Handheld XRF Measurements of Fluorine

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Agenda

- Introduction
- Conventional handheld XRF (HHXRF) technology
- Light element analysis HHXRF technology
  - Direct control of excitation conditions
  - Optional helium atmosphere
  - Optimized front-end geometry
  - Optimized detector
  - Live spectral analysis software
- Fluorine analysis HHXRF application examples
  - Semiconductor
  - Environmental
- Q & A

Welcome

Speakers

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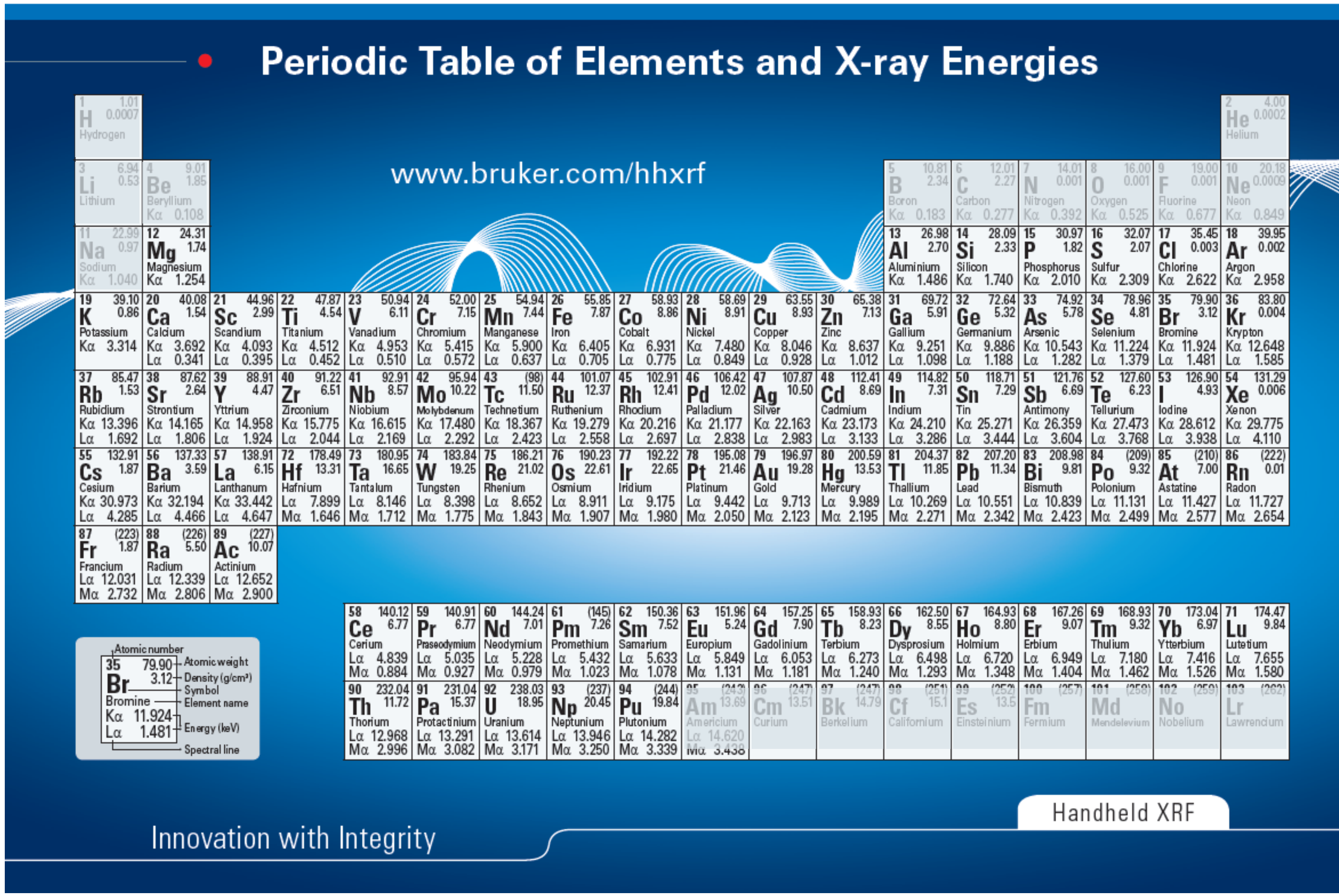
Handheld XRF Technology

- What does it do?
- How does it work?

