spectroscopy). The latter one is used in trace analysis.

4. Emission spectroscopy:

Many elements under suitable excitation condition emit radiations of characteristic wavelengths. This method involves the study of these spectral lines, the wavelengths and intensities of which provide a means for identifying and measuring the quantity of an element.

(a) Flame photometry: Here, the excitation is caused by injecting the sample into a flame either by the fuel or oxidant. The resulting flame concentrates the source of emitted radiation to a small space. The power of radiation from the flame at a wavelength characteristic of a particular element is very closely proportional to its concentration. Background luminosity interferes in this method and has to be corrected.

(b) Inductively coupled plasma sources have replaced the flame in recent techniques. The excitation can be done by radio-frequency induction or by a dc discharge. The plasma that

results is very energetic, capable of dissociating and activating a large number of elements, not accessible to gas flames. The dissolved sample is aspirated into the plasma. This method shows relative freedom from chemical interference.

5. X-ray fluorescence spectrometry:

In this method, a sample is irradiated by a powerful beam of x-rays, which can replace an electron from the innermost electronic shell of an atom and the lost electron is replaced by another electron from one of the outer shells, releasing energy in the form of characteristic X-rays. The wave-length of the resultant secondary or fluorescent x-rays is characteristic of the atom involved and the radiant power of the same can be used to assess the amount of the element giving rise to it, present in the sample. This technique is very useful for simultaneous multielemental analysis of environmental, biological, geological, agricultural and metallurgical samples, and can detect all the elements above $Z = 16$.⁴

6. Proton induced x-ray spectroscopy and Auger electron spectroscopy:

Bombardment of a substance by energetic particles like proton or radiations results in ejection of electrons from target atoms, leaving vacancies, followed by relaxation i.e. return to the normal configuration.

When a core electron is ejected, an electron from a higher energy level will drop into the vacancy. The excess

energy will be released either by emission of secondary (fluorescent) x-ray or by the ejection of another electron from one of the upper or intermediate levels, with whatever kinetic energy is available from the orbital transition. The later, dealing with electron emission, is known as Auger electron spectroscopy.

7. Electron microscope analysis:

A finely focussed electron beam is utilized to excite x-rays in a solid sample as small as 10^{-18} m^3 . The radiation produced in the sample is analysed in an x-ray spectrometer.

8. Polarography:

Here, a solution of an electrolyte in much higher concentration (supporting electrolyte) is subjected to a steadily increasing difference of potential between two electrodes. Then, under certain conditions, a current flows through the solution. From an examination of the curves showing the magnitude of the voltage on the electrode of interest, informations as to the nature and concentration of the material may be obtained.

Out of several modifications, the pulse polarography is recommended for trace analysis. Here the voltage is applied as a series of brief pulses of regularly increasing amplitude.

9. Anodic-stripping voltametry:

Here, a mixed deposit of metals by anodic voltametry is performed. A portion of the solution is electrolysed for 15 to 30 min. with a small mercury cathode at a sufficiently negative

potential. The mercury electrode is then made the anode, stripping off the metals deposited in the preceding step.

10. Mass spectrometry:

Here, the identification of various isotopes in a given sample depends upon the fact that particles of different charge/mass ratio move differently in electrical and magnetic fields. So the passage of a beam of ions of different charge/mass ratios through the same field leads to separation of component particles which can be collected individually.

The ions can be obtained from various sources, two of which are utilized in trace analysis.

(a) Spark-ionisation mass spectroscopy:

Here, the ionisation is brought about by spark. A high voltage radio-frequency spark is passed between electrodes, one of which contains or is made of the sample material.

(b) Chemical ionisation mass spectrometry:

When the sample is mixed with a suitable solvent in large excess (e.g. $10^4:1$), the latter serves as a source of reactant ions, which accelerates the ionisation process. The mass spectra from chemical ionisation sources are thus markedly different from conventional spectra with additional and more complete information.

11. Gas chromatography:

When a gaseous mixture is passed over a solid or an immobilized liquid, it is possible to separate the components

of the mixture. In this method, a column is folded or coiled on itself and filled with a porous granular solid. The pores are saturated with a liquid having a high boiling point. The sample gas, mixed with another gas, called the carrier gas, is made to pass through the column. The constituents of the sample are then eluted by suitable reagents and on leaving the column they pass through a detector. The components are then collected and analysed by any appropriate method. Recently, liquid chromatography which remained eclipsed for many years because of its gas analog has met with renewed interest as a result of modern design principles. Here, the column is a solid or liquid on a solid support. The carrier liquid with the sample is poured through it. Slow speed of elution was its main difficulty. This has been overcome in High Pressure Liquid chromatography, where a high pressure is applied to the liquid to force it through the column at a satisfactory rate.

12. Activation analysis:

Many elements become radioactive when bombarded with energetic particles such as protons, deuterons, alpha particles or neutrons. The resulting activity can provide data for quantitative analyses.

(a) Neutron activation analysis:

In this method, activation is done by exposure to neutrons with thermal velocities. The neutron is then captured by the atomic nucleus to become radioactive. The active isotopes

formed in this way from various elements vary widely in half-life, and often can be identified by this constant along with other pertinent informations, such as the gamma-ray energy spectrum.

