X-RAY TECHNOLOGY AND HIGHWAY RESEARCH
Report on an Equipment Symposium: Chicago, June 7-11, 1965

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The x-ray symposium sponsored by Philips Electronic Instruments in Chicago, on June 7-11, 1965, provided excellent training in x-ray spectroscopy. It has made possible a more thorough understanding of x-ray principles and brought us up-to-date on many of the latest developments in x-ray technology. The program or format of the symposium covered three areas:

1. A brief discussion of x-ray theory in general.
2. A rather detailed discussion of the principles of x-ray analytical instruments and their applications.
3. New developments in the field of x-ray spectroscopy.

In addition to discussion of these subjects, this report includes a final section covering specific applications of x-rays to highway materials.

Theory of X-Rays

X-rays can be considered to be of the same nature as light, since both travel in waves, and differ only in their respective wavelengths. X-rays have wavelengths in the order of 10^{-7} mm or 1 angstrom (Å), and visible light has a wavelength range of 4.0×10^{-4} mm to 7.5×10^{-4} mm or 4000 to 7500 Å. X-rays are produced in a vacuum tube where a high-voltage source causes an electron filament cathode to emit electrons toward an anode target. When a free electron X strikes an atom of the target element (Fig. 1), it excites and removes an electron e from one of the shells; for example, the atom's K shell ($n = 1$). Since electrons in an atom tend to return to their ground state, an electron from another energy level (for example, the L shell) will eventually fall back into the vacancy in the K shell, causing the difference in energy to be emitted as an x-ray photon. This example is known as "the K-alpha transition." The x-ray photon produced from this transition is a primary x-ray characteristic of the target element.

X-Ray Analytical Instruments

X-ray analytical instruments are distinguished from fluoroscopy and radiography type x-ray instruments by the type of radiation they produce.

Fluoroscopy and radiography instruments operate at high tube voltages up to several hundred kilovolts (kv) and always use short wavelength target elements such as platinum and tungsten to produce "hard" or high penetrating x-rays. Such penetration is necessary in fluoroscopy and radiography because it is important that the x-rays pass rapidly through the body without being absorbed. Analytical instruments operate at tube voltages up to 100 kv, but usually are in the 50 to 60 kv range. They use many target elements, including platinum and tungsten, but since high penetration is rarely necessary analytical instruments produce a relatively low penetrating or "soft" type of radiation. Analytical instruments can be divided generally into two groups: x-ray diffraction and x-ray spectroscopy. Diffraction instruments are used to determine the crystal structure and the chemical compounds present, while the spectrograph performs an elemental analysis.

