

Screenings

from the Soil Research Lab

IOWA ENGINEERING EXPERIMENT STATION
IOWA STATE UNIVERSITY of Science and Technology
AMES, IOWA

July - August, 1958
Vol. 2, No. 4

ABC's of yz X RAYS

'Way back in 19 ought '95, when you and I were young, Macbeth, a German Herr Prof. Wilhelm Röntgen (we called him Bill) was shooting high voltages through a vacuum tube when invisible rays seemed to zip through the shield and make some nearby chemicals brightly fluorescent.

"Ach! Was ist maken dem Chemicallen go geglitter?" exclaimed Bill, swearing off liquor and reaching for his hat.

There were no comic books in those days, so scientists weren't well up on what they were supposed to find out. Fortunately from his previous training Bill could pretty well work along on his own.

After thorough investigation the invisible rays were still unexplained. They were therefore called X rays, X signifying unknown, like Uncle Chester's signature. Nowadays they are sometimes called Röntgen rays except by Uncle Chester, who puts down X for everything, X, XX, XX X XXX X X. As a rule in school the plowheads drool, infants stool, and eggheads graduate but don't win elections.

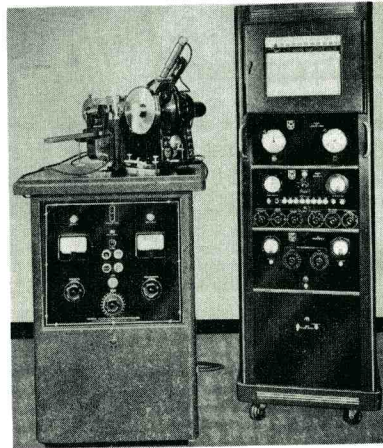
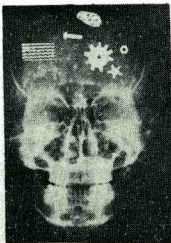
Where, why, and how?

The next decade was one of wild hypothesis and speculation on the nature of X rays, further illustrating suitability of the term X. In 1912 Herr Dr. Prof. Max von Laue stumbled onto a fantastic double-barreled discovery that still makes a physicist's eyes glisten and puts a lump in his throat.

In one gala experiment Von Laue and associates demonstrated the nature of X rays and also incidentally the internal structure of matter.

It's hard to grasp how they learned so much doing so little. Nowadays physicists walk on tile floors down guarded corridors, and the price has gone up.

Dr. R. L. Handy, professor-in-charge of the X-ray project. He also writes Screenings, or could you tell?



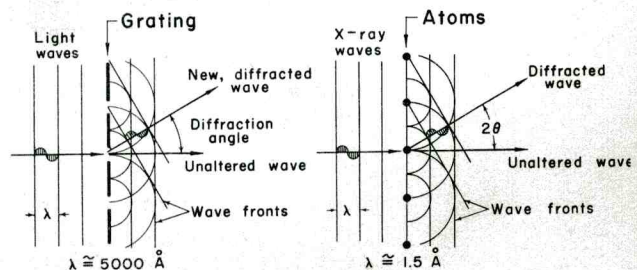
A modern X-ray diffractometer. The X-ray generator and tube are housed on the left. Rays are caught by a Geiger or scintillation counter which sends signals to the electronic recording unit, on the right, so it can draw those jiggly lines.

Von Laue took his clue from the diffraction grating, long known for its effect on visible light. A diffraction grating is nothing more than closely scribed lines on a glass plate. White light shining through the grating shows colored spectra, because individual slits are close enough that the light waves emerging will reinforce or annul at certain angles.

A grate day comin'

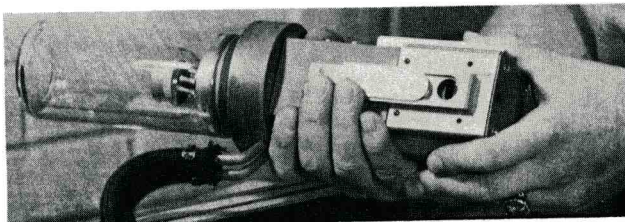
Perhaps a diffraction grating could demonstrate a wavelike character for X rays, but the suspicion was that their wavelength was extremely short, and how could one scribe a grating fine enough?

