

X-ray – A Boon for Elemental Analysis

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The characteristic X-rays coming out from an unknown sample due to the irradiation of gamma rays or X-ray photons or due to the bombardment of high velocity protons are used for elemental analysis in a sample. We describe here two techniques viz., Energy Dispersive X-Ray Fluorescence (EDXRF) and Proton Induced X-ray Emission (PIXE) which have the capability of nondestructive and multi-elemental analysis of the sample.

Introduction

X-rays are typically produced by bombarding a metal target in a vacuum tube (*Box 1*) with high speed electrons that are accelerated by tens to hundreds of kilovolts. These high speed electrons can eject electrons from the inner shells of the atoms of the metal target. The vacancies thus created are quickly filled by electrons dropping down from higher levels. The continuous X-ray is due to stopping of high velocity charged particles (including electrons, protons, etc.) by the target material. The energy lost is converted into a continuum of X-radiation called Bremsstrahlung, meaning breaking radiation.

The characteristic X-rays are emitted from heavy elements when their electrons make transitions between the lower atomic energy levels. The characteristic X-ray emissions are shown in *Figure 1* as two sharp peaks when vacancies are produced in the $n = 1$ or K -shell of the atom and electrons drop down from above to fill the gap. The transition from $n = 2$ to $n = 1$ levels ($n = 2 \rightarrow 1$) produce K_{α} lines and from $n = 3$ to $n = 1$, the K_{β} lines. The characteristic X-rays are generally used in X-ray crystallography whenever a monochromatic source is required.

We describe here proton induced X-ray fluorescence emission (PIXE) technique, which can be used for non-destructive simul-



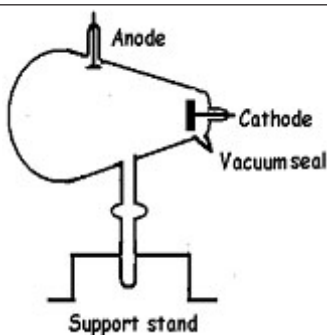
Box 1. X-ray Tubes

Crookes tube is a device invented by Sir William Crookes (1832-1919) in 1875. It consists of an evacuated sealed glass tube containing two metal electrodes. When a high voltage is applied between the two electrodes, due to electric discharge, the so-called cathode rays pass through the highly rarified air in the tube. The Crookes tube played an important role in the discovery of the electrons by J J Thomson in 1897.

X-ray tubes today are based on the 1913 design of William Coolidge, a physicist at the General Electric Research Laboratory. The characteristic features of the Coolidge tube are its high vacuum and its use of a heated filament as the source of electrons. There is so little gas inside the tube that it is not involved in the production of X-rays. This is in contrast to the somewhat bulky Crookes tube which depends on the residual gases inside that makes it unpredictable due their changing properties when heated. As the cathode filament is heated, it emits electrons. The hotter the filament gets, the greater the emission of electrons. These electrons are accelerated towards the anode by the high electric field and on striking the anode, X-rays are emitted. The major advantages of the Coolidge tube are its stability and its ease of controlling intensity. The Coolidge tube also has much longer life.



Sir William Crookes



Crookes Tube



William Coolidge



Coolidge tube

In the early 1950s the rotating-anode X-ray generator was developed which plays a very important role in the modern X-ray generators especially in X-ray diffraction (XRD) studies which is an indispensable tool in materials science. The modern diagnostic X-ray equipment also uses a rotating anode tube, which has a power rating of fifty kilowatts or more, needing an exposure time of only a small fraction of a second thus minimizing radiation hazard.

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taneous elemental analysis (see *Box 2* for two other techniques). This technique makes use of protons (instead of electrons) from accelerators. If these protons eject the electrons in the inner orbit of the target atom, then characteristic X-rays are produced due to the transition of electrons from the higher orbit to fill the vacant site of the lower orbits. Again this primary X-ray can produce secondary X-rays when they are irradiated on a particular target