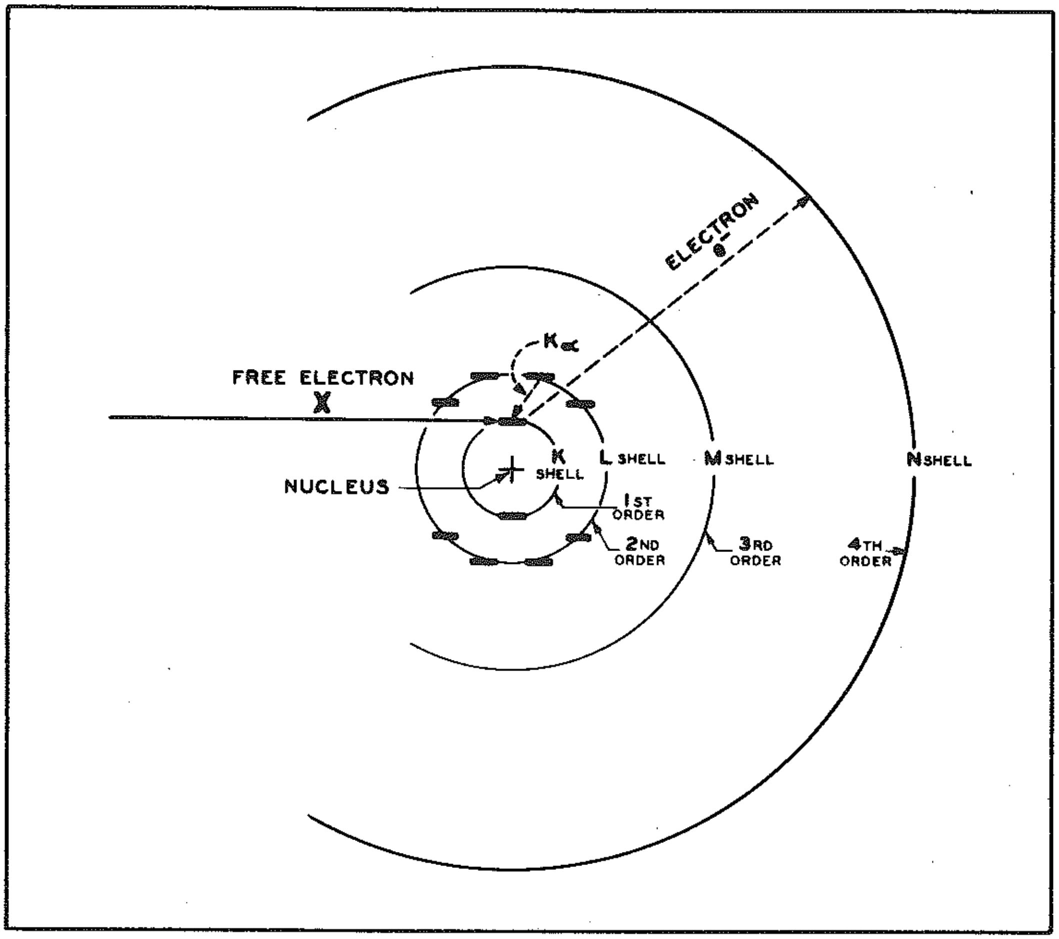

Figure 1. K-alpha transition.

1. X-Ray Diffraction: In x-ray diffraction instruments, a polycrystalline sample is bombarded by monochromatic primary x-rays of known wavelength emitted from the x-ray target, and the various crystal planes of the specimen material reflect the projected rays. The rays are reflected in accordance with Bragg's Law:

$$n\lambda = 2d \sin \theta$$

where

n = order number,
λ = wavelength of primary x-rays,
d = interplanar spacing, and
θ = angle of reflection.

These reflected or diffracted rays can be recorded by means of a powder camera or a diffractometer. If a powder camera (Fig. 2) is used, the diffracted rays form a set of concentric cones around the incident x-ray and expose a film strip revealing the interplanar spacings d that are characteristic of the crystal structure of the specimen. When a diffractometer (Fig. 3) is used to record the diffraction pattern, an x-ray sensitive detector is used in place of the film to receive the reflections from the specimen. The detector is mounted on a movable element or goniometer which is coupled mechanically to the specimen holder. Whenever the angular orientation of the slowly rotating specimen satisfies Bragg's Law, the incoming x-ray beam is reflected. The reflections, received as impulses, are electronically integrated and amplified and serve as a means of drawing peaks on a chart corresponding to diffraction lines on the film pattern. The angles of reflection θ can be read directly from the recording chart or measured from the film strip and the inter-