One day Von Laue heard of an unproved notion on what makes crystals pretty. Their flat faces could indicate an orderly internal arrangement of atoms. Ah, he thought, if a crystal is really composed of closely spaced atoms it could be a natural grating! Well worth a try.



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Friends of Von Laue shot an X-ray beam through a crystal of zinc sulphide and caught the invisible diffracted glitter on a photographic plate. Breathlessly they skittered to the darkroom to see what developed. Eureka! Spots! The experiment was a success. It proved the wavelike character of X rays, and the orderly internal arrangement of atoms in a crystal. Von Laue, like Röntgen, got the Nobel prize. Progress stems from uncommon sense.



A peek through an open window of an X-ray tube. Hoses are for water cooling of the target.

Equation

The Bragg Law reads

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

Where n is a whole number, λ is the X-ray wavelength, d is the distance between layers of atoms, θ is half the diffraction angle, $=$ is $=$, and 2 is 2 . If you want to play the hep physicist, derive the Bragg Law from the sketch. If it's any consolation this also won the Nobel prize for both Drs. Bragg.

Laying down the law

Significance of the Bragg equation? Let us take a crystal and reflect. The diamond seems very popular for one reason or another. Diamond gives a strong diffracted X-ray beam at an angle 2θ of 43.9° from the incident beam. What's the interplanar spacing?

Ans. The X-ray tube we're using gives a wavelength of 1.54\AA , and for a strong reflection n usually equals 1. Plugging in and turning the crank, we have

$$\begin{aligned} n\lambda &= 2d \sin \theta \\ 1(1.54) &= 2d \sin (43.9^\circ / 2) \\ d &= 2.06\text{\AA} \end{aligned}$$

From this, if we are of that turn of mind, we can figure out the size of the atoms in a diamond. Or if we X ray an unknown and have a strong reflection at $d = 2.06\text{\AA}$ we can suspect the presence of diamond and run right out and sell stock. Much money can be made this way if one is not adverse to travel.

About that

A WITH THE ° OVER IT...

Atomic dimensions are so tiny we need a tiny unit of measure--something less than an inch, if you please. The choice is the Angstrom, named after a Swedish physicist and abbreviated \AA . One $\text{\AA} = (10)^{-8}$ cm, or one hundred millionth of a centimeter, or one thousandth of a micron. This is rather small. The diameter of an oxygen ion, the building block for most minerals, is 2.7\AA .

Something to Bragg about

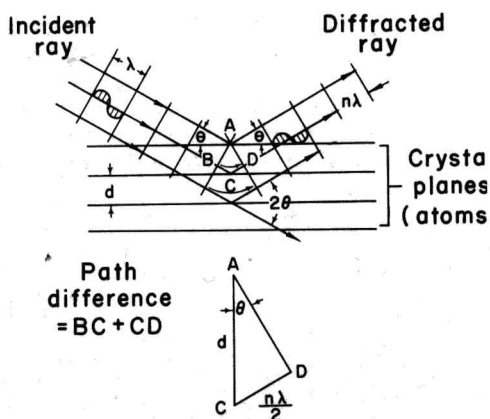
While Von Laue's discoveries were momentous, the practical use of X rays for analysis of crystals was a little hard to grasp. The mathematics proved hairier than a Grecian male stomach.

Then two British scientists, Sir William Henry Bragg and his son William Lawrence made a beautifully imaginative simplification. They visualized crystals as stacked layers of atoms which in effect reflect X rays something like a stack of mirrors.

Angle tangle

The only catch is that the incident angle must be right for "reflection" to occur. Why? Because X rays behave like light waves, and must be in phase in order to get anywhere. Out of phase they annul quicker than a high school marriage.

For adjacent reflected waves to remain happily married, the spaces between atomic layers must account for an X-ray path difference of a whole number of wavelengths, abbreviated $n\lambda$. If we let $n\lambda$ equal path difference and exercise reasonable care in trigonometry, the result is the Bragg Law, easily the most important equation in X-ray diffraction.



X RAYS FOR THE INSIDE STORY

But why all the fuss, Farnsworth? Everybody knows that real crystals are as rare as sin in Congress. But now with a little inside information we know a lot more about crystals, and we aren't at all sure about Congress.