Handheld XRF Technology

Conventional
Handheld XRF
Technology



Handheld XRF Applications

Alloy PMI and quality control

Scrap metal recycling

Precious metals

Geology, mining & exploration

Multiple HHXRF Applications

Applications & product development

Environmental

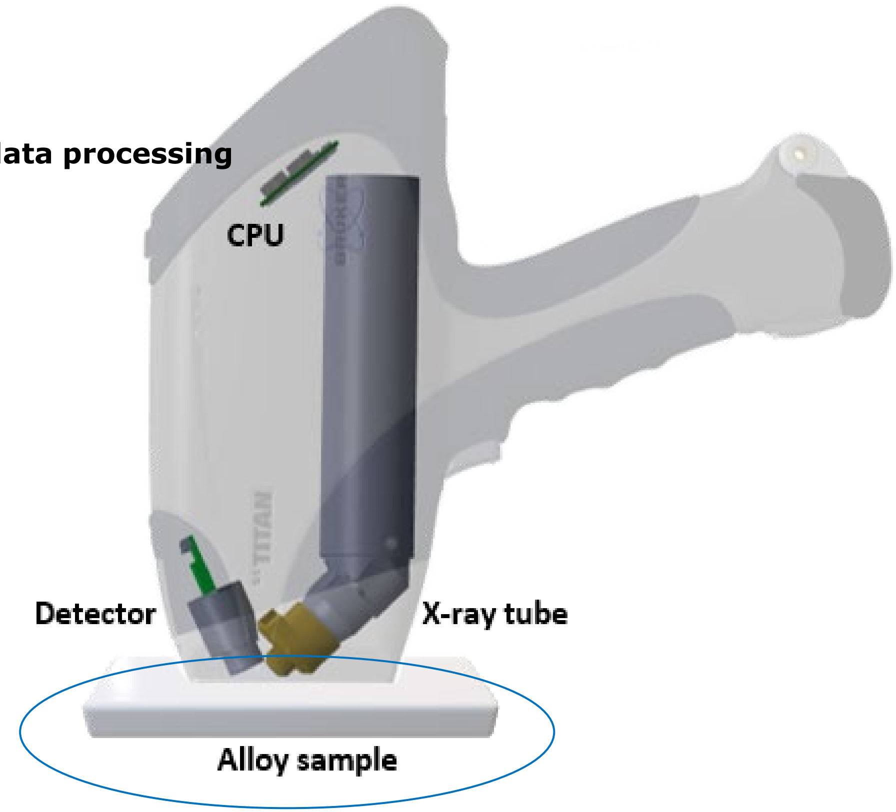
Research & education

Food safety & agriculture

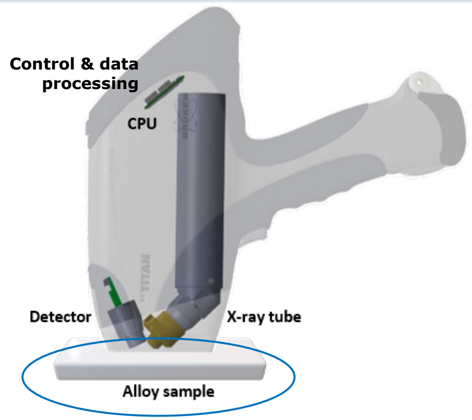
Conservation & archaeology

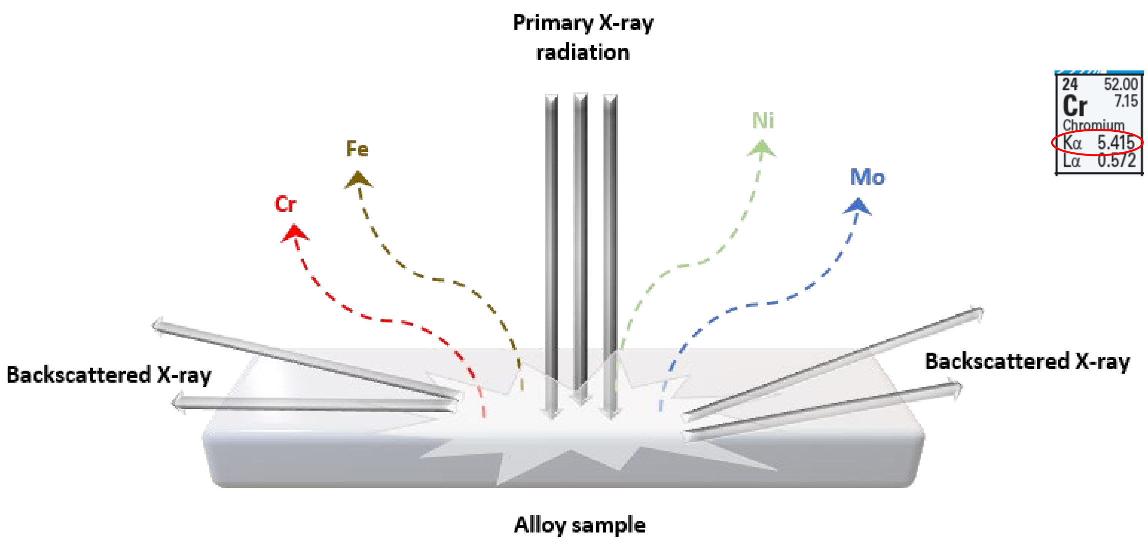
RoHS & consumer safety

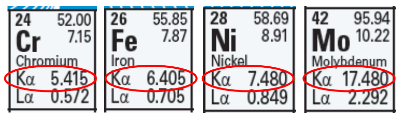
HHXRF Technology