In a sample, thus treated, radioactivity will be induced in each of the elements (capable of being so activated), present. The element is determined by measuring the intensity of radioactivity produced. To determine the amount of an element E , a sample containing a known weight of E is irradiated at the same time and under exactly the same conditions. After completion of the irradiation time (which is usually a few times the half-life of the desired isotope), the sample and the standard are normally treated to separate the isotopes of the element (being determined from other products), and the ratio of their activities then gives directly the ratio of the amounts of E .

The sensitivity of this method of analysis depends on the intensity of the activating source, on the ability of the element sought, to capture neutrons and on the half-life of the induced activity. The governing relation is¹

$$A = N\sigma\phi \left[1 - e^{-.693t/T_{1/2}} \right]$$

Where A = induced activity at the end of the period of irradiation (disintegrations/sec)

N = the number of atoms present of the isotope being activated.

σ = the neutron capture cross-section (cm^2)

ϕ = the flux (neutrons/cm²/sec)

t = irradiation time

$T_{\frac{1}{2}}$ = the half-life of the product.

(t and $T_{\frac{1}{2}}$ must be in the same units)

13. Radiometric (or radio-tracer method):

In this method a radioactive substance (tracer) is used indirectly to determine the quantity of an inactive substance. A reaction may be designed to form a compound or derivatives of the tracer and the element, such that it can be separated from the rest of the sample by filtration, extraction or volatilization or some other chemical procedure.

14. Delayed neutron counting method:

Delayed neutrons are emitted from nuclei which have been left in a highly excited state by neutron decay. Immediately after the neutron is emitted, neutrons are emitted and are counted for ten minutes and the element is detected from the count.

15. Gamma-ray spectrometry:

Gamma rays of characteristic energies are emitted by both natural and radioactive elements, which are identified by the energy carried by the emitted gamma rays. The intensity of the gamma ray flux at that particular energy gives a quantitative measure of the element.

The latest addition to this list is the particle Track Analysis or simply PTA, discovered and developed by Price and Walker.^{5,6} This simple method, adorned with high sensitivity,

TABLE 2.1

Relative advantages and disadvantages of PTA and other comparable techniques of trace analysis.

Techniques	Advantages	Disadvantages
1. Mass spectroscopy	Precision and accuracy	Costly, expertise needed, contamination.
2. Activation Analysis	Low cost, no contamination accuracy upto ppb level	$\pm 10\%$ accuracy, expertise and reactor within reach of the worker needed.
3. Fluorescence	Rapid & cheap	ppm level limit contamination
4. Delayed neutron counting	Rapid	ppm limit, Reactor needed, $\pm 10\%$ accuracy
5. Radiometric analysis	Cheap & rapid	ppm limit, large sample size
6. Pulse(A.C.) Polarography	Cheap & rapid	ppm limit
7. PTA	Cheap, rapid, contamination usually recognisable, small sample size, ppb level	$\pm 10\%$ accuracy.
8. Spectrophotometry	simple, apparatus portable	reliable upto ppm level $\pm (5 \text{ to } 10)\%$ accuracy only one or a small group of elements at a time

reliability and economy, has its applications to all branches of Science in trace analysis. The method is introduced in the following sections. The advantages and disadvantages of PTA and other competing techniques are shown in table 2.1.

2.2 PARTICLE TRACK ANALYSIS:

This method is based on the changes in physical and chemical properties of matter by passage of charged particles through an insulating solid by creation of regions of radiation damage, the tracks. These regions distinguish themselves from the surrounding undamaged bulk in the form of pits or holes and are preferentially attacked by suitable chemical reagents, called etchants. These etched pits are enlarged to a diameter of 10^{-4} to 10^{-3} cm and can be conveniently observed as particle tracks under an optical microscope. Each insulator, used as Solid State Nuclear Track Detector (SSNTD) shows tracks only for incident ions which produce primary ionisation along the path at a rate which is greater than a characteristic critical value for it.⁸ Thus it is possible to use this effect selectively to detect highly ionising particles even in the presence of large amounts of other radiations. This method was applied for uranium and boron estimation in water by Fleischer and Lovette⁹ and in plants and soils by Nagpaul et al.^{10,11}

2.2.1. CHARACTERISTICS OF TRACK STORING MATERIALS:

Almost any insulating material can store tracks of particles; but no tracks have been observed in any metal or good

conductor. Materials with electrical resistivity of about 2,000 ohm-cm or more are capable of recording tracks indefinitely. Metals and semi-conductors have electrical resistivity in the range from 10^{-6} ohm-cm to 2,000 ohm-cm. Hence they cannot store tracks.¹²

One of the most striking features of all the track recording materials is their specific threshold for recording tracks of various ions. A series of measurements reveals that there exists both a charge and an energy threshold for a given detector.^{10,11}

The usefulness of the threshold characteristics can be visualized by considering figure 2.1, where the damage density in various nonconducting solids are plotted as a function of velocity and of energy per nucleon for a number of nuclei. The figure indicates a wide variation in response of various detectors to different nuclei. Thus heavy nuclides at energies ≤ 100 MeV/nucleon leave tracks in all of the detectors, while He tracks are observable only at low energies in CN and at very low energies in lexan and proton tracks have been observed only in CN.^{7,11}

Due to the threshold selectivities of the detectors, one can suitably choose them for specific experiments to avoid background problems. For example, one can use lexan to record fission fragment tracks and be confident about elimination of back-ground interference due to light particles.