For one thing we know that internal crystalline structure is much more common than previously supposed, and frequently doesn't show on the outside. In fact, the vast majority of solid materials have crystalline structure. Metals, woods, rocks, clays, plastics, etc., are mostly crystalline. Even our secretary is included, from her hair, muscles and bones right down to her toenails. This is pure speculation, of course.

In a soil lab, X ray diffraction is the only sure way to identify many minerals, particularly clays too fine to see adequately under a microscope. For chemical reasons these are the most important grains to know. Without X ray we stumble and stab in the damnable dark.

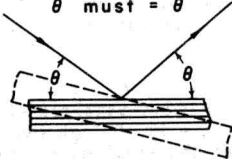
TAKE A POWDER

Many techniques have been worked out for measuring X-ray diffraction angles. Often single crystals are oriented in the X-ray beam, and diffractions are recorded on photographic film.

Unfortunately this won't work very well for fine-grained materials such as soils; how in holy hosiery are you going to orient individual crystals when they're too small to see?

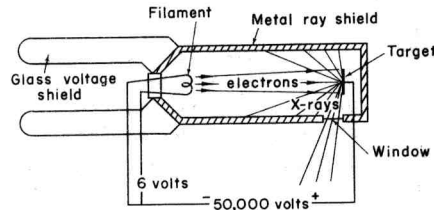
The solution is rather simple, because only crystals nearly perfectly oriented will reflect X rays. Therefore one X rays a powder--if orientation is random, a few of the crystals will surely reflect. To increase the number of orientations and assure getting all reflections, samples are ground very fine and are often rotated or spun while in the X-ray beam. Even so, fewer than a third of the crystals in the powder will diffract. On the other hand if you're facing a machine gun it's not the bullets that miss that count.

For diffraction, a crystal must be oriented;
 θ must = θ



Cameras but no lenses

An X-ray diffraction "camera" looks about as much like a conventional camera as a crippled yo-yo. It won't click and it won't focus; all it does is steady the subject and hold the film.



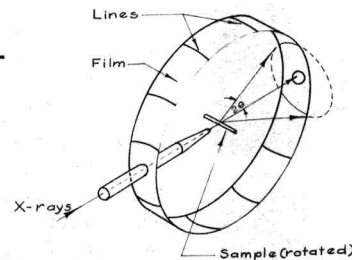
ABOUT X-RAY TUBES...

Practically any vacuum tube, including your TV picture tube, can generate X rays if the voltage is high enough. Electrons stream from the heated filament to the plate, and the higher the voltage across the tube the faster the electrons travel. In the neighborhood of 20,000 volts, they hit so hard that other electrons are displaced in the plate, now called target. When they find their way back into orbits energy is released as X rays, similar to the gamma rays from nuclear reactions.

Wavelength depends on target material. Heavy elements such as tungsten give short wavelengths which have greater penetrating power and are known as hard X rays. These are most useful in medicine or industrial radiography. Soft X rays of longer wavelength are more satisfactory for X-ray diffraction, because of better diffraction angles and less secondary fluorescence, or emission by the sample.

The most commonly used powder camera dates back to about 1917 when it was simultaneously dreamed up by Hull in the U.S. and Debye and Scherrer in Germany. In a Debye-Scherrer camera the powder sample is put at the center of a circle and shot with a beam of X rays. Diffracted rays are caught by film arranged around the circumference.

As the powder sample rotates in the beam one can imagine the tiny glints of light that reflect from individual crystals the instant they reach proper orientation. The glints are recorded on special fast film which has emulsion on the sides to better conserve the X-rays. The camera must be loaded and unloaded in a darkroom.



X-rays may be observed for line-up purposes by use of a fluorescent wand. Arrow shows the sample supported at the center of the Debye-Scherrer camera where it is rotated with an electric motor. Film fits in the cassette around the outside.

Diffracted rays from any one d spacing will be at a constant 2θ angle with the incoming beam of X rays, so their locus is a cone. This causes arcs, or halos, on the film. Diffraction angles are easily measured from the film and converted to d spacings by the Bragg equation.

Take an order

An X-ray diffraction film has many lines, partly because n in the Bragg equation is not always equal to one. It can equal 2, 3, or even more if we could count. Each value of n gives a different diffraction angle and a new line. But the angles are entirely predictable. When $n = 1$ we say we have a first-order reflection; $n = 2$ gives a second-order reflection, and so on.