HHXRF Technology



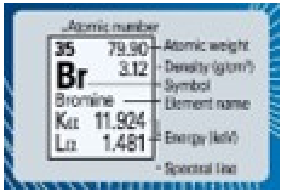




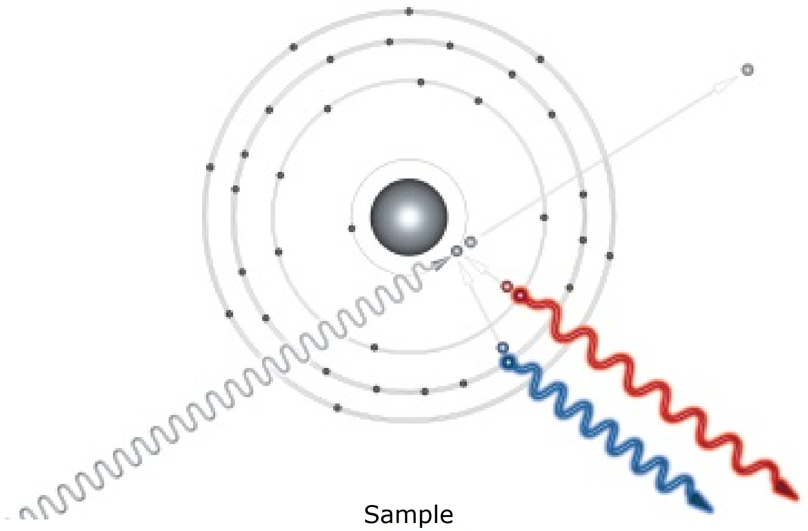
HHXRF Technology

Energy Dispersive (ED) X-ray Fluorescence (XRF) Spectroscopy

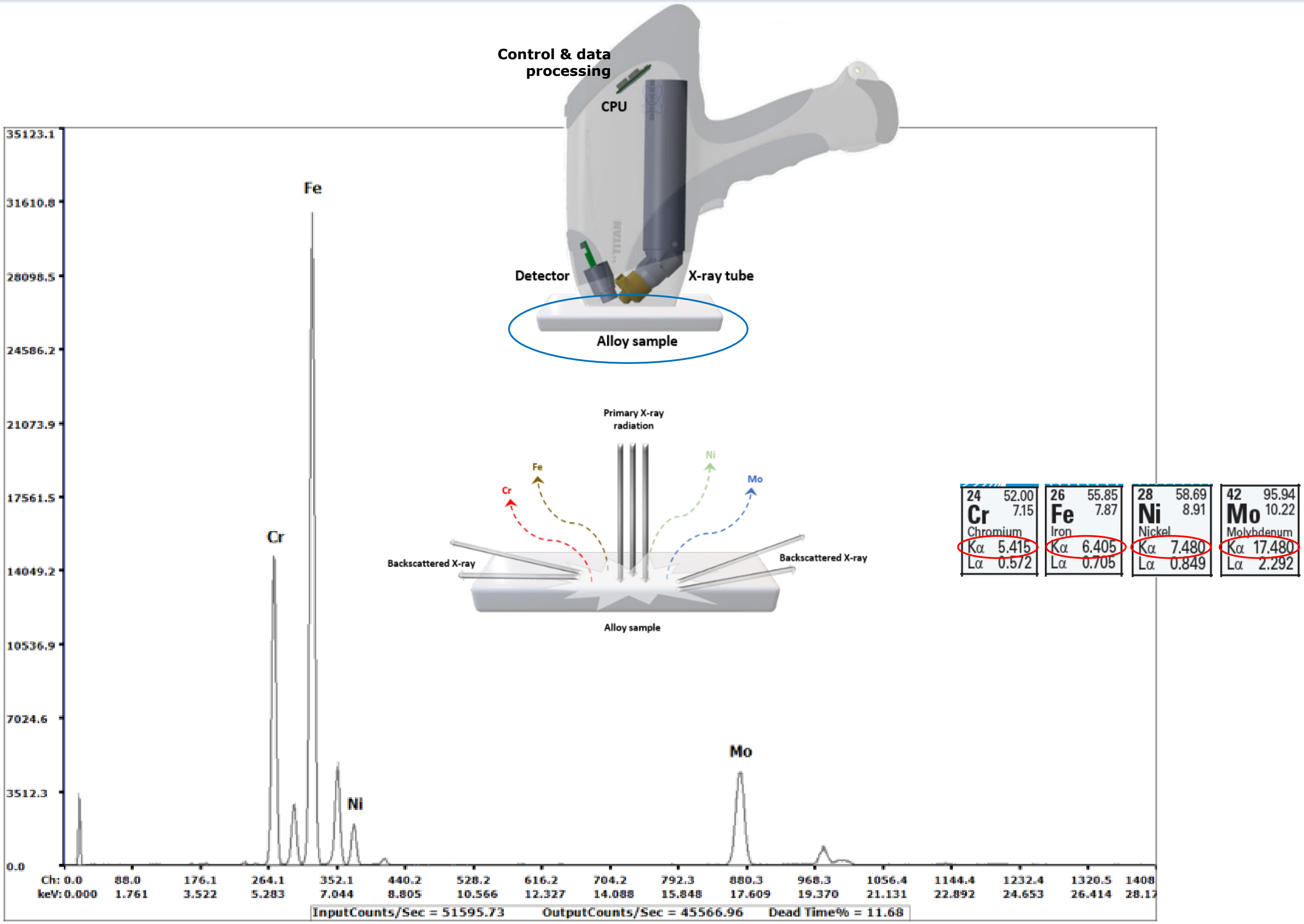
- Energy from an EDXRF source aimed at a sample can eject the elemental atoms’ inner orbital electrons
- Outer electrons move into the voids to regain stability
- While moving in, the outer electrons generate energy characteristic of the element
- These characteristic energies are the fluorescent X-rays of the element