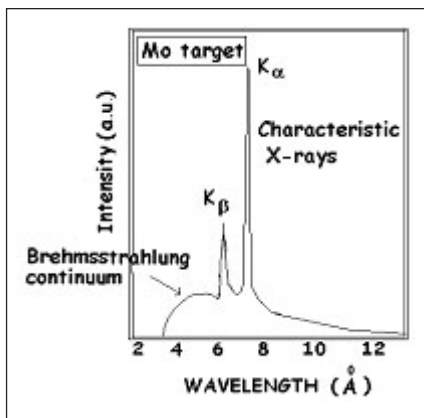


Figure 1. Characteristic X-ray emission using Mo target.

material. The irradiation of γ -ray or X-ray photons on the target material leads to the ejection of the electrons from the inner orbits (K, L, M , etc.). This results in the characteristic X-rays of the target material. The use of proton beam as an excitation source definitely offers some advantages over other X-ray techniques. For example, the elemental analysis process itself is faster due to higher rate of data accumulation over the entire spectrum especially for the lower atomic number elements. The overall sensitivity is also better because of the lower Bremsstrahlung background as the more massive protons undergo lower deceleration (and hence lower energy loss) compared to electrons. This is in contrast to higher background during electron excitation.

Box 2. Electron Spectroscopy for Chemical Analysis (ESCA)

One of the most important techniques used in materials science for characterization is ESCA which is also known as X-ray Photoelectron Spectroscopy (XPS). This is a method generally used for characterising the top few atom layers on the surface of a solid. ESCA can provide information on the elemental composition of a surface (C, O, N, etc.) as well as insights into the chemical bonding of species existing on the surface.

In ESCA, a monoenergetic soft (about 1.5 kV) X-ray beam is directed towards the sample under ultrahigh vacuum. When the sample absorbs the X-ray photon, it is ionized, ejecting a free electron. The energy of the electron emitted is less than that of the incident X-ray photon by an amount equivalent to the binding energy E_b of the electron to the atom.

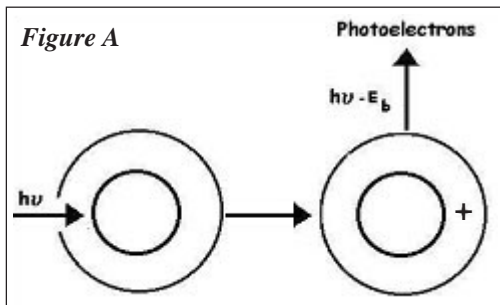
The kinetic energy E_k of the ejected electron, called photoelectron, depends on the energy of the incident X-ray photon $h\nu$, (see Figure A). It can be expressed as :

$$E_b = h\nu - E_k + \phi,$$

where ϕ is the correction for the spectrometer work function. This relation forms the basis of ESCA. Since $h\nu$ is known, a measurement of E_k determines E_b . The value of E_b is specific to the atom concerned. Measurement of E_b serves as a 'fingerprint' to identify the atom. A plot of E_b vs. intensity of the emitted electron is the XPS spectrum. Qualitative analysis can be performed from the positions of the peaks. The peak height is dependent on the concentration of the element, the mean free path for the electrons in the material and the efficiency of absorption of X-rays. Since all of these parameters cannot be exactly known, this method is generally used only for quick and semi quantitative analysis.

Box 2. continued...





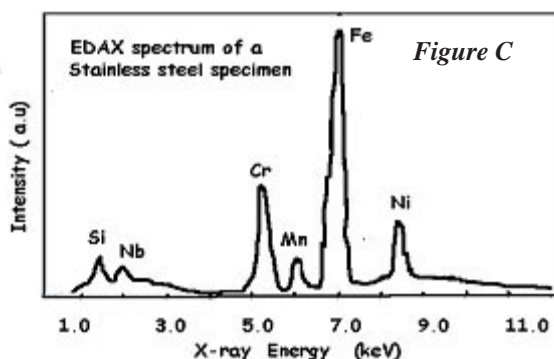
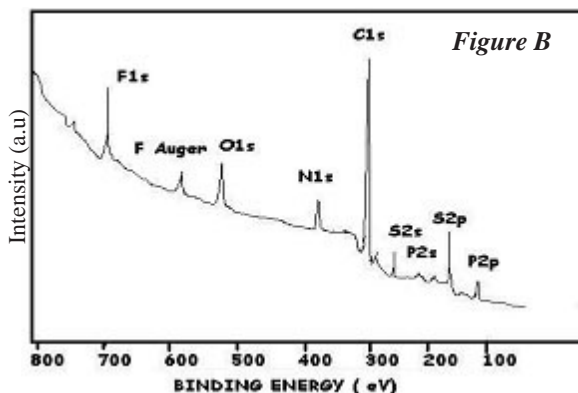
ESCA can be used to detect all elements except hydrogen and helium. It is most useful for solids, including powders and soft materials, organic films and polymers. It has very high surface sensitivity (usually nanometer depth) which makes it one of the most important surface analysis techniques today.