For example, diamonds are a girl's best friend and have a major spacing of 2.06Å. Girls, at what angle will the second-order reflection occur?

As if you didn't know,

$$2(1.54) = 2(2.06) \sin \theta$$

$$\theta = 48.4^\circ, \text{ or } 2\theta = 96.8^\circ$$

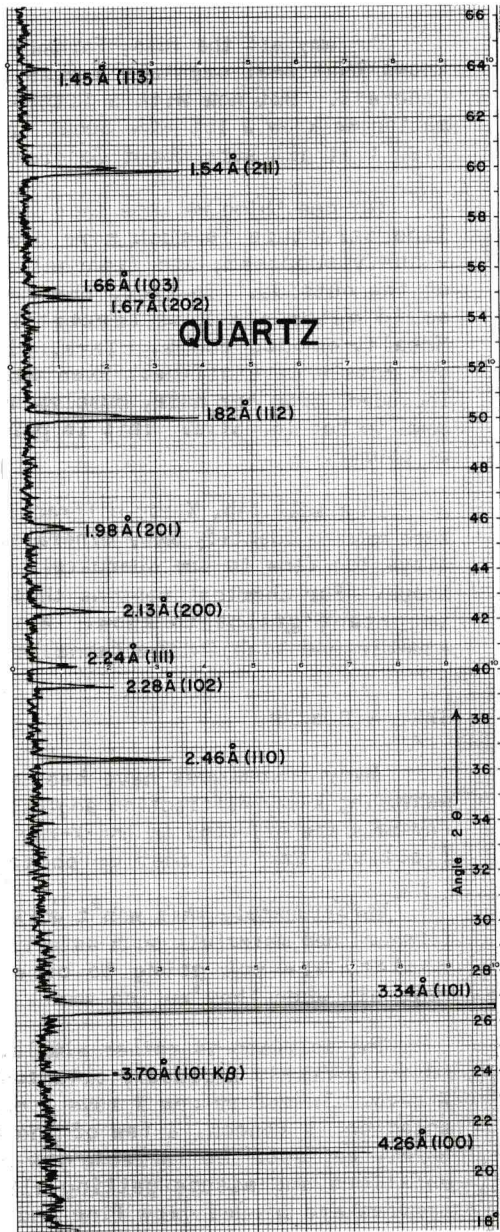
Note the 2θ angle is much higher. In fact, it is the same as for a d spacing of 1.03Å. Actually diamond is a bad example; it's so perfect the second order annuls. We should have used something cheap, like zircon.

KEEPING COUNT

Film detection of X rays is a little slow and messy and doesn't look very scientific. Better to have some blinking lights.

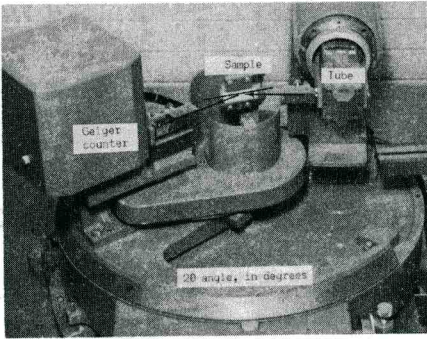
In 1928 Geiger and Muller invented a counter tube that measure X-ray intensity directly, and in 1935 the tube was adapted for X-ray diffraction. Only as recently as 1945 was the instrument perfected, partly due to some tricky re-design by an American named Friedman.

Soon afterwards the first commercial diffractometer came out, built by the then North American Philips Co. (Norelco). At present two very warm competitors for the U.S. diffractometer trade are Philips Electronics, Inc. (new name) and General Electric (Progress is our most important product). Both make exceptionally fine instruments, and we don't mean electric shavers or vacuum cleaners, although they're okay too.



X-ray diffractometer chart for quartz. Peaks occur at specific 2θ angles, converted to d spacings by the Bragg Law. Numbers in parentheses are Miller Indices for crystal planes.

Opposite is a Debye-Scherrer film for quartz. The 2θ angle is 180° at the center of the hole, 0° at the small mark. Bracket shows the approximate amount covered by the strip chart, which correlates with lines in the light half of the film. Extra lines in the dark half are from unfiltered X rays.



