

Slide Intro

Even the routine use of X-ray analytical equipment requires a solid understanding of the physics behind it — and of how the instruments work.

Because of this, and because X-ray systems are quite expensive, two separate specializations have emerged: one in X-ray diffraction, and another in fluorescence analysis.

At this event, you'll hear from experts in both fields who will go into detail.

I'm not one of those experts. I'm a former service technician — someone who had to work with both methods simply because the job required it.

So today, I'll try to give you a simple comparison of XRD and XRF — their similarities and their key differences.

I hope this approach feels fresh and useful. And above all, I hope it helps you better understand both techniques.

Slide Why Tao

You've probably heard of Confucius — a court philosopher, scholar, and teacher of high-ranking Chinese officials some 2,500 years ago.

Around the same time, a Chinese peasant named Lao Tzu was also thinking about philosophy. He observed that everything in nature is made of two opposite forces: yang — the male principle, and yin — the female.

These two forces, in balance, define the nature and the momentary state of things. He called this underlying essence the Tao.

Now, the title of my talk is, of course, a joke — a playful reference to this ancient philosopher.

But be careful: in his writings, Lao Tzu warned that “The Tao cannot be defined. And those who ignore it may die before their time.”

Artists often depicted him riding a buffalo — looking quite annoyed.

Slide Diffraction versus fluorescence

X-ray fluorescence and X-ray diffraction are like yin and yang.

Fluorescence helps us find elements. But when we do diffraction, this same light becomes noise.

Diffraction peaks in a fluorescence spectrum are also a problem.

Diffraction shows the crystal structure, but not the atoms.

Fluorescence shows the atoms, but not the structure.

XRD phase analysis is an absolute method.

It measures real intensities and needs no standards.

For someone used to fluorescence — a comparative method — this feels like magic.

Both use X-rays and may look similar. But in truth, they are opposites — just like the instruments.

Let's look at some examples.

Slide X-ray tubes

The slide shows pictures of X-ray tubes.

The dimensions of the two tubes are different. The XRF tube is significantly larger.

Both are vacuum tubes with heated cathode wires. These are second-generation X-ray tubes — the first generation had cold cathodes.

The X-ray diffraction lamp must have a point focus. When viewed at a very small angle, the point remains sharp. Its anode is water-cooled and has neutral potential, so its cathode must be negatively charged.

In contrast, the XRF tube must irradiate the entire surface of the sample. This requires a large spot focus behind a front Be window. The cathode wire surrounds the anode, and the electron paths curve, as shown in red on the schematic.

To create these curved trajectories, the tube body must be at the same potential as the cathode. Since the body must be grounded (0V), the anode must have a high positive voltage. As a result, the cooling water must be a very good insulator — otherwise, the anode would short-circuit.

So, XRF systems use a deionized water cooling system. Internal water circulates in a closed loop, with an internal pump and a heat exchanger connected to an external cooling system.

Both tubes are vacuum tubes, but their cables, hoses, and high-voltage generators are different.

Slide X-ray tube spectra

Both tubes accelerate electrons toward their anodes.

The negative acceleration of electrons in the anode material produces X-rays in two ways:

Ionization and recombination of K-shell orbitals — this gives characteristic lines of the anode atoms.

Bremsstrahlung radiation — acceleration itself causes the electrons to emit continuous X-ray spectra.

For diffraction, only the characteristic $K\alpha$ line is used. The rest of the spectrum is considered noise.

For fluorescence, the continuous spectrum is important, but the characteristic lines are also useful.

Slide X-rays – Particles or Waves

God gave us the freedom to see X-rays as either waves or particles — and Planck gave us a formula to switch between them.

In the right units, Planck's constant times the speed of light is almost one — which means we can switch between energy and wavelength without thinking too hard.

Slide Bragg's Law

Bragg's Law is the same in both methods — but while spectrometers use a perfect crystal to read the spectrum, diffractometers grind the crystal to powder so that all Bragg peaks fall into a single plane.

Slide Goniometers

Both instruments use a goniometer — XRD with divergent optics, WDXRF with parallel.

In Bragg-Brentano geometry, the primary X-ray beam is divergent. Slits limit both the primary beam and the detector aperture.

The Bragg-Brentano geometry has two requirements:

The first one is equal distances from the sample to the tube focus and to the detector.

The second requirement is the incidence angle must equal the detection angle.

In modern instruments, the sample remains fixed. The tube and detector arms move in a vertical plane at equal angles to the sample surface.

In front of the detector, usually a filter to absorb scattered $K\beta$ radiation is used.

In parallel geometry, the sample surface acts as a full X-ray source.

A soller slit (a parallel array of absorbing plates) collimates the beam.

The resulting wide, parallel beam hits the analytical crystal and then goes to the detector.

Another soller lens is placed in front of the detector.

In parallel optics, distances to the sample don't matter — only angle equality is required.