Figure B shows a schematic ESCA spectrum of an organic compound containing different elements

and the identification of these elements from the binding energy of electrons in different orbitals.

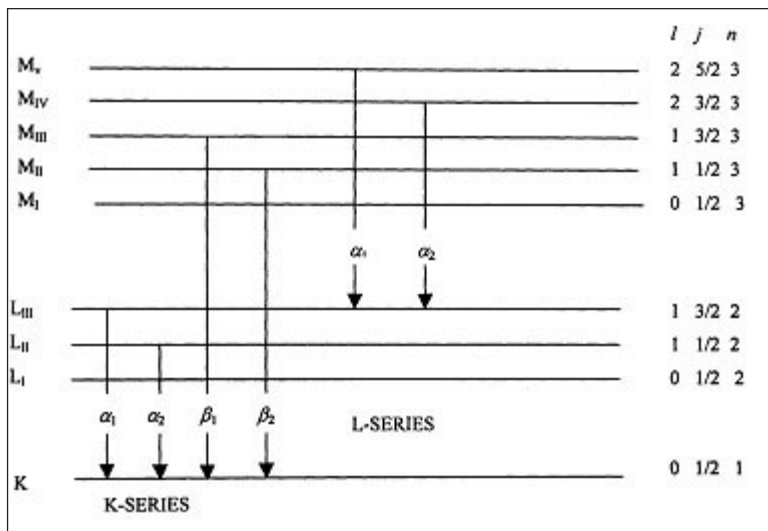
Energy Dispersive X-Ray Analysis (EDAX)

This technique is generally associated with scanning electron microscope. In this technique, an electron beam of 10-20 keV strikes the surface of a conducting sample which causes X-rays to be emitted from the point of incidence. The energy of the X-rays emitted depends on the material under examination. By collecting and analyzing the energy of these X-rays, the constituent elements of the specimen can be determined. The X-rays are generated in a region of about 2 microns in depth. The electron beam scans across the material and an image of each element in the sample can be acquired. In this method however, elements of low atomic number are difficult to be detected. The detector, which is a lithium doped silicon (SiLi), is protected by a Beryllium window and operated at liquid nitrogen temperatures. The absorption of the soft X-rays by the beryllium decreases the sensitivity below an atomic number of 11 (Na). When an X-ray strikes the detector, it will generate a photoelectron within the bulk silicon which in turn generates electron-hole pairs. A strong electric field attracts the electrons and holes towards opposite ends of the detector. The size of the current pulse thus generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. The X-ray spectrum obtained gives information on the elemental composition of the material under examination. Figure C shows a schematic EDAX spectrum of a stainless steel sample from which the elemental composition can be obtained.



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Figure 2. Structure of X-ray levels.



Production of Characteristic X-rays

As mentioned above, characteristic X-rays are produced due to the transition of the electrons in different shells which leads to different characteristic X-rays, viz. $K_{\alpha 1}, K_{\alpha 2}, K_{\beta 1}, K_{\beta 2}, L_{\alpha 1}, L_{\alpha 2}, \dots$, etc., The partial energy level diagram showing the transitions leading to K and L series of X-rays is shown in Figure 2.