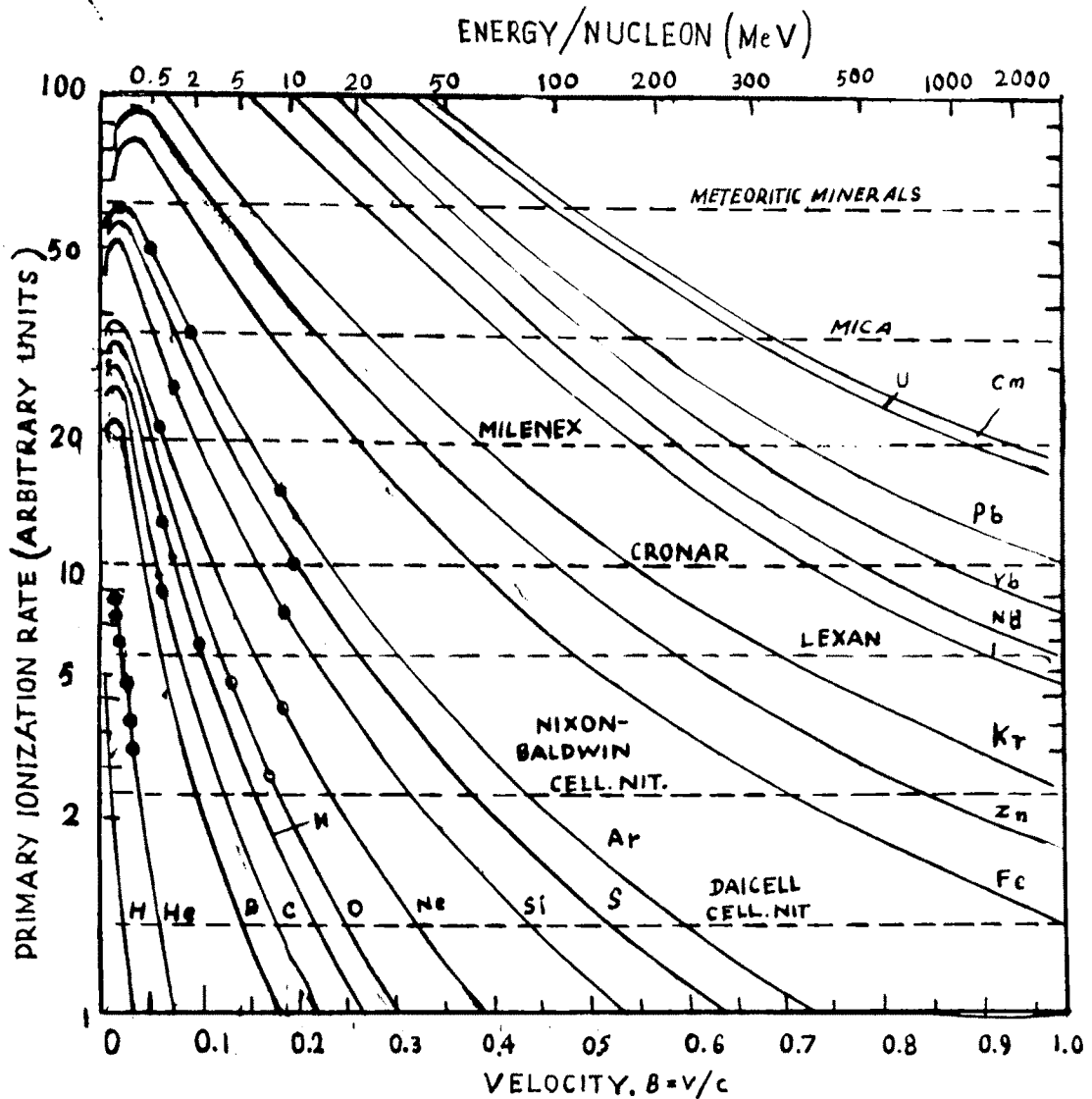


Fig. 2.1: Damage density in various nonconducting solids are plotted as a function velocity and energy per nucleon for various nuclei. Each detector has a level below which no tracks are etched and one above which all particles create tracks. (After Fleischer et.al. 1975).

2.3. TRACK FORMATION IN SOLIDS:

Most tracks are ionisation induced defects--- the result of the interaction of a charged particle with the electron attached to the atoms in the detector. They are narrow ($\sim 50\text{\AA}$ radius), stable, chemically reactive sites of strains, composed mainly of displaced atoms. A fast atom of atomic number Z passing through a solid would soon turn into an ion due to its interaction with the surrounding electrons. The ion acquires a net positive charge Z^* which is given as⁶

$$Z^* = Z (1 - e^{-130\beta/Z^{2/3}}) \quad (2.1)$$

Where β is the speed of the ion relative to that of light. The type of collision of the ion inside the solid depends on its velocity. At high velocities, the dominant interaction is the electrical force between the ion and electrons attached to the atoms within the solid. The effect of this force is either (a) to excite electrons to higher energy levels, or (b) to loosen them from their atoms and eject them.

