

## **IMAGING AND CHARACTERIZING - TRACE ELEMENT ANALYSIS**

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### **Summary**

This chapter outlines various physical methods for the investigation (bulk and surface) of different substances – optical and electron microscopy, holography and interferometry, laser spectroscopy, holography and interferometry, remote sensing of the Earth's surface. It covers various types of analysis of impurities and tracers at the surface or in the bulk of materials, different aspects of applied nuclear physics in elemental analysis of substances, and their industrial, biological and environmental (monitoring) applications.

### **1. Introduction**

Surface characterization means knowledge of the physical properties of the surface of objects, including their roughness, chemical composition, atomic structure, structure of surface defects, and so on. On the atomic and sub-atomic level, an investigation of the surface state can be performed by different techniques – optical and electron

microscopy, tunneling and force microscopes. The nuclear microprobe provides elemental analysis at the submicron level.

Generally speaking, the term surface examination can be applied not only to microsystems but also macrosystems, for instance, study of the Earth's surface, i.e. global examination of its lands, mountains, oceans and seas, and even atmosphere. Modern imaging systems also provide characterization of the bulk of various objects under examination.

For many years, optical measuring techniques have provided detailed and comprehensive information concerning not only the morphology of objects, but also in the fields of heat and mass transfer, and fluid dynamics. The high spatial and temporal resolution of the measurements enables great insight to be gained concerning the thermo- and fluid dynamical properties of a given system. Optical methods also supply valuable evidence on the formation of phase interfaces, on particle movement, and on the size distribution of droplet swarms. One of the most fruitful optical techniques is holography, which allows various interferometric methods for measuring processes of heat and mass transfer to be used.

One of the major problems of modern technology is the high purity often required in the starting materials used in a given process. Tolerable impurity limits can be as low as  $10^{-12}$  of the main matrix mass. The ability to measure concentration of trace elements is thus of fundamental importance. Interest in trace elements, especially in biological and environmental systems, has been steadily increasing during the last few decades. Important fields of interest are animal, human and plant biology, food production, medicine and environmental pollution. The interest in trace elements covers toxic elements as well as essential elements, some of which may also occur in toxic concentrations. Another important aspect of trace elements in both organic and nonorganic matrices is that they sometimes display a specific pattern (often called fingerprint), which may be indicative of the origin or the history of a sample.

Efforts in space research have similarly led to scientists seeking possibilities for checking ideas regarding star evolution, starting from investigation of details of the Earth's own satellite – the Moon. Samples of lunar soils and dust have been subjected to many tests, the determination of elemental abundance being one of the main interests of such studies.

One of the most fruitful approaches in such determination has been activation analysis that will be considered in Section 7.2.

## **2. Optical Microscopy**

The optical microscope is perhaps the most widely used scientific instrument. Although they can image tiny objects such as bacteria and cells, the resolution of optical microscopes is limited by the value of the wavelength of visible light; the highest resolution of optical microscopes is only 0.2  $\mu\text{m}$ . In order to probe atomic structure, another illumination source with a shorter wavelength is needed, and such a possibility is provided by particles with nonzero mass – electrons, neutrons, ions of different

elements.

In any form of microscopy, there are two basic elements that must be present. First, for an image to be formable there must be some respect in which the events occurring in the specimen vary from point to point; this variation supplies the contrast mechanism of the microscopy in question. Second, the arrangement of optical devices and detectors observing the events (or in scanning systems the manner in which the particles inducing the events are delivered to the specimen) must allow a detected event to be accurately referred to the point in the specimen at which it occurred; this arrangement supplies the imaging system of the microscopy.

## **2.1. Historical Development**

The first compound microscopes appeared in Holland around the end of the sixteenth century and their invention is usually attributed to the spectacle maker, Hans Jansen. However, Dutch microscopist Antoni van Leeuwenhoek is also often cited as the father of microscopy, since the single-lens instruments he pioneered from about 1670 (essentially high-powered magnifying glasses) were superior in performance to the compound instruments until about or even after 1800. In the first few decades of the 19<sup>th</sup> century, lenses corrected for chromatic and spherical aberrations were being developed, notably by the British amateur scientist J.J. Lister. This work culminated in the designs of German physicist Ernst Abbe who also formalized the theory of image formation in 1877. By 1880 instruments were in use which had attained the theoretical limit of resolution for light microscopy. The most significant development in the 20<sup>th</sup> century was the development by Zernike in the 1930s of "phase contrast" microscopy, allowing details to be seen in thin transparent sections which are almost invisible using standard microscopy.