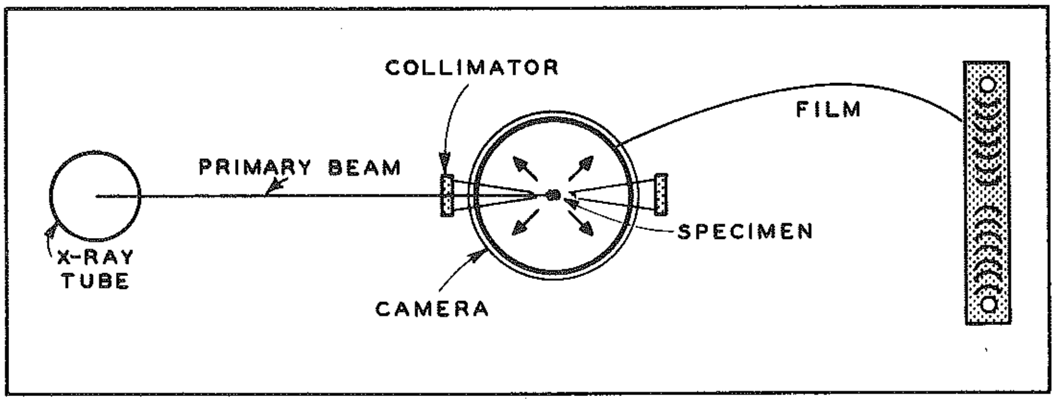

Figure 2. Powder camera.

planar spacing d can be calculated from Bragg's Law, since n, λ, and θ are all known. A set of interplanar spacing values is in effect a fingerprint of the unknown structure. By reference to a data file, the chemical compounds or metallurgical phases can be identified.

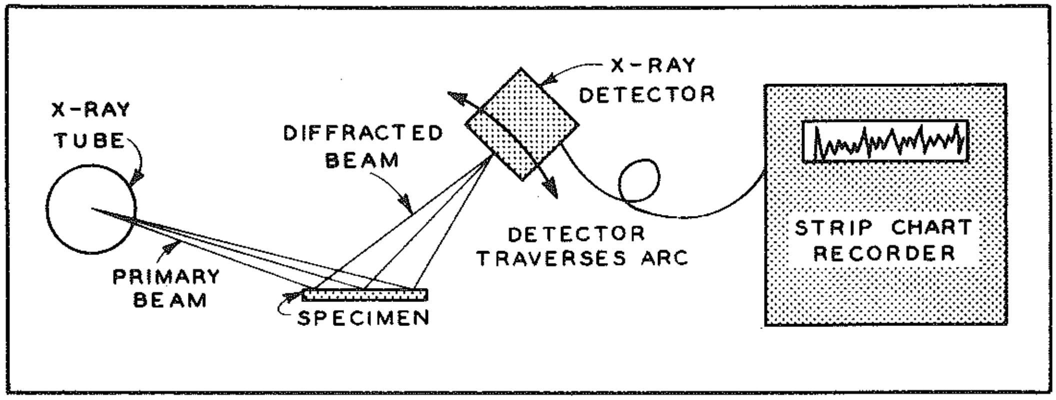

Figure 3. X-ray diffractometer.

2. X-Ray Spectroscopy: There are generally considered to be three types of spectrographic instruments: the spectrometer, the automatic spectrometer, and the electron probe microanalyzer. In all spectrographic instruments, primary x-rays from the tube target bombard and excite the atoms of the specimen, causing the emission of secondary x-rays characteristic of each element in the specimen (Fig. 4).

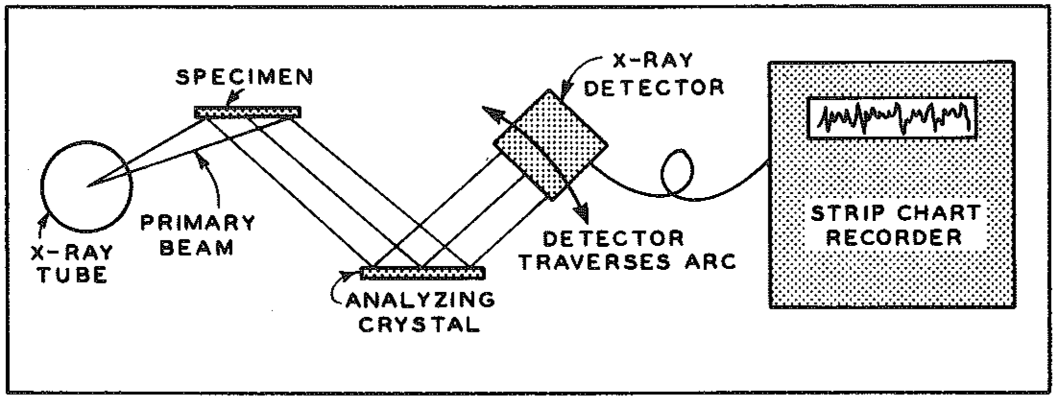

Figure 4. X-ray spectrometer.