The ejected electrons, called delta rays, can produce further excitation and ionisation if it is carrying enough energy. The original ionisation and excitation occur close to the path of the ion, while secondary excitation and ionisation can spread to larger areas. However, most of the ejected electrons are confined around the core of the track region.

When an ion slows down in a solid, it reacquires orbital electrons one by one as its velocity becomes comparable to the

orbital velocities of less tightly bound electrons. Thus below about 50 Kev/amu, the more abundant mode of energy loss is interactions between the moving ion with whole atoms or ions in the stopping medium. The damage produced by atomic collision consists of displaced atoms and the resultant vacancies.

A quantitative calculation of total damage along a track depends on the relative importance of (a) the primary damage that results from the excitation and ionisation caused directly by the heavy ion and (b) of that part of the secondary damage which is caused by the delta-rays during their passage close to the path of the ion.

Experiments to this effect show that in inorganic solids, the major source of radiation damage is the primary ionisation, while in polymers, both primary and secondary ionisation and excitation contribute in track formation. Excitation can lead to chain breaks in polymers and hence to a reduced molecular weight, which in turn, helps to increase the etching rate in them.⁶

2.3.1. TRACK FORMATION MECHANISM:

Track formation in solids depends upon the total rate of energy loss (dE/dx) of the track forming particles. For each solid there is a critical rate of energy loss such that particles losing energy more rapidly than this value produce continuous tracks with unit efficiency, while, those, depositing

appreciably less energy per unit length produce no track. The value of this critical energy loss varies from solid to solid; but in a given material, it is the same for all particles.⁸

Particles lose energy in different ways as it passes through a solid. Several methods have been put forward to explain track formation mechanism in SSNTDs, predicting different modes of energy loss, which involve the conception of deposition of energy in a highly restricted region. These models⁶ are

- (i) Direct atomic displacement model,
- (ii) Thermal spike model,
- (iii) Total energy loss model,
- (iv) Secondary energy loss model,
- (v) Restricted energy loss model, and
- (vi) Primary and secondary energy loss model.

These models are not applicable; some are unrealistic, and yet others are not quite adequate to explain the experimental data. Another model, namely, primary ionisation model or ion explosion spike model is quite satisfactory regarding these points so far.

2.3.2. POSSIBLE TRACK FORMATION MECHANISM: ION

EXPLOSION SPIKE OR PRIMARY IONISATION MODEL:

When a charged particle passes through a solid, there is a burst of ionisations along its path resulting in the formation of an electrostatically unstable array of adjacent ions. These ions eject one another from their normal sites

into interstitial positions (Fig. 2.2a). Thus a local electrostatic stress is produced in the region (Fig. 2.2b). The elastic relaxation (Fig. 2.2c), that follows spreads the strain more widely to create long range strains. In polymers, de-excitation following excitation can lead to breaks in the long chain molecules. The breaks produce new chain ends forming new species those are highly reactive chemically (Fig.2.3).

For track formation it is required that the coulomb repulsive force within the ionised region be sufficient to overcome the lattice bonding forces, i.e., the local electrostatic stress must be greater than the local mechanical or bonding strength. If two ions in a material of dielectric constant ϵ and an average atomic spacing a_0 have received an average ionisation of n unit of charges e , the force between them is $n^2 e^2 / \epsilon a_0^2$. Hence the electrostatic stress is $n^2 e^2 / \epsilon a_0^4$. The mechanical tensile strength σ_M of a material of Young's Modulus Y is approximately $Y/10$. Hence the condition of track formation is

$$n^2 e^2 / \epsilon a_0^4 > Y/10$$

or $n^2 > R$. (2.2)

Where $R \left(\equiv \frac{Y \epsilon a_0^4}{10 e^2} \right)$ is called the stress ratio, which is

a measure of the relative sensitivities of various track storing materials. It follows from (2.2.) that tracks will be formed most easily in materials of low mechanical strength,