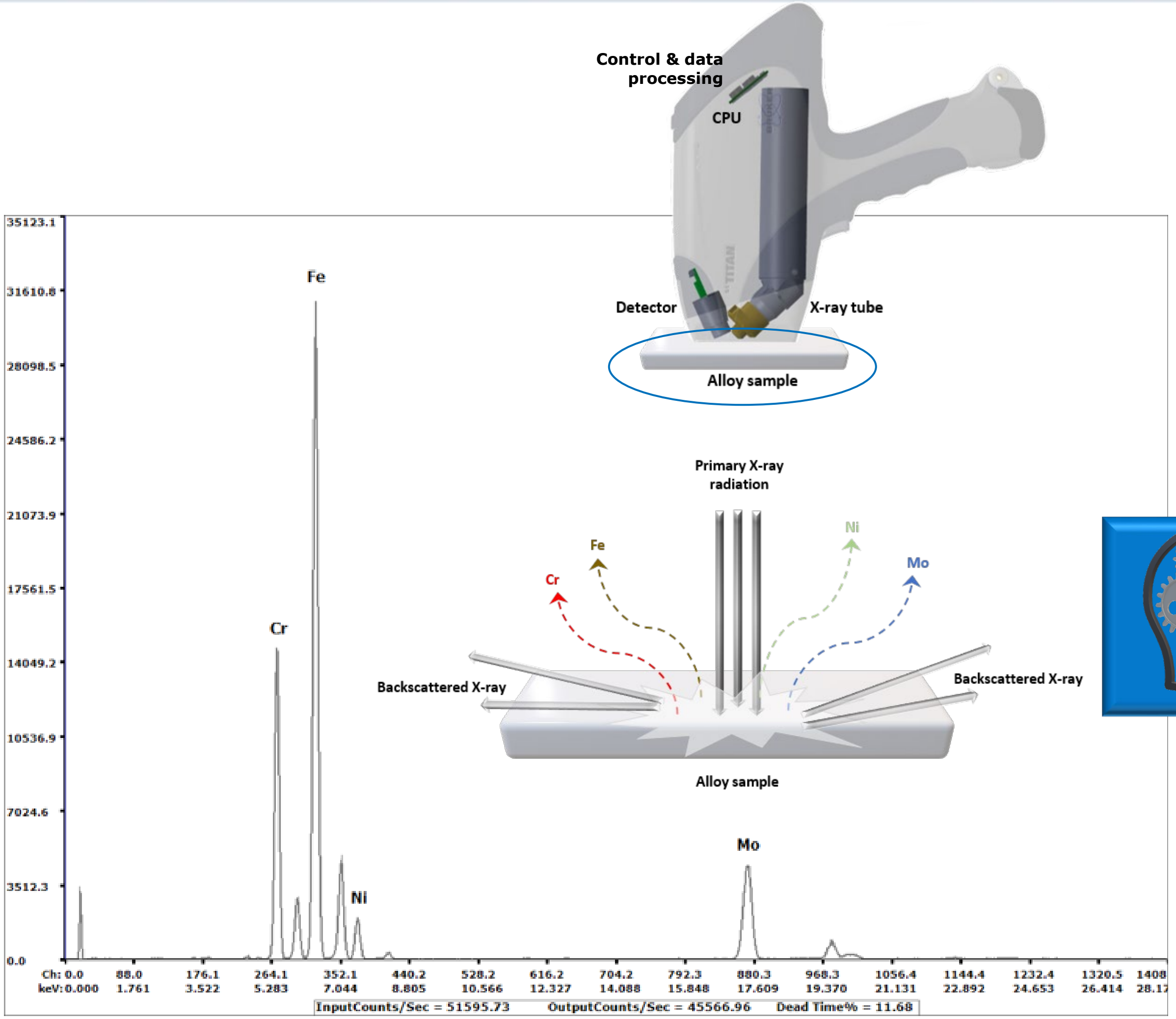
Electron orbitals of element’s atom

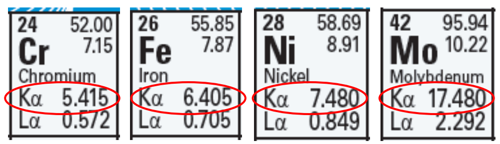


HHXRF Technology



HHXRF Technology



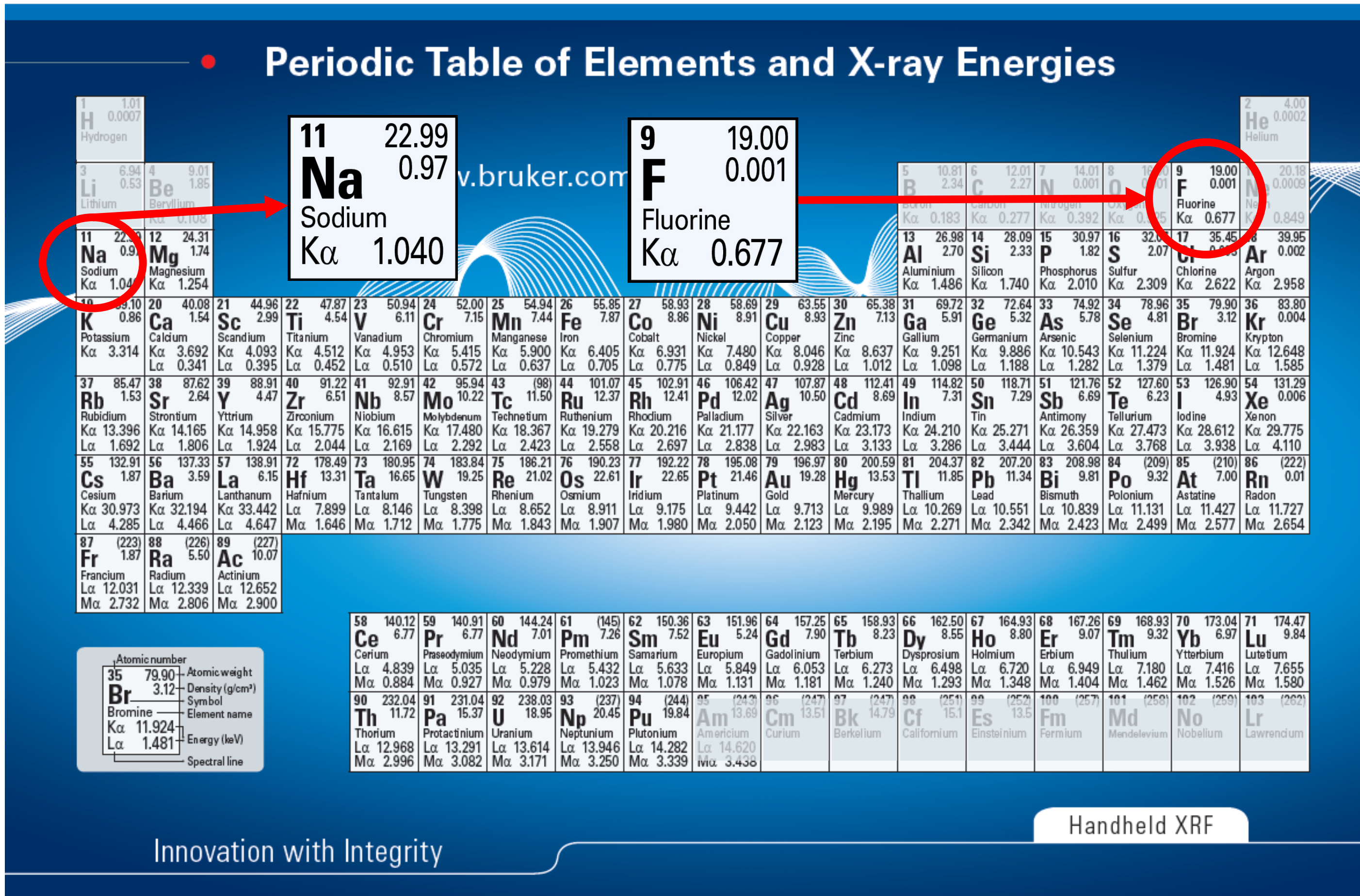


HHXRF light element analysis technology

- How is it different?