## **2.2. Resolution Limits and Aberrations**

Parallel light rays arriving at the lens will not be focused to an infinitely small point. The ray optics model presented in Figure 1 ignores the wave-nature of light. Light waves consist of oscillating electric and magnetic fields, whose strength or "amplitude" varies as a function of position and time. At a given moment in time, the electric field of a parallel beam of light may be thought of as a "plane wave" — a series of peaks and troughs in amplitude running perpendicular to the direction of propagation. The distance between two peaks is the wavelength  $\lambda$  and for visible light it is around 500nm. A property of waves is that they interfere with each other; the crest or peak of one wave coinciding with the trough of another will result in a canceling out of the amplitudes of both waves, whereas two peaks coinciding doubles the amplitude.

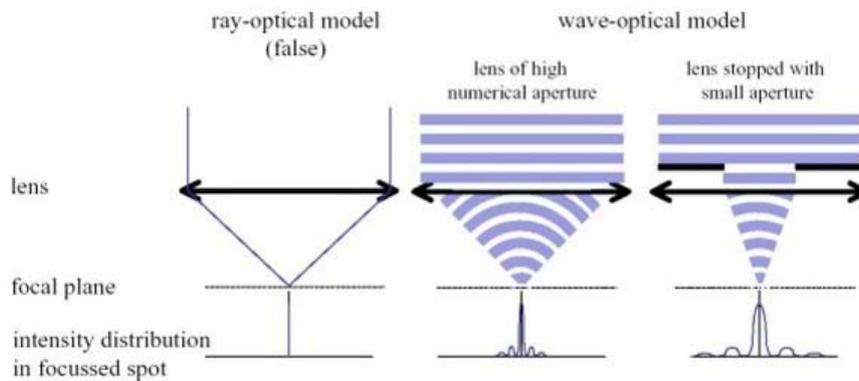


Figure 1: Focusing of parallel light to a point

This means that many plane waves arriving towards a point from different angles combine to yield complicated interference patterns, with localized intensity maxima and minima. However, Abbe showed that no combination of waves of a given wavelength can be found which concentrates all the intensity into a zone whose size is less than about  $\lambda/2$ . This size is achieved if plane waves of equal amplitude arrive towards a point from all directions. The action of the lens can be seen as breaking up the incident plane wave into a range of plane waves all arriving at the focal point from different angles. The greater the angle subtended by the lens at its focal plane, the greater is the range of angles contributing (Figure 1). A plane wave arriving at a lens, will thus be focused into a disc (known as the Airy disc) at least  $\lambda/2$  in diameter, no matter how good the lens is. But this size will increase if the lens diameter is small compared to its focal length or if a small aperture is centered on the principal axis close to the lens. In addition there will be subsidiary maxima in the form of rings around the central disc caused by the interference of waves scattering or "diffracting" from the edge of the lens, or aperture if there is one. (The terms "scattering" and "diffraction" are sometimes used almost interchangeably, but most authors reserve the use of diffraction to cases in which the scattered waves interfere with each other to cause intensity peaks and troughs).

Similarly, light emitted or reflected from a particular point on the object will be focused not to a perfect point but into a blurred disc, again, at least  $\lambda/2$  in diameter. The resolving power of the lens approaches this theoretical optimum as the ratio of its diameter to its focal length increases. Conventionally, objective lenses are classified in terms of their numerical aperture (NA) which is defined by the relation

$$NA = \frac{\sin \alpha}{n},$$

where  $\alpha$  is the half angle subtended by the lens at its focal point and  $n$  is the refractive index of the medium between the lens and its back focal plane — see Figure 2.

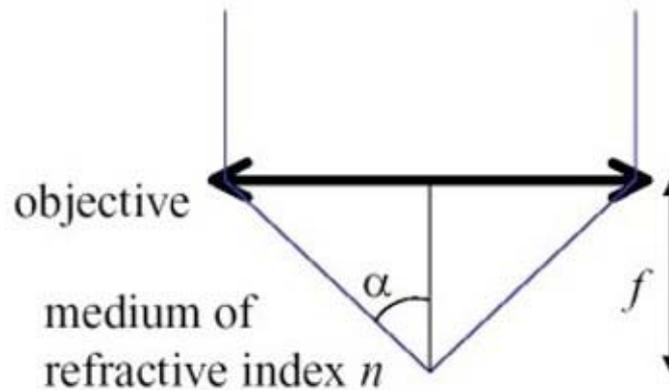


Figure 2: Definition of the numerical aperture, NA

Modern objectives combine very short focal lengths with wide acceptance angles leading to values of  $\sin \alpha$  approaching 0.9. This is in practice the maximum value that can be achieved in air ( $n = 1$ ) but "immersion lenses", designed to function with a film of high refractive index ( $n = 1.5$ ) oil occupying the space between lens and sample (or cover slip) can increase NA to about 1.4. Such a lens will reproduce detail down to the scale of about  $0.2 \mu\text{m}$ .