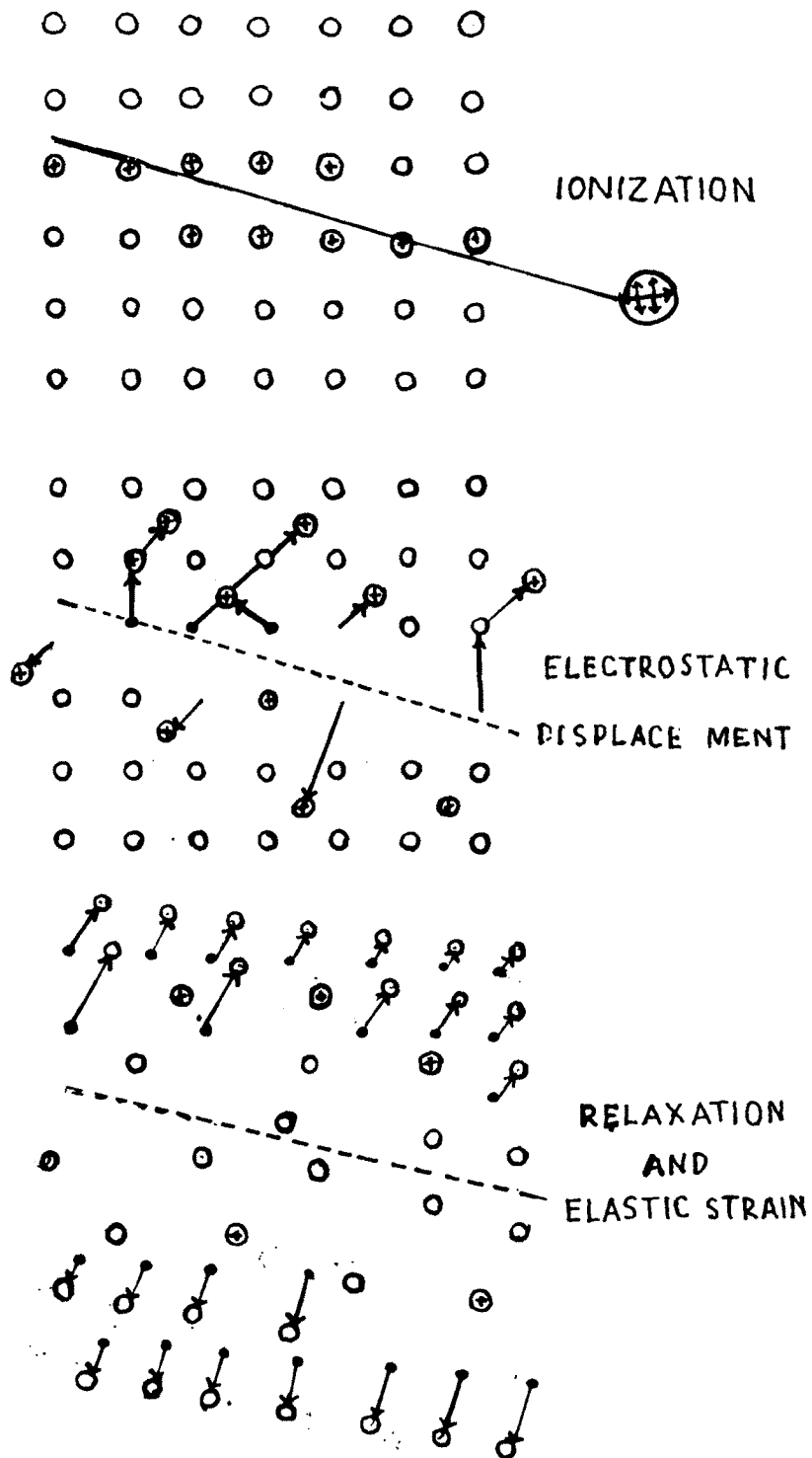


Fig. 2.2 THE ION EXPLOSION SPIKE MECHANISM FOR TRACK FORMATION IN INORGANIC SOLIDS.