The spectrometer usually has two detectors:

A proportional gas detector for light elements (early periodic table)

A scintillation counter for the rest

Thought experiment:

Q: What if we place two tiny detectors side-by-side on a diffractometer?

A: We'll get the same spectrum in half the time.

This is the principle of modern detectors — over 100 small detectors stacked next to each other.

Q: How will the spectrometer speed change if we replace the scintillation detector with a position-sensitive one?

A: Ideally, no change. In practice — a bit slower. In parallel optics, the scintillation detector uses its full area. Dividing it doesn't increase the number of counted photons.

In diffraction, a position-sensitive detector maps angles into space — so stacking small detectors speeds things up.

But in parallel optics, dividing the detector doesn't help — the same photons just hit smaller pieces.

Slide WDXRF Goniometer

This is a rare look inside a real WDXRF goniometer — working under vacuum, at 37 degrees, with temperature-stabilized crystals mounted in a rotating turret.

It takes six hours to stabilize — and one wrong move to lose it all.

What you see here is hidden for a reason — precision needs silence.

Slide Modern Detectors

Modern detectors are based on silicon — like SSDs for fast diffraction scans, and SDDs for fluorescence.

In the diagram (top right), multiple strips are aligned perpendicular to the goniometer plane. Each strip has its own preamplifier and works as a separate detector. There are usually more than 100 strips, covering a total angle of 2–5 degrees.

SSDs work without cooling and in the best case can reach ~8% resolution. That's enough to skip the $K\beta$ filter, doubling measurement speed by avoiding absorption losses.

SDDs have concentric strips with a gradient negative voltage. This electric field causes the charge to drift to the center where the amplifier is built. The central node is the gate of a tiny transistor — just nanometers wide — which keeps the capacitance extremely low.

That's why even a single photon of Na can leave a clear, measurable pulse.

SSD are electrically cooled — achieving ~2% resolution for much sharper energy peaks.

Slide Detector Electronics

Behind every good detector, there's smart electronics.

XRD and WDXRF use a single energy window — simple and fast — while EDXRF relies on a multichannel analyzer: far more complex and expensive, but capable of reading the entire spectrum.

Slide Critical Sample Thickness

How does fluorescence yield of a line depend on the element concentration in the sample?

It is proportional to:

the concentration c of the element in the sample,

a coefficient K that reflects the system's ability to excite this element (tube settings, element type, etc.)

It is inversely proportional to how strongly the other elements absorb this line — described by the mass absorption coefficient, μ/ρ (mu-rho).

The term in brackets shows how sample thickness affects the yield. It includes the sample's density, thickness, and the absorption coefficient.

As thickness increases, the bracket value quickly approaches 1.

There is a certain thickness that gives 99% of the maximum yield. This is called the critical sample thickness. Beyond it, the sample is considered “infinite” — its thickness doesn't affect the fluorescence yield for that element.

In practice:

Polymers and light materials may need centimeters of thickness.

Metals can reach critical thickness with just 1 micron.

Rocks/minerals reach it with a few millimeters.

So remember: XRF analyzes only a thin surface layer.

Example 1: If a bar tests as 99% gold, that only means the surface (~1 micron deep) is gold. There's no guarantee what's inside.

Example 2: A sweaty fingerprint on a steel sample may leave enough sodium to be calculated as 2.3% Na in the sample — even though there's no sodium in the bulk material.

Now let's consider a sample that's infinitely thin.

We can develop the formula using a Taylor expansion, stopping at the first term. For such thin samples, density and thickness lose meaning — it's better to think in terms of surface density (mass per unit area).

In this case, the fluorescence yield becomes independent of the other elements in the sample.

This is the principle behind total reflection XRF (TXRF).

Slide Total Reflection

The total reflection spectrometer is interesting for several reasons:

TXRF is very rare — you could call it exotic. But there is one here.

It competes with ICP-OES. TXRF's detection limits are not as low as ICP-OES but better than AAS.

The instrument is expensive and requires chemical sample preparation, just like ICP-OES.

Minor advantage: TXRF doesn't use compressed argon gas.

Major advantage: TXRF is almost an absolute method. It works with an internal standard instead of calibration curves.

The device's optical layout is closer to a diffractometer than a fluorescence system.

A monochromator selects only the $K\alpha$ line from a molybdenum or tungsten tube. This monochromatic beam hits a quartz carrier at a very small angle (like in grazing incidence XRD — GIXRD), and is completely reflected without entering the substrate.

In this geometry:

The detector is placed very close to the sample.

No vacuum is needed.

The substrate doesn't produce background.

The reflected beam goes in a safe direction — this reduces background noise.

Low background = high sensitivity.

Detection limits are between AAS and ICP-OES.

The sample is applied as a droplet on the quartz. After drying, a thin film remains.