These secondary x-rays are directed against a single crystal, called an analyzing crystal, used as a wavelength sorter. The face of the crystal is cut parallel to a pre-selected set of parallel atomic planes of known interplanar spacings. Depending on the angular orientation of the analyzing crystal, the radiation of a particular element is diffracted according to Bragg's Law and permitted to pass to a detector. The current pulses from the detector tube are amplified and can be recorded as peaks on a paper strip chart as with the diffractometer. The position of the peaks on the chart indicates the angle of reflection θ, and since the interplanar spacing d of the analyzing crystal is known, the wavelengths λ of the elements present can be calculated from Bragg's Law. For example, if the angle θ is 40°, d is 1.284 Å, and $n = 1$, the wavelength is $1\lambda = 2 \times 1.284 \times 0.642$, or $\lambda = 1.54$ A. Reference to wavelength data tables indicates this is the wavelength for copper K_{α}. Thus the presence of copper is established as being one of the elements in the specimen. Also, the relative intensities of the peaks serve as an indication of the amounts of each element present. The current pulses can also be counted electronically in a decade scaler with a timer to obtain average counting rates. The data can be read directly from decade tubes or printed on paper tape.

a. The X-Ray Spectrometer is a very versatile instrument. It finds its widest applications in laboratories that handle a wide variety of samples, both on a routine and non-routine basis. It is capable of handling liquid, powder, and solid samples and is able to determine elements, both qualitatively and quantitatively, from sodium (atomic number 11) upward. With special x-ray tubes and long d spacing analyzing crystals such as lead stearate, this range can be extended downward to boron (atomic number 5). Completely unknown samples can be analyzed qualitatively in about 1 hour and, if proper standards are available, a quantitative analysis can be performed in a few minutes. Routine quantitative analyses for specific elements can be performed in many cases as fast as 10 seconds, after calibration curves are established.

b. The Automatic X-Ray Spectrometer is designed for laboratories that run large numbers of routine samples on a strict time schedule. For example, the quality control laboratory of a steel company that maintains a very close control of the blast furnaces, must have a complete analysis of a certain heat of steel in the matter of 3 or 4 minutes. The automatic x-ray spectrometer can be programmed to analyze automatically from one to four samples for any combination of up to 15 elements selected for 24 programmed element or background positions. The analysis can be completed with the data printed out on paper tape within a very few minutes.

c. The Electron Probe Microanalyzer (EPM) is a relatively new entry in the field of x-ray spectroscopy. It combines the features of an optical microscope and an x-ray spectrometer. The specimen area to be analyzed is first detected visually by using the microscope and then subjected to analysis by means of the spectrometer. The EPM operates on the same principle as the conventional spectrometer except that the specimen acts as the target of the x-ray tube (Fig. 5). This allows an extremely small focal point or spot, in the order of 1 micron in diameter. The very small focal point permits analysis of individual precipitates or inclusions in metals, minerals, and other solids. It is also possible to measure such composition gradients as occur in alloy phases, biological tissue, or corrosion layers. In addition, it is possible to analyze individual airborne dust particles or any other particulate matter. The x-rays emitted from the specimen target are directed to the analyzing crystal and thence to the detector, where the x-ray photons are converted to current pulses counted in the same manner as the conventional spectrometer. The EPM appears to have a great future since there are few techniques that can detect the order of 10^{-13} to 10^{-14} grams of an element or perform chemical analysis on areas as small as 1 micron.