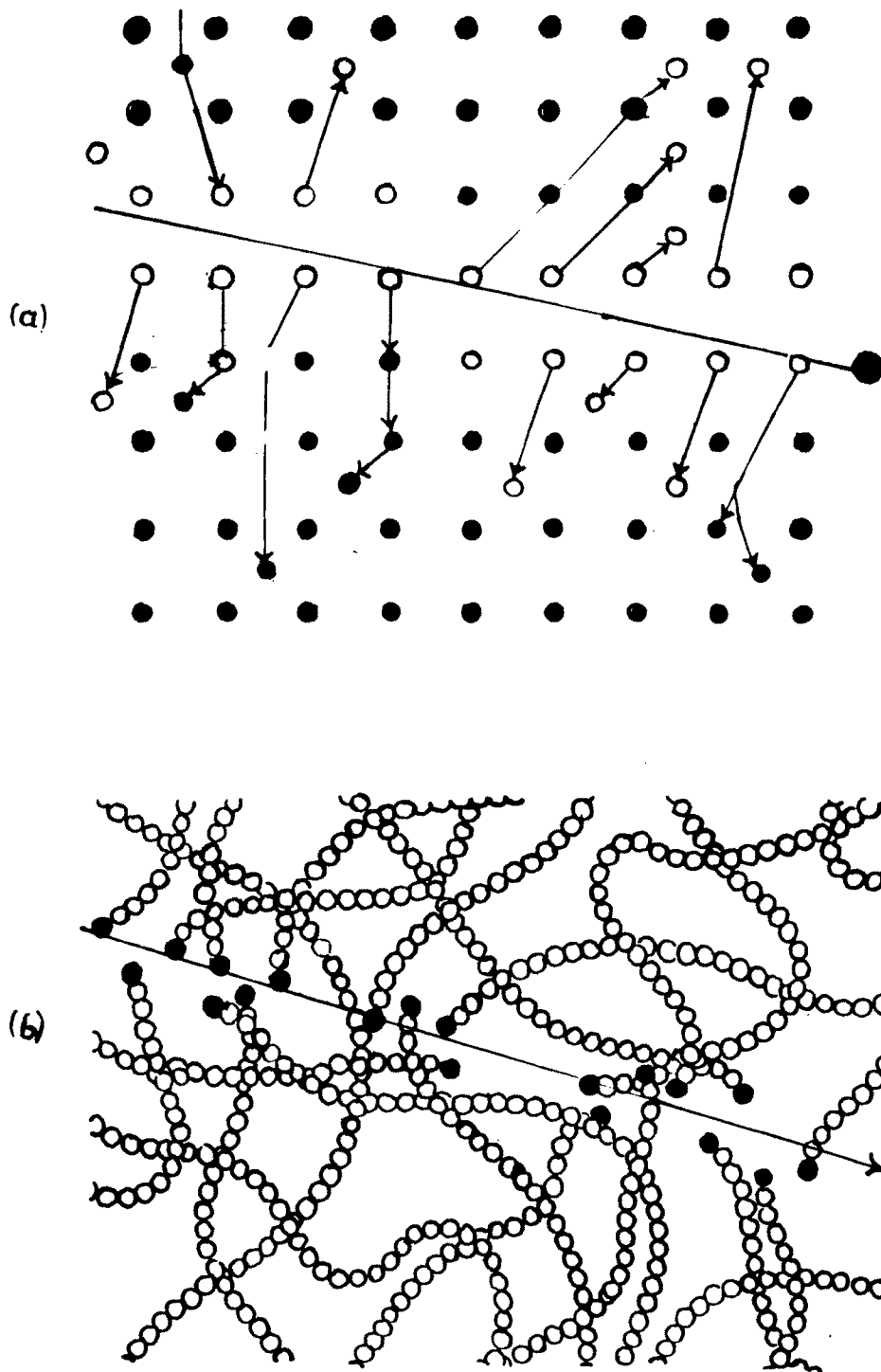


Fig. 2.3: The atomic character of a particle track in (a) A crystal and (b) A polymer. In the crystal the damage is continuous disorder composed of vacant lattice sites and interstitial ions or atoms. In the polymer new chain ends and other chemically reactive sites are formed. (After Fleischer et.al. 1975)

low dielectric constant and close interatomic spacing. The average value of R in some plastics have been found as 0.01, and in some inorganic glasses the same has been found to vary from 0.5 to 0.7 while in some crystal R was found as 4.5. Hence plastics are more sensitive detectors than glasses and crystals.⁶

In detectors like mica, there must be at least one ionisation per atomic plane traversed by the charged particle ($n > 1$) and in other materials it is likely that $n \sim 1$ so that the damage is atomically continuous. In plastics, these can be formed even when there are only 1 to 3 ionisations per 20 atomic spaces along the track. Again excited electrons ($\sim 2\text{eV}$) can also lead to free radical and broken bond formation, with a spacing of about one per atom distance along a track for which the density of ionisation is only ~ 1 per 20 atom distances. Hence primary ionisation is not the sole track producing factor in plastics. Primary ionisation and excitation together can give a continuous trail of damage. That there is adequate primary damage to explain track formation in polymers is further supported by calculations of Fain et al (1971) who include effects from ionisation of inner shells and concluded that about 0.6 ionisations per atom distance are produced at the threshold in cellulose nitrate.⁶

The following equation derived by Bethe¹⁷ for primary ionisation produced by charged particles while passing through atomic hydrogen accounts for all the etching rate measurements

made so far.¹⁶

$$J = \frac{aZ^*{}^2}{\beta^2} \left[\ln \frac{\beta^2}{1-\beta^2} + K - \beta^2 - \delta(\beta) \right] \quad (2.3)$$

where Z^* = effective charge of the particles

a = a constant depending on the nature of the medium

K = a constant depending on the plastic and etching conditions,

β = ratio of the velocity of the particle to that of light,

$\delta(\beta)$ = A relativistic correction term on account of polarisation of the medium by the electromagnetic field of the moving particle.

2.3.3. RESTRICTIONS IN TRACK FORMATION:

Track formation will not be possible if electrons from the adjacent material can attach themselves to the ionised atoms formed due to the passage of an energetic charged particle along its path. Due to the large abundance of free electrons ($\sim 10^{20} \text{ cm}^{-3}$) in metals, this is actually the case, and hence no track will be formed in metals and good semiconductors.

The ionised region along a track is essentially a region of high concentration of holes, which may move away, thereby suppressing permanent track formation. It is seen that at room temperature, if in a material, the track mobility is less than about $10^2 \text{ cm}^2/\text{V}/\text{Sec}$, tracks can be formed. That is why metals and many semiconductors including silicon and

germanium, are not track storing materials.⁶

2.3.4. OTHER TRACK FORMATION MODELS:

Since the discovery of the particle etch technique, a number of models have been put forward to show how ion-induced tracks are formed in Solids. There is still no general agreement as to the mechanism of track formation nor the appropriate parameter against which to plot etching rate or threshold or track diameter.¹⁷ Ali and Durrani¹⁸ proposed the concept of reactive cells, created along and around the path of the primary ionising particle, as responsible for registration of tracks.

Groeneveld et al (1979) have reported the new evidence of occurrence of coulomb explosion in nuclear track formation in solids and for free molecular system with properties close to solid-state.

The plausibility of a new track theory model for formation of etchable tracks in SSNTDs has been put forward by Katz.¹⁹ According to this theory, polymer clusters for the sensitive targets for radiation damage by delta rays. A quasi-threshold for track formation can be expected when about 20% of these clusters, intersected by a passing ion, are damaged to enhanced etchability.