HHXRF light element analysis technology

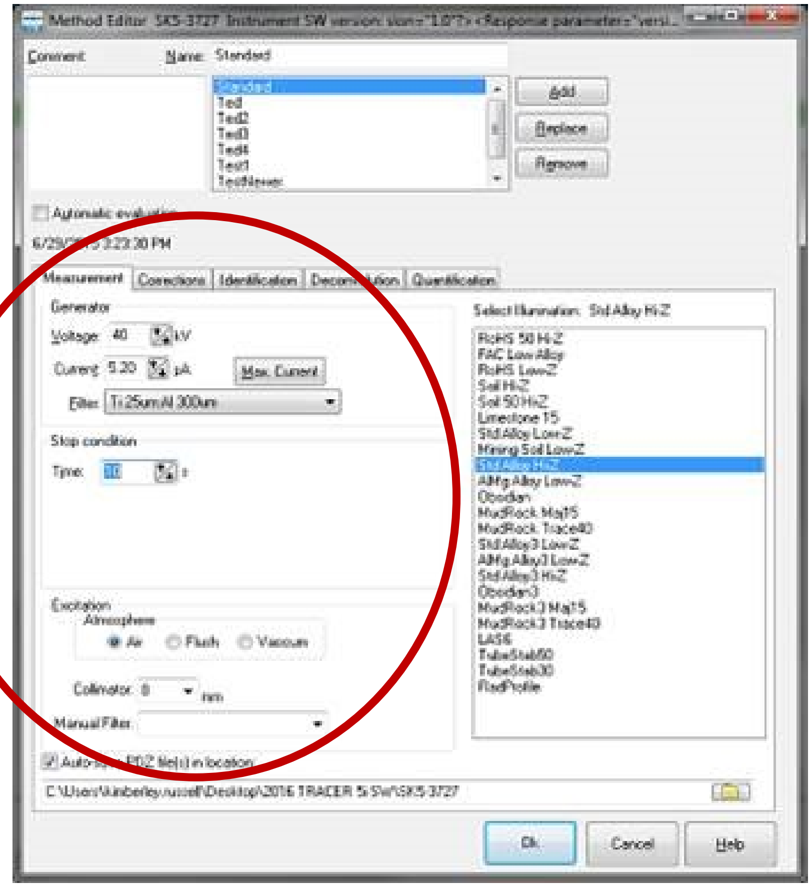
Light Element
Handheld XRF
Technology



HHXRF light element analysis technology

Direct user control of settings to optimize HHXRF measurements

HH Screen for user control of measurement settings



PC screen for user control of measurement settings

HHXRF light element analysis technology

Optional helium atmosphere for light element detection capability

- Fluorine is a low atomic number element with an XRF measurement depth of about 1µm, a very weak signal at 0.677 keV, and is absorbed by all materials
- To get a strong enough XRF signal, air and other materials absorbing the fluorine signal between the sample and detector need to be removed
- The instrument nose needs to be purged with helium which absorbs the fluorine signal much less than air (N_2, O_2, Ar) does
- In addition to purging the nose, its protective window needs to be removed to provide a non-obstructive path for the F signal

HHXRF light element analysis technology

Optional helium atmosphere for light element detection

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	N/A	N/A
Mg	932	0.12
Al	462	0.59
Ca	25	13.13
Fe	46	29.36

Air atmosphere and
3 µm prolene window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	548	0.31
Mg	155	1.44
Al	165	3.36
Ca	27	14.00
Fe	50	26.40

Lab helium atmosphere and
3 µm prolene window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	312	0.62
Mg	122	2.13
Al	134	4.41
Ca	24	14.04
Fe	50	25.87

Lab helium atmosphere and
no window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	356	0.52
Mg	127	1.95
Al	143	4.07
Ca	25	14.15
Fe	50	26.36

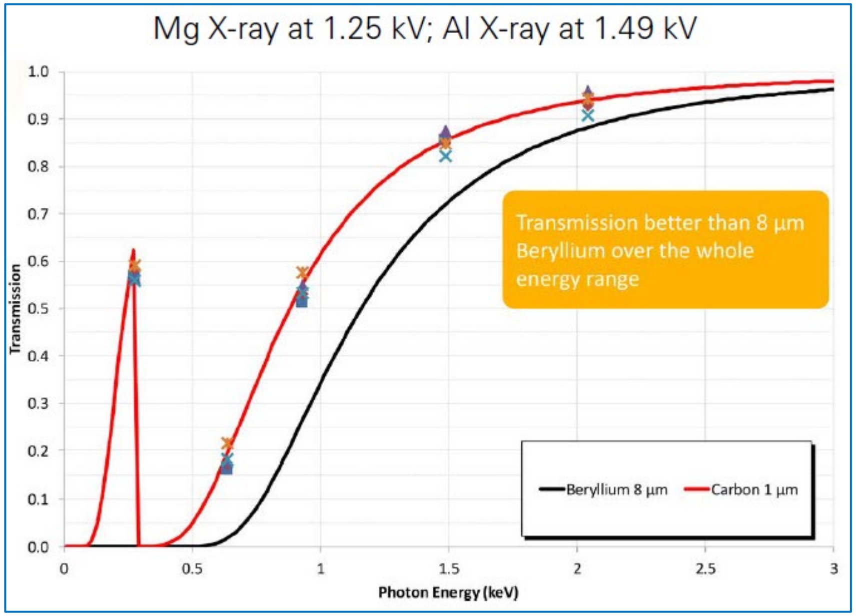
Balloon helium atmosphere and
no window

HHXRF light element analysis technology

1 µm Graphene window high resolution SDD for sensitive, clean spectra

- The TRACER 5g incorporates a large area Silicon Drift Detector (SDD). Conventional HHXRF 8 µm beryllium windows have been replaced with 1µm graphene windows to provide extra sensitivity and clean spectra for light element HHXRF analysis