X-ray diffractometer setup for measurement of 2θ angles. Arrows show paths of the incident and reflected X-ray beams. As the Geiger counter moves and scans the arc, the sample is turned to maintain equal angles with both rays.

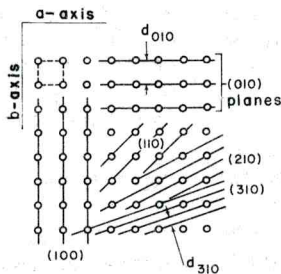
Robot

A diffractometer is nothing more than a glorified powder camera with a Geiger counter scanning the arc formerly occupied by the film. Counts are fed to a ratemeter, and the counting rate is continuously recorded on a strip chart. While the machine scans through different 2θ angles the chart runs and a pen draws peaks. As with the diffraction halos on the film, each peak represents a particular d spacing. The 2θ angles can be read right off the chart and converted to d's through the Bragg equation.

Plane talk, please

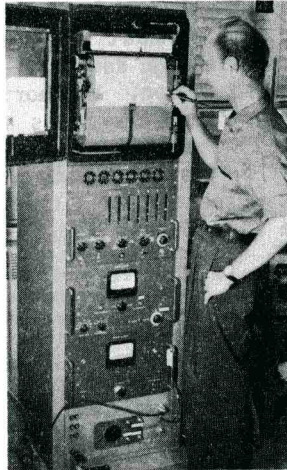
Why so many peaks? Higher order reflections contribute, but in addition there are a lot of ways to slice a crystal and still have a plane full of atoms. Just look at crystal faces--they go in all directions, practically. A glance at the sketch shows why. Different directions give different interplanar spacings, which in turn gives different diffraction angles.

Obviously we need nomenclature. Fortunately a system of Miller Indices was worked out years ago by mineralogists to describe faces on a crystal. We now know the faces are parallel to interior atomic planes. Once a crystal structure has been worked out, a Miller index number can be salvaged for every d spacing.



Routines and Shortcuts

Enough of theory! There is left but one major question: how do you use it? With every



Dr. Elmer A. Rossauer, a recent addition to the staff, looks over the flickering lights. Elmer graduated from the University of Bonn, West Germany. The recorder is hard at work spelling out quartz.

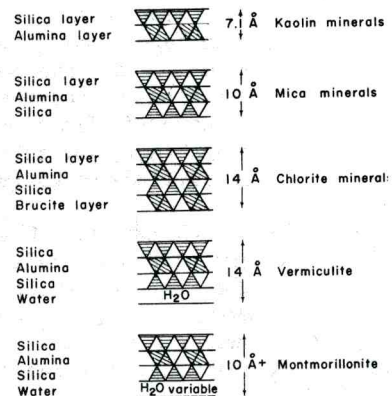
crystalline material giving different lines and d spacings it isn't long before we're submerged in data sufficiently deep to drown. Two unknowns can double the number of diffractions, and you don't know which peaks belong to what. Four unknowns can spell only confusion.

Fortunately, A.S.T.M. to the rescue! The American Society for Testing Materials has published some 7000 Diffraction Data Cards compiled by many workers and gleaned from the stacks of science under cover. Cards are catalogued by the three strongest lines for each material. For convenience in sorting, the lines can be punched around the edge of the card or run out through I.B.M.

Special topic: clay minerals

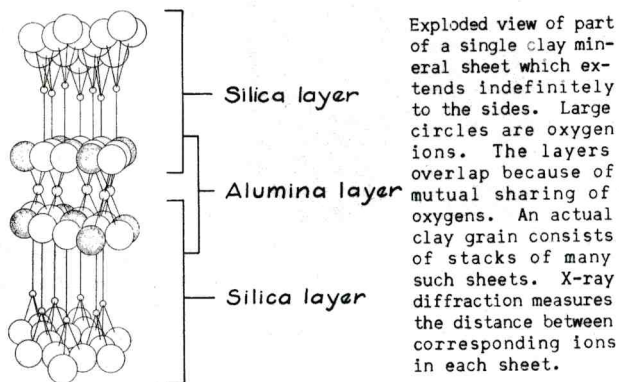
Clay minerals are the feminine fraction of soils--vital, soft and intriguing, but ultimately hard to reason with. X ray has opened the door to understanding, but clay identification requires special knowledge and technics.