### 2.3. Soft X-ray Microscopy

For years physicists have wanted to construct an X-ray microscope that would exploit the ability of soft X-rays to detect small structures. The need for such an instrument is clear. As mentioned above, the resolution of light microscopes is limited by the comparatively long wavelength of visible light. And transmission electron microscopes, although they have a much higher resolution, are weak in penetrating power and are therefore limited to very thin specimens. Moreover, in transmission electron microscopy the biological specimen is usually stained and mounted in a vacuum chamber.

Between ultraviolet radiation and short-wavelength X-rays lies the soft or long-wavelength X-rays ( $1 - 10 \text{ nm}$ ). Until the 70s of XX century researchers had worked little with this radiation, primarily because it was difficult to generate in the laboratory.

X-rays traditionally have been generated by accelerating electrons and slamming them into a solid target. The efficiency of this method is quite low – typically  $<10^{-3}$  of the electron energy is converted to X-rays. It is even lower for soft X-rays, which tend to be absorbed in the target. Hot plasmas, generated by high-power lasers or electric discharges, produce soft X-rays copiously, but these sources are not in common use. Synchrotron radiation comes close to being the ideal universal source because of its intensity, tunability, and small size and divergence.

Soft X-rays have proved to be useful in analyzing the structure of objects that range in size from the chromosome of the living cell, through the hot plasma in fusion experiments to the corona of the sun.

Soft X-ray photons interact with matter chiefly through absorption. The variation of the number of absorption events from point to point in the specimen provides the contrast

mechanism of soft X-ray microscopy. In the transmission X-ray microscope (TXM) the variation is detected by counting the transmitted photons. It is possible to do X-ray microscopy by counting showers of secondary particles rather than unabsorbed photons. There are two cases to be distinguished, according to whether electrons or photons are detected; the former is electron-emission X-ray microscopy (EXM) and the latter is fluorescence X-ray microscopy (FXM). Because of the difference in range of the particles, FXM detects showers occurring anywhere within moderately thick specimens, while EXM detects only showers occurring within a few nanometers of a surface of the specimen facing the detector. EXM is thus potentially useful as a method of surface-layer microscopy. In addition, because of the variation of fluorescence yield with Z, FXM is mainly useful for the imaging of medium- or high-Z features. We may note finally that the shower-counting microscopy is dark field (features are bright against a dark background) and that absorption microscopy is bright field (dark features against a bright background).

The simplest method of imaging is a contact X-ray microscopy. Behind the specimen is a screen, X-ray resist, or film that records the intensity of the X-rays that pass through it.

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their principles of operation, resolution, applications in different scientific and technological fields are given.].

### **Biographical Sketches**

**Tsipenyuk Yuri Mikhailovich**, graduated from the Moscow Institute of Physics and Technology (MIPT) in 1962, becoming candidate of sciences in 1969, and doctor of physico-mathematical sciences in 1979. From 1961 until the present time he has worked at the P.L.Kapitza Institute for Physical Problems, Russian Academy of Sciences, now are being the leading scientist of this Institute. In addition he is Professor of physics of the Moscow Institute of Physics and Technology. His scientific interests include: electron accelerators, fission of atomic nuclei, activation analysis, investigation of the solid state by neutron scattering, and superconductivity. In 1997 he was made Soros professor and in 1997 he became a Member of the New York Academy of Sciences. Y.M.T. has published more than 120 papers in scientific journals, and is the author of three monographs: "Physics of Superconductivity" (in Russian, 1995, MIPT Publishing, Moscow), "Nuclear Methods in Science and Technology" (IOP Publishing, 1997), "The Microtron: Development and Applications" (Taylor and Francis, London 2002), in addition to being the coauthor of a textbook on general physics for high school "Basics of Physics" (FIZMATLIT, Moscow, 2002).

**Michael Walls** was born in Liverpool and studied physics at the University of Sheffield before undertaking a Ph.D. at the Cavendish Laboratory in Cambridge. His thesis (1987) was based on theoretical and experimental studies in Electron Energy-Loss Spectroscopy (EELS) of surfaces and interfaces in the electron microscope. He then spent eighteen months performing post-doctoral research in the Laboratoire de Physique des Solides at the Université Paris-Sud, where he investigated using EELS the decomposition of carbonates under electron beams, and helped to develop algorithms for the elimination of EELS quantification errors due to fine structure in the spectrum. He returned to Cambridge in 1989 to conduct research on a range of materials using the scanning tunneling microscope (STM). In 1991 he joined the present laboratory, the Centre d'Etudes de Chimie Métallurgique in Vitry-sur-Seine where his research includes; the development of new microscopic techniques for of impurity element site determination using Energy-dispersive X-ray spectroscopy, the analysis in the transmission electron microscope (TEM) of the structure of metallic multilayers grown by electrochemical methods, the observation by atomic force microscopy (AFM) of corrosion processes in steels and of the formation of biofilms on metal surfaces, including steels and tantalum. He is also involved in the development of algorithms for quantitative analysis of AFM and STM and TEM images.