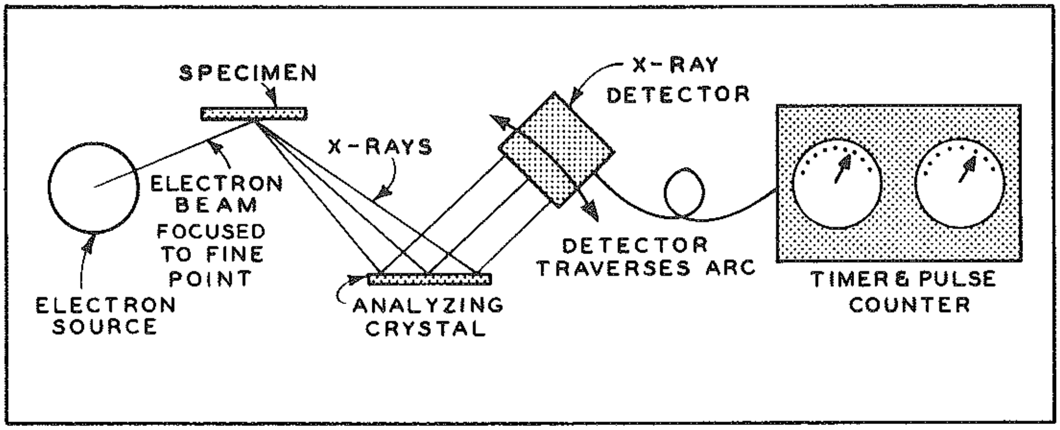

Figure 5. Electron probe microanalyzer.

Some general applications of analytical x-ray instruments in modern industry and government are:

Agriculture - analysis of insecticides for evaluation of insect-killing properties, discovery of trace amounts of harmful elements in plants and foods, and determination of harmful elements such as selenium in animal feeds.

Petroleum - detection and analysis of impurities and additives in gasoline and lubricants.

Plastics - determination of structure and composition of resins and plastics for most efficient application characteristics.

Electronics - detection of trace impurities in germanium, silicon, and other materials used for the manufacture of crystals, diodes, and other components.

Atomic Energy - structure study and element analysis of radiocative materials.

Government Inspection - detection of contraband drugs, determination of dutiable elements in unprocessed raw materials, detection of impurities in food and drugs, forensic investigations, and geological surveys.

Medicine - evaluation and detection of elements present in blood, and the study of structure of dentine and dental enamel.

Metals - elemental analysis of alloys, and of furnace feed and slag; determination of plating and coating thickness; analysis of retained austenite in steel; determination of steel surface hardness and residual stresses; determination and identification of alloy phases, and possible metallurgical history of materials, as well as study of preferred orientation.

Space Technology - development of new alloys and ceramics for missile and rocket components, and solid propellant research.

Chemicals - analysis of raw materials, mixes, and finished products.

Mining - structure studies of minerals, and the analysis of ore, tailings, concentrates, drilled cores, and exploration samples.

New Developments

Many dramatic developments have taken place in the field of analytical x-ray instrumentation in the last few years. Some important examples include thin film mylar window and demountable x-ray tubes, long d spacing analyzing crystals, vacuum path spectrometers, improved detector systems, and highly stabilized electronic equipment.

The limits of detection have been lowered significantly for most elements, in some instances a whole order of magnitude. Silicon in steel, for example, can now be detected at 0.001 percent; formerly, 0.02 percent was considered good. For many elements, the limit of detection is in the parts-per-million range. For instance, it is now possible to determine iron, cobalt, and nickel in petroleum samples at the three parts-per-million level.

The speed and accuracy with which many analyses can be performed has been greatly increased. For example, in the analysis of brass, copper at 60 percent, zinc at 33 percent, and lead at 1.3 percent can be determined with standard deviations of ± 0.10 percent, ± 0.08 percent, and ± 0.02 percent, respectively. The analysis time for these elements is about 30 seconds. Manganese in steel in the range of 0.3 to 0.4 percent can be determined within 10 seconds with a standard deviation of ± 0.004.