The selection rule of these transitions is given as

$$\Delta l = \pm 1; \Delta j = 0, \pm 1, \Delta n \geq 1, \tag{1}$$

where n, l and j are the principal, orbital and total angular momentum quantum numbers respectively. The energy of the characteristic X-ray emitted from different elements is different and thus it gives the unavoidable signature of the particular element contained in the sample. Moseley (see Box 3) found that the square root of the frequency ν of each series varied smoothly as the atomic number Z of the target element. By plotting $\sqrt{\nu}$ against Z , he established the law

$$\sqrt{\nu} = C(Z - \sigma), \tag{2}$$

where C is the proportionality constant that is independent of Z and σ is the screening constant whose value lies between 1 to 2 for

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Box 3. Moseley's Work

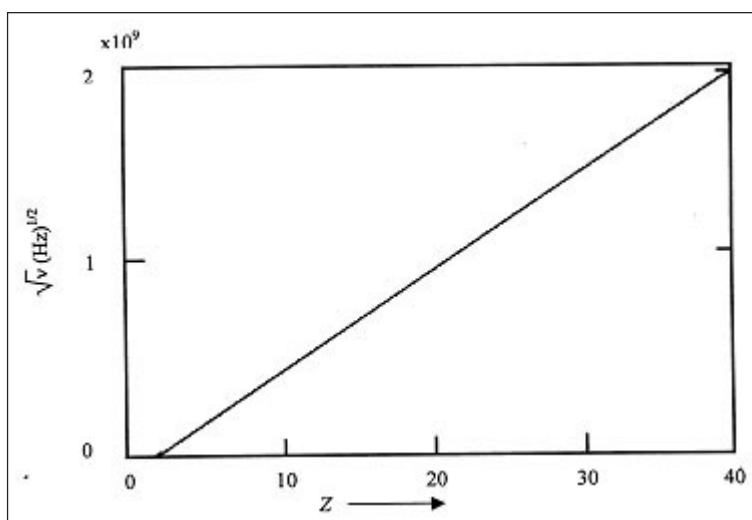
In 1913 H Moseley observed regularities in X-ray spectra. The spectrum observed was characteristic of the material used as target in the X-ray tube. The spectrum consisted of a continuous spectrum upon which was superimposed a line spectrum. He studied such line spectra of thirty nine elements from aluminium to gold. In most cases the line spectra consisted of two groups of lines – the K series and the L series, however for heavier elements other series of lines appeared. For a given target element, frequencies of K lines were higher than the L lines. For heavier elements other series of lines appeared at still lower frequencies. By interpreting the regularities, Moseley was able to establish the identification of Z , the atomic number from which it was known that different elements emit different characteristic X-rays having different energies.

the K series and is in the range of 7.4 to 9.4 for the L series. Moseley's plot of $\sqrt{\nu}$ against Z is shown in *Figure 3*.

By interpreting the regularities, Moseley was able to establish the identification of Z , the atomic number from which it was known that different elements emit different characteristic X-rays having different energies. In some cases, the characteristic K_{α} X-ray photon is used up to eject an electron from the L shell and hence no radiation will come out. This type of radiationless transition is known as Auger effect and the electrons are called Auger electrons. One consequence of the Auger effect is that the lines of a given series are not as intense as would be predicted from the number of vacancies created in the associated orbitals. The fluorescence yield is defined as the ratio of the number of photons emitted per unit time to the number of vacancies formed during the same time. Mathematically, the fluorescence yield ω_K is expressed as

$$\omega_K = \Sigma (n_K)_I / N_K, \quad (3)$$

Figure 3. Moseley's plot of $\sqrt{\nu}$ against Z .

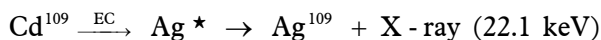


The Compton peak in the spectrum provides information on the velocity distribution of electrons and also for examining electronic structure of solids.

where $(n_K)_i$ is the rate at which photons of spectral line i are emitted and N_K is the rate at which K shell vacancies are produced. Auger effect can also occur in higher orbits. In that case the electrons from the L shell, M shell and N shell are known as primary, secondary and tertiary Auger electrons respectively.