Most clay minerals have a sheet structure and can be grouped according to thickness of the sheets. The thickness depends on the number of structural units such as the silica and alumina layers, and is easily measured by X ray.



Most interesting of the clay minerals is montmorillonite, which drinks water between the plates, expands, and turns soil into a very sticky

mud. You know; gumbo (local term). X rays show montmorillonite to be the most abundant clay mineral in Iowa soils, although kaolinite, illite and vermiculite are also common. Montmorillonite expansion is limited by many chemicals and soil stabilizers. In fact, identification of montmorillonites is aided by treatment with glycerine or ethylene glycol, which causes a uniform expansion and gives a nice X-ray peak.



FINALLY, CHEMICAL ANALYSIS!

Look out, Hornblower, there's alligators afoot. We don't want to sound like instrument salesmen, but the fact is that X-ray diffraction units are easily converted for spectro-chemical analysis. This means a chemical analysis in a matter of minutes where formerly it took days. And all this without destroying the sample, whether it's harsh as hair on a goat or delicate as a buzzard's sigh.

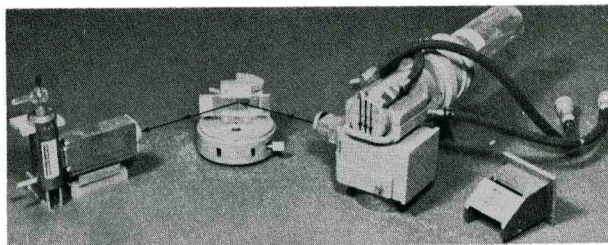
How now? Examine Bragg's Law. Previously we knew X-ray wavelength, or λ , and solved for d . Now we'll use a known d and solve for λ , a very usable idea since λ is characteristic of the elements giving off the X rays.

The technique is to brighten the sample with hard X rays, usually from tungsten, so that elements in the sample give off a secondary emission or fluorescence. These rays are analyzed by diffraction from a crystal with a known d spacing. The right combination of wavelengths is sufficient to identify an element.

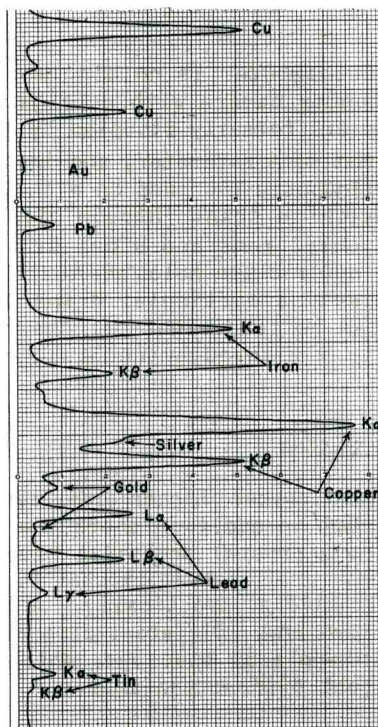
Drawbacks? Elements with low atomic numbers give off such soft X rays they are absorbed by the air. An enclosed helium atmosphere helps. Even so, sodium, oxygen, carbon, and other low-number elements can't be measured. Quantitative analysis requires calibration curves.

IN THE NEXT ISSUE: Tall tales from the Pleistocene.

RLH



Arrangement for X-ray fluorescent analysis. Hard X rays shoot down (triple arrow) and irradiate the sample. X rays given off by the sample are analyzed by diffraction through a known crystal (center) and detection by a Geiger tube (left).



X-ray spectrogram of a Roman coin with quite a weird display of elements. Note the iron. Undoubtedly a secret alloy nobody else knows about. Or maybe one day they decided to clean up the shop and make money.

ACKNOWLEDGEMENTS

Iowa Highway Research Board Project HR-48, X-Ray Diffraction Analysis of Highway Materials, was set up to investigate the composition and changes in soils and other highway materials to better understand their behavior and lead to more intelligent use. Funds are supplied by the Iowa State Highway Commission.

BACK ISSUES!

Now available? Genuine, unexpurgated, uncorrected reprints from Vol. 1, No. 5 on! Going rate 10¢ per copy, but any loose change in the cup will help. Subjects: soil-lime, soil-lime-fly ash, Mexico City clays, loads on pipe, and progress of soil-cement.