2.4 PLASTIC DETECTORS:

Dielectric materials, such as glass, mica and plastics have been extensively used as Solid State Nuclear Track Detectors for particle identification and estimation of

concentrations. While the former two are used for fission fragments, various organic materials-polycarbonates and polymers (plastics) are used for both fission fragments and alpha particles. The most widely used plastics are cellulose nitrate (Diacell, LR-115, CA-80), cellulose acetate butyrate, Lexan and Macrofol polycarbonate etc.

Cellulose nitrate (CN) ($C_6H_8O_9N_2$) is known to record the tracks of low-energy protons, deuterons, tritons and alpha particles. This plastic is known for the following original properties.²⁰⁻²²

- (i) A high sensitivity with minimum detectable ratio $Z/\beta \sim 30$;
- (ii) An easy and very simple etching possibility
- (iii) A very high precision of sheet thickness ($< 1/\mu m$)
- (iv) An excellent flexibility, permitting to fill exactly non-plane surfaces.
- (v) Good reproducibility regarding different batches.

It has been improved to achieve few more properties, some major ones of which are

- (vi) The dosimetry of medium energy protons and consequently of medium energy neutrons.
- (vii) Detection of low neutron cross-section capture elements such as $^{14}N, ^{17}O$.
- (viii) The imaging of tumoral cells for neutron capture therapy.
- (ix) A large improvement for track counting methods both spark and optical.

Lexan polycarbonate ($C_{16}H_{18}O_3$), due to its uniformity, reasonable sensitivity and availability in large areas and in a variety of thicknesses, is the most thoroughly studied detector. It is insensitive to track-producing high energy photons, deuterons and alpha particles, all of which are common in nuclear reactions. Some uses of it are^{6,24-27}

- (i) identification of fission fragments ($Z=30$ to 60 with $\Delta Z \simeq 1.5$ to 2 ,
- (ii) isotope abundance measurement,
- (iii) imaging of tissue-section,
- (iv) uranium trace analysis, and
- (v) as molecular sieve.

Unirradiated lexan is optically transparent at wavelengths more than 2750\AA and has absorption peak at 3050\AA . It is also practically free from uranium.

Recently, the plastic CR-39 ($C_{12}H_{18}O_7$) is emerging as the most sensitive track detector. It is an optically clear, amorphous, radiation sensitive, thermoset material—an ideal polymer for detection. It can detect light charged particles such as neutrons, protons and alpha particles as well as light heavy ions over a wide range of energy. It is free from nitrogen and therefore does not produce background proton tracks from the reactions of thermal neutrons with nitrogen. It can detect and record tracks of alpha particles upto $\simeq 60$ MeV ($\equiv Z/\beta \sim 10$). Choudhury et al showed that it can record alpha particles upto 30 MeV and protons upto 11 MeV.²⁰⁻²¹

2.5. OBSERVATION OF PARTICLE TRACKS:

The damage trails of ^{235}U , first seen in mica by Silk and Barnes²⁸ by an electron microscope faded away by constant bombardment of electrons. The same were first revealed by Price and Walker by using hydrofloric acid as etchant. Subsequent works by Fleischer and Price established the general realisation of track etching by proper choice of chemical reagents. The etching technique, known as chemical etching, is adorned with simplicity, as only common chemicals are required to enlarge the tracks to sizes observable under an optical microscope.²⁹

2.5.1. BASICS OF TRACK ETCHING:

Due to large free energy association, radiation damage trails are much more chemically reactive than normal material. Although initial tracks are only about 50\AA or less in diameter, prolonged chemical attack makes them large enough (micron range) to be seen under an optical microscope. There is permanent record of tracks of particles in the form of etched pits which are not always merely magnified versions of the original tracks. Although different solvents give differently shaped tracks, by adjusting the etching parameters they can be made quite faithful.²⁹

The condition for revelation of tracks is given by the relation

$$\theta_c \geq \sin^{-1} V_g/V_t \quad (2.4)$$

where V_g is the general rate of attack perpendicular to the surface and V_t that along the track and θ_c is the critical angle of etching of the tracks.

Etching of tracks is one of the most important phenomena in particle detection by SSNTD. The knowledge of etch rate is highly useful as it considerably affects the etching efficiency (η).³⁰

$$\eta = 1 - V_g/v_t \quad (2.5)$$

The etching rate depends upon (i) the composition of the material, (ii) nature of the damage produced, (iii) etchant parameters and (iv) the duration of etching.

Since etching is, in essence, a diffusion process, its temperature dependence is obvious, and is given by the relation

$$V_g = Ae^{-E_b/KT} \quad (2.6)$$

where A is a constant, E_b the activation energy for bulk etching and K , the Boltzmen constant.

V_g is shown to be a linearly increasing function of the etchant concentration. For lexan, V_g increases at the same rate with the etchant concentration.

The etched pits are in the form of hollow cones and can be measured easily to identify the charge and energy of particles individually. The registration sensitivities of various dielectric detectors depend upon the chemical constituents of the etchant.