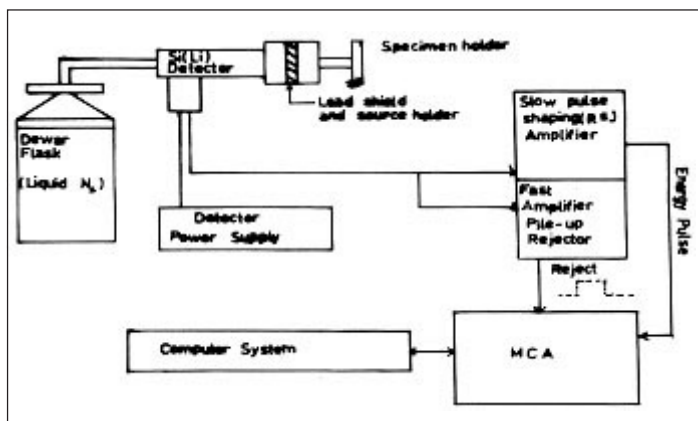
Experiment and Analysis

Quantitative estimation of elements is of importance in environmental, biological, agricultural, metallurgical, geological, archeological, semiconductor, medicinal and forensic sciences. The different radioactive sources used for the energy dispersive X-ray fluorescence (EDXRF) are given below with their energies.



In addition to the above radioactive sources, I^{125} may also be used. Americium can excite K -lines of elements with $Z \leq 69$. Cadmium can excite K -lines of elements with $Z \leq 44$ and L lines of $Z \geq 69$. Lastly, iron can excite K -lines of elements with $Z \leq 23$. The interaction of γ -ray or X-ray photons with matter can be divided into three processes viz. photoelectric effect, Compton effect and pair production (see Box 4). Of these, the photoelectric effect largely favours the production of the characteristic X-ray as the photons used are only in the range of a few keV. The Compton

Figure 4. EDXRF set-up.



peak in the spectrum provides information on the velocity distribution of electrons and also for examining electronic structure of solids. The profile of the experimental set-up of EDXRF is shown in Figure 4. Here, the γ -ray or X-ray photon from the radioactive source in the annular groove is made to fall on the sample to be analysed. The char-

Box 4. Interaction of Photons with Matter

1. **Photoelectric effect:** The photoelectric effect is the principal mode of interaction of low energy photons with matter. In this process, photon of energy E_g is wholly absorbed by an electron of the atom and the electron is ejected with an energy E_e given by

$$E_e = E_g - E_b,$$

where E_b is the binding energy of the electron in the atom. Absorption of a photon due to photoelectric effect decreases sharply with increase of photon energy, but increases rapidly with atomic number Z of the absorber material. The probability of photoelectric absorption is directly proportional to Z^5 and E_g^{-3} .

2. **Compton effect:** For intermediate energy photons over a wide range (~ 0.1 to 10 MeV), the interaction is dominated by Compton scattering. In this process, the photon interacts with a free or loosely bound electron, transfers a part of its energy to it and gets scattered as photon of corresponding reduced energy. The energy and momentum of the incident photon are shared between the scattered photon and the recoil electron.

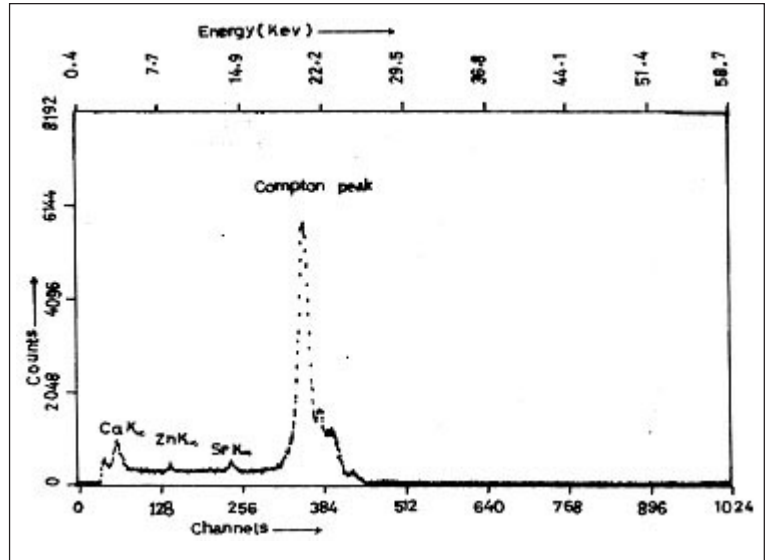
3. **Pair production:** When the energy of a photon exceeds twice the rest mass of an electron (1.02 MeV), there is a probability that the photon is converted into an electron positron pair. This process can occur only in the presence of nuclear Coulomb field which helps to balance energy and momentum. In *EDXRF*, the X-ray energy being in keV range, this process does not take place.