If we rewrite the earlier formula for thin samples, the monochromator lets us simplify it further. The Kr coefficient becomes:

The hard part is knowing I_0 . But if the sample contains an element with a known concentration, we can calculate it — or just add a known element (internal standard).

That way, we can measure the sample once, without calibration curves.

In practice, gallium (Ga) is used as the internal standard because it's a rare element.

An Italian Story

I want to tell you about an experiment done quite recently. The article shown on the slide is from 2022. Technology is advancing quickly — it's no longer crazy to imagine putting 32 multichannel analyzers in one system.

Our colleagues from three Italian institutions decided to build an SSD-based detector and a special diffraction system. The SSD had good enough energy resolution.

The innovation: they managed to connect a multichannel analyzer to each strip in the detector.

So, the setup included:

32 strips (each one a small detector)

32 charge amplifiers

32 multichannel analyzers — all based on DSP

Everything is installed in a vacuum chamber, with a goniometer and a molybdenum tube.

The article mostly focuses on the semiconductor technology used for the detector and electronics. The diffractometer itself is only briefly described — it's not completely clear what the full purpose is.

I wrote to one of the authors, asking for digital data to show in the talk. Unfortunately, he didn't respond. So, I can only speak based on the published images.

The slide shows the left part of Figure 1 from the article. It explains the construction of the diffractometer. The only unusual part is the vacuum system — but that's normal in fluorescence setups.

Their technology has good energy resolution — not as good as SDDs, but close.

In the diagram, two orange lines point to the right part of the figure — an image of the laptop screen. I've taken that section and placed it on the next slide so we can look at it in detail.

Slide Color Diffraction

It's always exciting to show something new. You can call it whatever you want — here are three name ideas for this image:

Angularly distributed X-ray fluorescence

Energetically distributed X-ray diffraction

Color diffraction

The graphic is unusual and needs some time to understand.

Let's start with the colors. Intensity is represented by color — black is zero, dark blue to yellow means increasing intensity, and red is maximum.

The x-axis shows the energy of the registered photons.
The y-axis shows the angle at which they were detected.

In the middle, there are two vertical red lines — the strongest intensities. These are the $K\alpha$ and $K\beta$ lines of the molybdenum tube.

If we take a vertical cut through the $K\alpha$ line and convert the color to numbers, we get a classic diffractogram.

Since the detector separates $K\alpha$ and $K\beta$, we can take a second cut through $K\beta$. The same peaks, but shifted in angle, are visible.

If we had the digital data, we could combine both diffractograms for better statistics, or use the $K\beta$ line, which is a singlet, to calculate the crystal lattice parameters more accurately.

What about the arcs passing through the $K\alpha$ and $K\beta$ maxima? These arcs represent diffraction from the continuous spectrum — not just the tube lines. They carry the same information and can be combined into the analysis.

All other diffraction besides the Mo $K\alpha$ line is usually ignored — just counted as background.

There are two vertical lines without diffraction — the fluorescent lines of iron, at 6.4 and 7.08 keV. They come from FeSO_4 in the sample, as mentioned earlier (also mixed with CaCO_3).

Another interesting feature is the copper fluorescence line. You can see a bright dot connected by an arc to the $K\alpha$ line of molybdenum. Even the $K\beta$ of copper is faintly visible. Its origin is unclear — possibly from the tube optics, or the tube itself, if Mo is deposited on a copper base.

There are also two weak lines matching bromine ($K\alpha$ and $K\beta$). They're on a horizontal line, not on arcs. That suggests the bromine is not in the sample but somewhere on the detector arm — maybe in a plastic part or as vapor from vacuum oil.

One more guess: the horizontal lines seen across the image might result from X-rays being captured by two adjacent detectors, splitting the energy randomly. The tails of high-intensity peaks can show up at lower energies.

In summary:

The Italians successfully built a prototype for energy-dispersive diffraction.

It shows what's possible — and perhaps what's coming next.

The main limitation: their detector doesn't cover low-energy lines like Ca or S (< 4.5 keV).

The next step might be to build a detector with focusing strips and very low-capacitance gates on field transistors.

Conclusions

XRD and XRF are fundamentally opposite but complementary. Their instrumentation and applications are like yin and yang.

An exception is the TRXRF spectrometer. Most of all its part coming from the diffraction machines but it is an interesting near absolute quantity measurement XRF machine.

Detector and system design are evolving rapidly. Modern technologies such as silicon semiconductor detectors and digital electronics are transforming both methods. Probably will have commercial color diffraction systems in next 5-10 years.

съответен - corresponding

съответствие compliance

FeSO_4 — Iron sulfate

CaCO_3 — Calcium carbonate

adjacent - съседен

capacitor

capacitance

capacitance of a capacitor

voltage drop across the capacitor

electric potential

"In an X-ray tube, the anode is maintained at a high positive voltage relative to the cathode, enabling electron acceleration and X-ray generation upon impact."