2.5.2. ETCHING CONDITIONS:

The etching conditions are largely based on trial and error method; yet certain guidelines are to be followed.⁶

(a) The etchant should be so chosen that it slowly dissolves away the material at a constant rate. Since the tracks are to be enlarged to optically visible sizes, bulk attack is necessary.

(b) The attack rate, which is controlled by temperature and concentration of the etchant, can be varied by changing the concentration or by adding other chemicals to the etchants and also by changing the temperature.

(c) Etchants capable of revealing dislocation can reveal tracks also.

(d) Stirring the etchant during etching ensures uniformity of temperature of the etchant, and hence, is important.

(e) The surfaces to be etched should be optically smooth in order that submicroscopic cracks or scratches may not obscure tracks or produce confusion.

2.5.3. THE DIFFERENT CATEGORIES OF TRACKS:

(a) Sharp tip cone: Such type of cone is formed before the etching solution can reach the stopping point of the particle.

(b) Round-tip cone: This type of cone is formed by the action of the etching solution after it has reached the stopping front of the particle.

(c) **Joined cones:** Ordinarily, the etching solution, etching over both the surfaces of a sheet forms two separate cones along the trajectories of the energetic particles penetrating the sheets. However, if etching is continued long enough these two cones merge to form a joined cone.

2.6. ENVIRONMENTAL EFFECTS:

The important objective of the track study in SSNTD is to obtain good identification of the incoming particle and determine their energies and the incident flux. This is influenced by various environmental conditions during storage and handling. The environmental effects may be classified as

(a) Pre-irradiation effects:

Possible impurities like H_2O_2 , H_2O and O_2 in commercially available detectors, pre-treatment with ultraviolet or gamma rays increase the bulk etching rate.

Pre-treatment with laser beam is found to enhance the track revealing properties of CR-39 detector and hence reduce etching time.

(b) During irradiation, treatment with active agents, like O_2 , O_3 , H_2O_2 and even H_2O causes chemical effects so as to increase the track etching rate of polymers, whereas neutral environments such as vacuum or N_2 atmosphere decrease the track etching rate V_t .

The registration efficiency of alpha particle tracks of CN increases when an electric field is applied across the plastic sheet during irradiation.

(c) **Post-Irradiation effects:** Exposure to ultraviolet or high energy photons and electrons or other particles which do not themselves make tracks can have significant effects on the properties of track detectors—mostly plastics. Ultraviolet light, in presence of oxygen, increases the track etching rate V_t . Irradiation by lightly ionising radiation can either promote cross-linking of a polymer and hence decrease general etching rate or can cut the long chain molecules, converting them into shorter, more rapidly etchable materials.

V_t is found to increase for tracks kept in an environment containing oxygen even if the samples were protected from ultraviolet rays.

The sensitivity of charge registration in an irradiated sample increases when the latter is kept in a spark discharge chamber.³⁴

At room temperature, latent tracks in plastics are quite stable, but at higher temperatures, low charge tracks fade away and high charge tracks become shorter. At high temperatures, the free radicals or ions may recombine around the damage trail or react with the adjoining molecules to form more chemically stable species. This leads to a reduction in track etching rate.⁶

2.7. TRACK COUNTING:

For many track studies, it is required that simply the track density or total track count be measured. The most direct commonly used counting method is manual observation through normal optical microscope using an eyepiece with a calibrated

grid and counting the number of tracks in a series of fields of view. It is desirable that the microscope be equipped for viewing the reflected as well as transmitted light simultaneously.⁶

Manual track counting is very labour intensive, time consuming and carries the risk of observer bias, which can compromise experimental accuracy. The highest track density that have been successfully measured accurately by human observers using optical microscopy is 10^4 tracks per/sq.mm. Elimination of human element would permit the introduction of more quantitative standard. Again for attaining high statistical precision, a large number of tracks are to be counted.

It is a general procedure to aim at making the tracks more clear and easy to read using various means. The individual tracks can be located reproducibly by using a comparator microscope or a photosensitized grid or even by means of a congruent transformation of the track detectors' co-ordinate systems.

A spark counting method applicable with plastic detectors such as Macrofol or Lexen has been successfully demonstrated.³⁷ But the process possesses severe limitations for precession work with accuracy roughly of $\pm 10\%$ to $\pm 20\%$, provided the track density is limited to less than $10^3/\text{cm}^2$.³⁵

Tracks can also be counted automatically. This provides with a saving of both time and labour, but there is every

possibility of loss of information.

A more sophisticated automatic system an optical microscope under computer control (Argonne Optical Track Scanner-AOTS), has been demonstrated with comparable accuracy to manual scanning for plastic detectors such as Macrofol, Lexan etc. Here an accurate measurement of track density limit of roughly 10^5 tracks/cm² has been established. The AOTS system is the first microscope system ever built, that possess automatic focussing capability. This system has now been modified to improve its utility and called the Handford Optical Track Sensor (HOTS), which has also some limitations and these are tried to be corrected in the Automated Scanning Electron Microscope (ASEM).

An image analysis system capable of rapid, fully automated scanning identification and measurement of etched nucleon tracks has been reported by Few³⁸. Reliable and efficient selection criteria which reject all non-track defects have made its precision approaching or exceeding that of a skilled human observer.

The automated systems are yet to be within the reach of small laboratories.

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