Large area SDD with graphene window

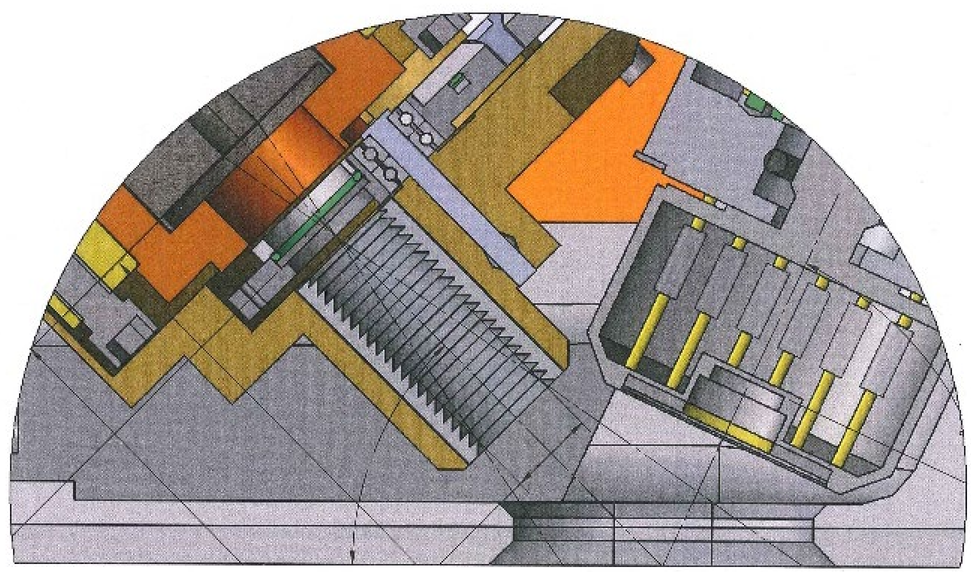


Transmission of beryllium and graphene windows

HHXRF light element analysis technology

SharpBeam™ front end geometry increases light element sensitivity

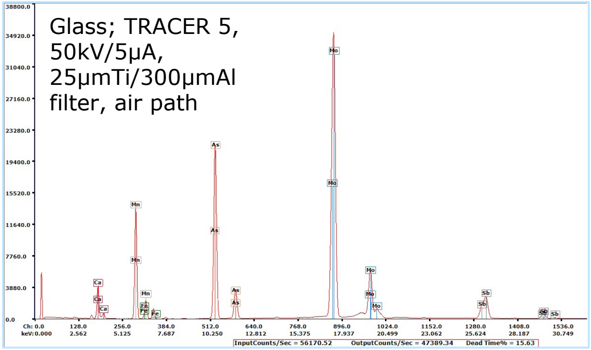
- SharpBeam™ front-end geometry maximizes count rate, increases light element sensitivity, provides a well-defined measurement spot, and minimizes detection of X-ray scatter

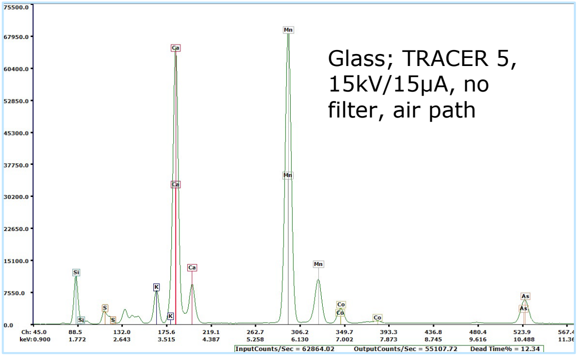


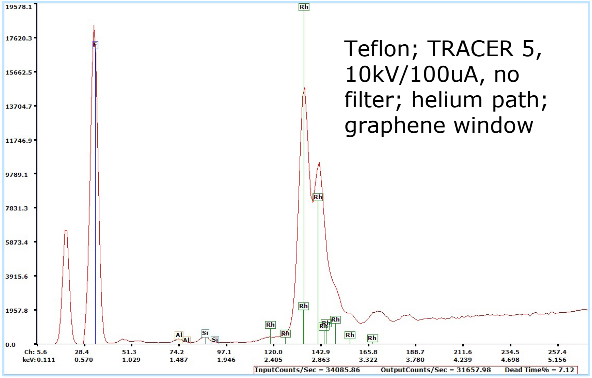
HHXRF light element analysis technology

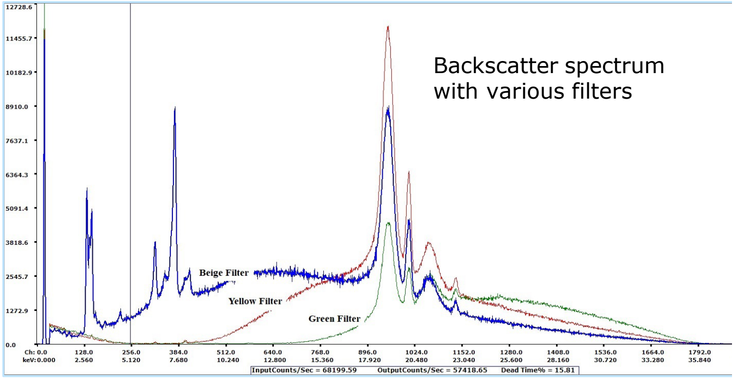
Live spectra analysis software guides measurement optimization of analysis and provides immediate information on sample composition

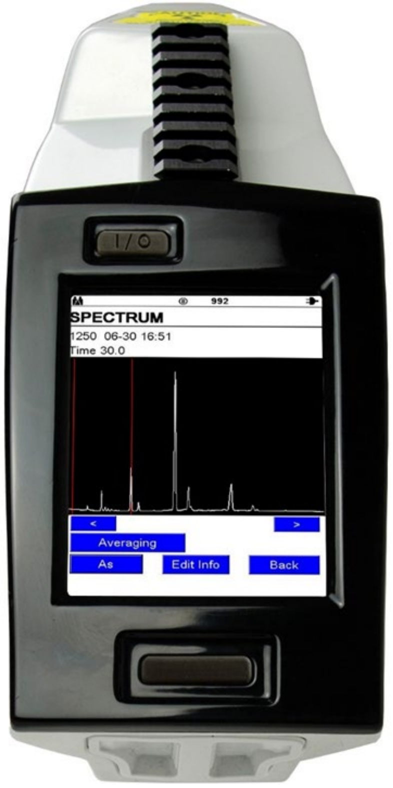
- Live spectra analysis software helps guide optimum measurement conditions (e.g., kV/μA, filter, path, time), especially important when developing new applications











HHXRF light element analysis technology

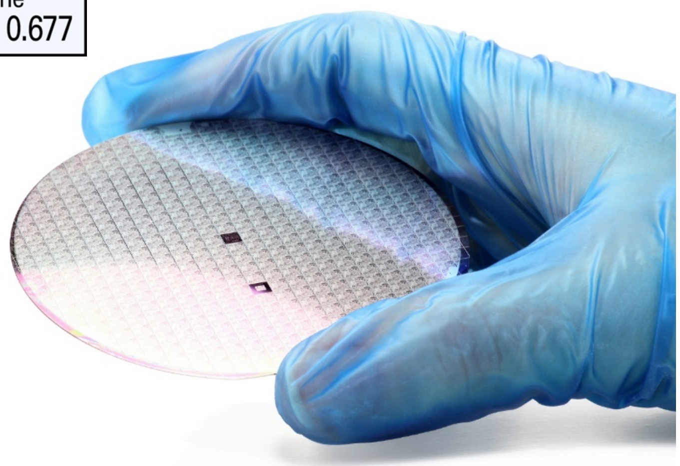
The TRACER 5g platform enables light element HHXRF analysis of fluorine with:

- Direct control of excitation conditions (e.g., kV/μA, filter, atmosphere, time)
- Optional helium atmosphere to minimize absorption of the light element signal
- SmartBeam™ front-end geometry to maximize the count rate
- Large area SDD with a graphene window for extra sensitivity and clean spectra
- Live spectra analysis via handheld and PC software to optimize measurement conditions