The most dramatic improvement in x-ray analytical techniques has been the extension of low atomic weight element detection from sodium (atomic number 11) down to boron (atomic number 5) in the last three or four years. The low atomic weight or "light" elements have always presented special difficulties for x-ray detection, for two reasons: 1) the characteristic x-rays fall in the wavelength range of 64 Å for boron to 11.9 Å for sodium, and are so strongly attenuated even by air that most of the radiation is lost before reaching the detector; and 2) the long wavelengths of these elements require long _d_ spacing analyzing crystals to satisfy Bragg's Law so that diffraction may occur. This ability to detect the low atomic weight elements is especially significant, since for the first time the element oxygen can be determined directly. Formerly, oxygen could only be determined by indirect means based on calculations of the oxides of the metals present. Carbon in steel, nitrogen in fertilizers, and fluorine and boron in minerals are some other significant benefits of this recent ability to determine the "light" elements. Previously, analysis for these elements often required special equipment, difficult separations, and long, tedious wet chemical techniques.

SPECIFIC APPLICATIONS OF X-RAY METHODS TO HIGHWAY MATERIALS

Cement

Cement can be analyzed to directly determine the compounds present. Calcium oxide, calcium hydroxide, tricalcium aluminum silicate, calcium sulfate, complex silicates containing iron, and calcium and magnesium carbonates are determinable. This permits rapid analysis for checking against specifications, comparing different cements, and choosing special purpose cements having high or low contents of specified compounds such as tricalcium silicate. The hydration of concrete mixes can be studied to determine the rate of formation of complex hydration products.

Metals and Alloys

X-ray methods have found broad industrial applications in metals analysis. Determination and identification of alloy phases, and possible metallurgical history of materials with respect to previous heat treatment, quench, and anneal can be investigated. Micro-constituents and segregation in alloys can be studied. Metallic elements in alloys can be identified and determined. X-ray methods thus are useful for checking metals against specifications according to crystal structure and alloy content and for direct comparison of different samples. Analysis of weld beads and study of weld failures due to the effects of the welding process on the parent metal with respect to the development of segregations and inhomogeneities can be conducted. Plating thickness of zinc, cadmium, tin, copper, and nickel on steel and other base metals can be readily measured as a specification check.

Aggregates, Soils, and Clays

These materials can be identified according to mineral type and analyzed for the chemical compounds present to exclude inferior materials. Such analysis by other methods is long and tedious or impossible. Potentially expansive clay in limestone coarse aggregate can also be detected. Inhomogeneities such as small veins in minerals can be studied. Slag aggregates, which seem to be used increasingly, are already analyzed industrially by x-ray methods.

Coatings

Identification and determination of compounds and elements in the pigment, extender, and dryer components of paints and concrete curing compounds would be greatly facilitated by x-ray methods. Other instrumental methods are less well suited for the task than x-ray, and chemical methods are prohibitively time-consuming.

Rubber, Plastic, Wiring Insulation, etc.

The crystallinity characteristics of such materials can be compared in relation to physical properties. It would be impossible, for instance, to say whether a change in hardness of these materials was due to crystal structure or a change in the amount of plasticizer added to the sample. Inorganic materials such as graphite, metals, and sulfur can also be detected and determined. This provides a powerful lever to be used in conjunction with spectrophotometric methods for comparing, identifying, and analyzing rubbers and plastics.

Concrete Additives and Admixtures

X-ray methods offer large improvements in speed and selectivity for analysis of concrete additives such as fly ash, retarders, anti-shrinking mixtures, and patching compounds. The x-ray data would aid identification and determination of the ingredients and also permit comparison of similar products.

Corrosion Studies

Analysis of dynamic systems is possible by x-ray methods. This means that it is possible to study a system or chemical reaction while it is actually taking place. For example, it would be possible to study corrosion cells and corrosion reactions by watching the formation and rate of formation of the complex corrosion products. In addition, the chemical compounds present in the corrosion products can be identified and determined quantitatively. This would be especially valuable in investigating the mechanism of zinc corrosion, where the corrosion products are often mixtures of several compounds. Knowledge of the mechanism of a reaction can often be used to stop or inhibit the reaction.