characteristic X-ray emitted from the sample is detected by a Si(Li) detector cooled at liquid nitro-gen temperature (77° K). Generally, in most of the detectors, the charge is so small that the signal pulses obtained, if used without an intermediate amplification, will be lost as noise. So the output signal from the detector is fed to the pre-amplifier. This signal is again amplified using a linear amplifier and it is made near gaussian in shape. Lastly, the amplified pulse is fed to the multi channel analyser (MCA) fitted to a personal computer so that the complete spectrum of the X-ray peaks of the different elements can be seen online. The elements present in the unknown sample are classified according to their characteristic X-ray lines. The concentrations of the elements are related to the intensity of the X-ray lines.

The EDXRF spectrum of a kidney stone is shown in *Figure 5* from which it can be seen that the major constituent is calcium with smaller quantities of zinc and strontium. For this analysis, the



Figure 5. EDXRF spectrum of a kidney stone.



kidney stone was washed with distilled water to remove possible blood constituents. After drying, it was grounded into fine powder and mixed with a binder (cellulose powder) and pressed into a thin pellet of 2.5 cm in diameter. The pellet was used for irradiation. The area under the peaks is used for the calculation of the concentration. The set-up was calibrated using standard radioactive source and the geometry was kept constant for all the subsequent measurements. This technique can be effectively used for non-destructive analysis of archaeological specimens.

A schematic diagram of PIXE set-up is shown in *Figure 6*. The high-energy protons (within the range of 2.5 MeV to 3.0 MeV) are made to bombard the sample to produce characteristic X-rays of the elements contained in the sample. These X-rays are detected as in EDXRF technique. A typical PIXE spectrum of a kidney stone is shown in *Figure 7*. The elements detected are Ca, Fe, Zn,

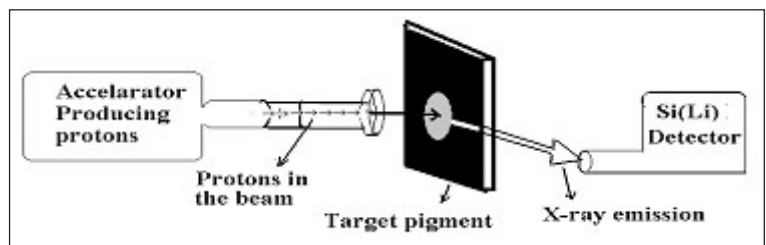


Figure 6. PIXE experimental set-up.



Sr with their concentrations 7.7%, 25 ppm, 10.5 ppm and 1.2 ppm respectively. The concentrations were calculated using coal fly ash as standard sample. It can be seen from *Figures 5 and 7* that the background is substantially lower in EDXRF (*Figure 5*) compared to PIXE (*Figure 7*). This means that the sensitivity of EDXRF is also better.

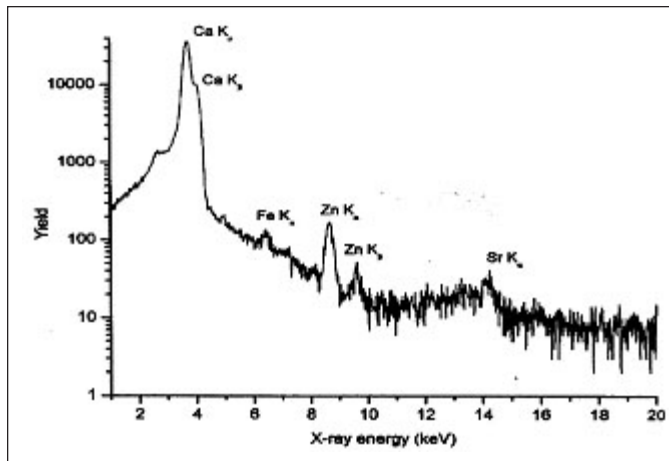


Figure 7. PIXE spectrum of a kidney stone.

Conclusion

EDXRF and PIXE are becoming important tools for the elemental analysis of unknown samples and their applications are increasing everyday for detecting elements at trace quantities and also for their multi-elemental detection capability. These techniques are particularly useful for non-destructive evaluation of specimens, an important advantage for the study of old art work and archaeological samples.

Suggested Reading

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