Fluorine analysis HHXRF application examples

Semiconductor application

9 19.00
F 0.001
Fluorine
Kα 0.677



- Fluorine is the most reactive chemical element and the lightest of the halogen group
- Fluorine compounds are used for a variety of semiconductor manufacturing applications including chemical vapor deposition, plasma etching, and cleaning
- A challenge in using fluorine (F) compounds for applications like these is the ability to measure it during manufacture, especially as a coating or residual
- The semiconductor industry needed to find a solution. Handheld XRF was proposed for its portability, in-situ measurement capability, ability to provide fast results, and its nondestructive nature

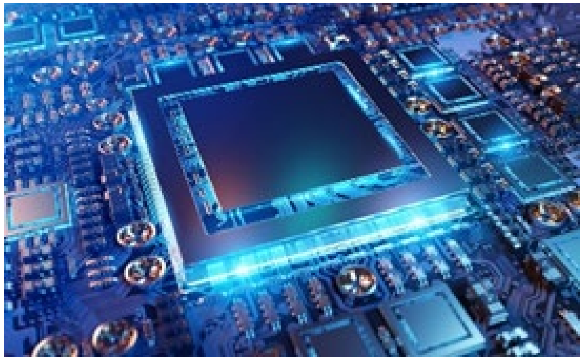
Semiconductor application

Fluorine in semiconductor manufacturing

- Yttrium oxyfluoride (YOF), a plasma-resistant material, is replacing yttrium oxide (Y_2O_3) as the protective material in plasma process chambers for the manufacture of 3-D stacking circuits
- It has become critical to detect F to differentiate which Y compound is being used

YOF

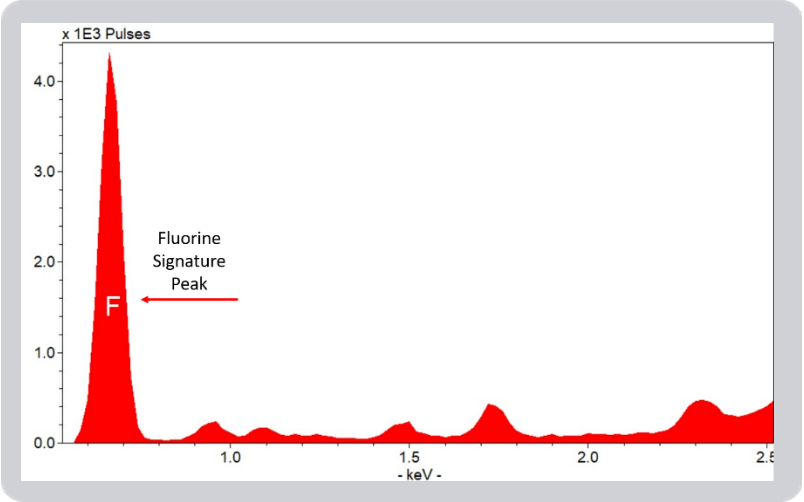
Y_2O_3



Semiconductor application

Feasibility

- Feasibility of measuring the low energy fluorine signature peak with a TRACER 5g was first established using polytetrafluoroethylene (PTFE) tape
- TRACER 5g settings were 10kV/100µA, helium purge, 8 mm spot size, no protective window, 30 seconds measurement time
- A clear fluorine peak at 0.677 keV in PTFE tape was detected by the TRACER 5g

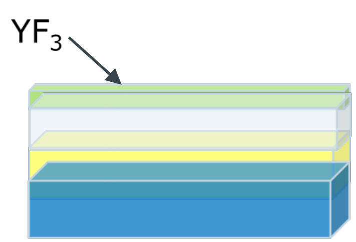


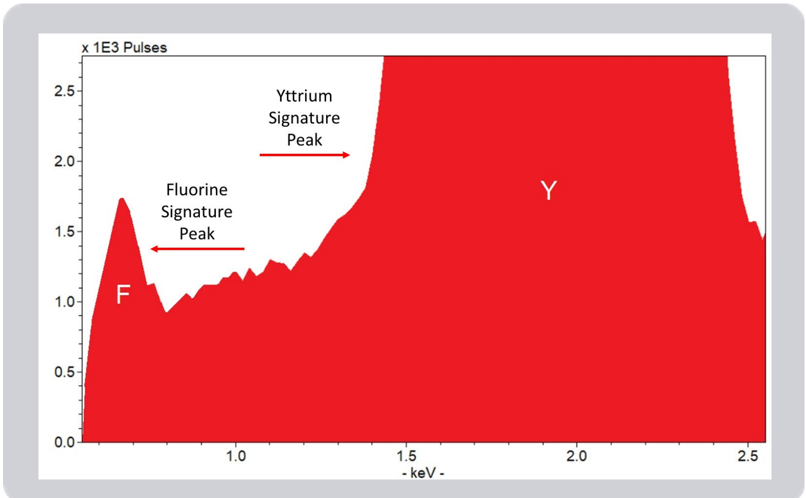
Polytetrafluoroethylene (PTFE) tape measurement with TRACER 5g

Semiconductor application

Data

- An yttrium fluoride (YF_3) coating used in the semiconductor industry was tested
- TRACER 5g settings were 10kV/100µA, helium purge, 8 mm spot size, no protective window, 30 seconds measurement time
- A clear F peak at 0.677 keV in YF_3 coating was detected by the TRACER 5g making it possible not only to identify the presence of F, but also to distinguish Y-compounds containing F to those without F





Yttrium fluoride (YF_3) coating measurement with TRACER 5g

Environmental application

Fluorine in ski wax

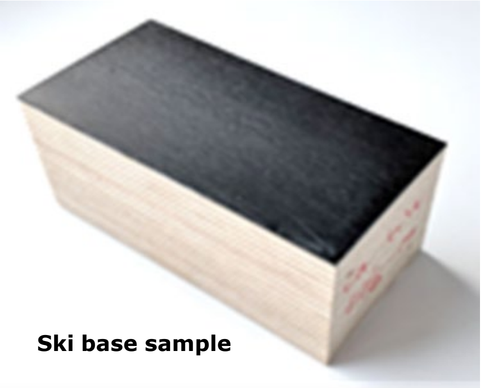
9 19.00
F 0.001
Fluorine
Kα 0.677

- Persistent Organic Pollutants, or POPs, are referred to as "forever chemicals" because they are almost impossible to get rid of when they get into our water sources and soil
- PFOS (perfluoro-octane-sulphonate) and PFOA (perfluoro-octanoic acid), referred to as fluorine-based PFAS, are in the Stockholm Convention's POPs list of harmful substances
- PTFE (Polytetrafluoroethylene), a particular type of PFAS, is a common ingredient in ski waxes to help reduce professional skiers race times, even if by seconds
- A challenge in promoting the phasing out PFAS for ski and snowboard waxes is the ability to ensure fluoro-waxes are not sold at retail stores or used on the slopes

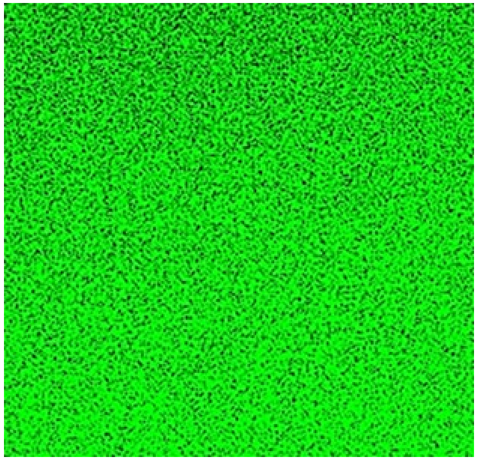
Environmental application

Sample presentation

- Five samples with ski bases and different wax compounds were measured to test if fluorinated ski wax samples can be reliably identified from fluorine-free ski wax samples
- All ski base samples were identical, but four of them had different types of fluorinated ski wax and one of the ski base samples had fluorine-free ski wax
- A ski base sample was analyzed with a micro-XRF system to confirm uniformity of sample surface via a F distribution map of a 1 x 1 cm area with 50 µm pixel size



Ski base sample

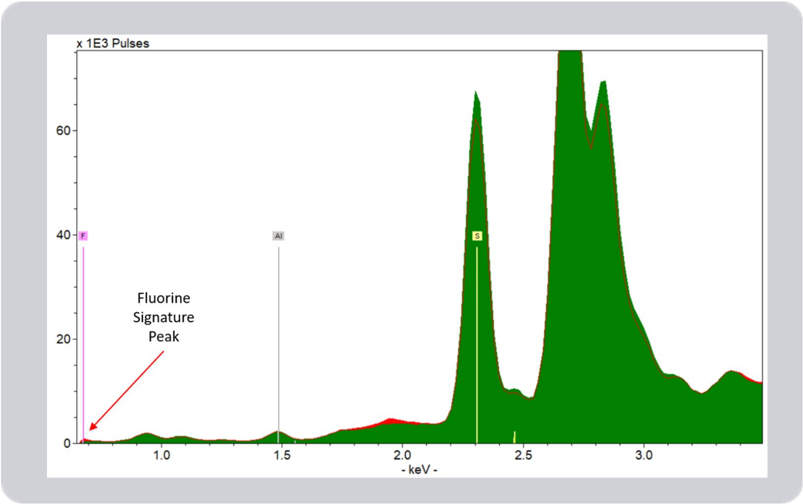


Micro-XRF was used to measure and map the distribution of F on the ski base to confirm uniformity of sample surface

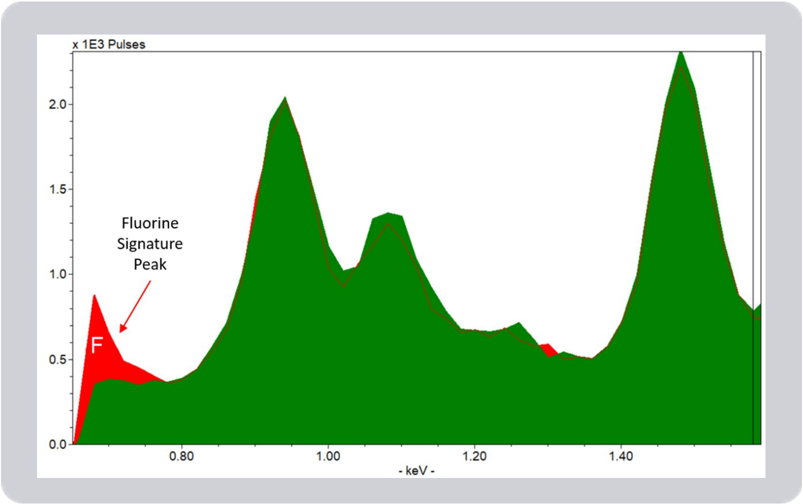
Environmental application

Data

- TRACER 5g settings were 10kV/180µA, helium purge, 8 mm spot size, no protective window, 180 seconds measurement time
- Test spectra from the TRACER 5g showed a small, but clear F signal in all ski base samples containing fluorine-based ski wax
- In comparison to other elements, such as aluminum (Al), sulfur (S), calcium (Ca) and iron (Fe), the fluorine signal was small
- Magnification showed a clear F peak in all fluorinated ski wax samples which made it possible to clearly distinguish them from fluorine-free ski wax



Fluorine peaks are small compared to other elements present, but when the Y axis is magnified, the peaks become clear.



Tracer 5g measurement can successfully distinguish fluorinated ski wax from fluorine-free ski wax.

Summary

- Fluorine analysis is a challenge for conventional handheld XRF
- The TRACER 5g's combination of direct user control of settings, optional helium atmosphere, SmartBeam™ geometry, large-area SDD with graphene window, and live spectral analysis software enable fluorine analysis with HHXRF
- The TRACER 5g's F signal at 0.677 keV in PTFE tape is clearly visible
- The TRACER 5g's F signal at 0.677 in YF_3 semiconductor coatings is clearly visible which makes it possible to distinguish from fluorine-free coatings
- Magnification of TRACER 5g data shows a clear F signal in fluorinated ski wax samples which makes it possible to distinguish them from fluorine-free ski wax
- The TRACER 5g's fluorine limit of detection (LOD) is highly dependent on the application; it is typically between 1% to 10% depending on measured material and measurement conditions

Q & A

Any Questions?

Please **type in** your questions for our speakers in the **Questions Box** and click **Submit.**

Thank You!

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