Hazardous Waste Management Program

Work in Progress: Developing a portable XRF method to screen for PFAS in consumer products

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Hazardous Waste Management Program of King County

Agenda

- Project Rationale and Background
- Study Overview
- Preliminary Results
- Future work

Acknowledgements

Study team

University of Washington

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Collaborators/Contributors

Eurofins Environment Testing Northern California, LLC, Sacramento, California

Forever Analytical, South Bend, Indiana

Washington State Department of Health

UW Dept. of Occ. & Env. Health Sciences

Public Health - Seattle & King County

Lead & Toxics; Best Starts for Kids

King County

Hazardous Waste Management Program; Water and Land Resources Division; Wastewater Treatment Division; Solid Waste Division; Parks and Rec Division

California Department of Toxic Substances Control (donated samples)

Middlebury College, Vermont (donated samples)

Project funding

- WA State Legislature
  - 2023 - 2025 supplemental budget proviso (Engrossed Subsitute Senate Bill 5950)

- Additional funding:
  - King County Haz Waste Program
    - Graduate intern
  - Public Health – Seattle & King County (Best Starts for Kids, Lead and Toxics Program)
    - Product samples and lab analyses
  - Council of State and Territorial Epidemiologists
    - Applied Epidemiology Fellow

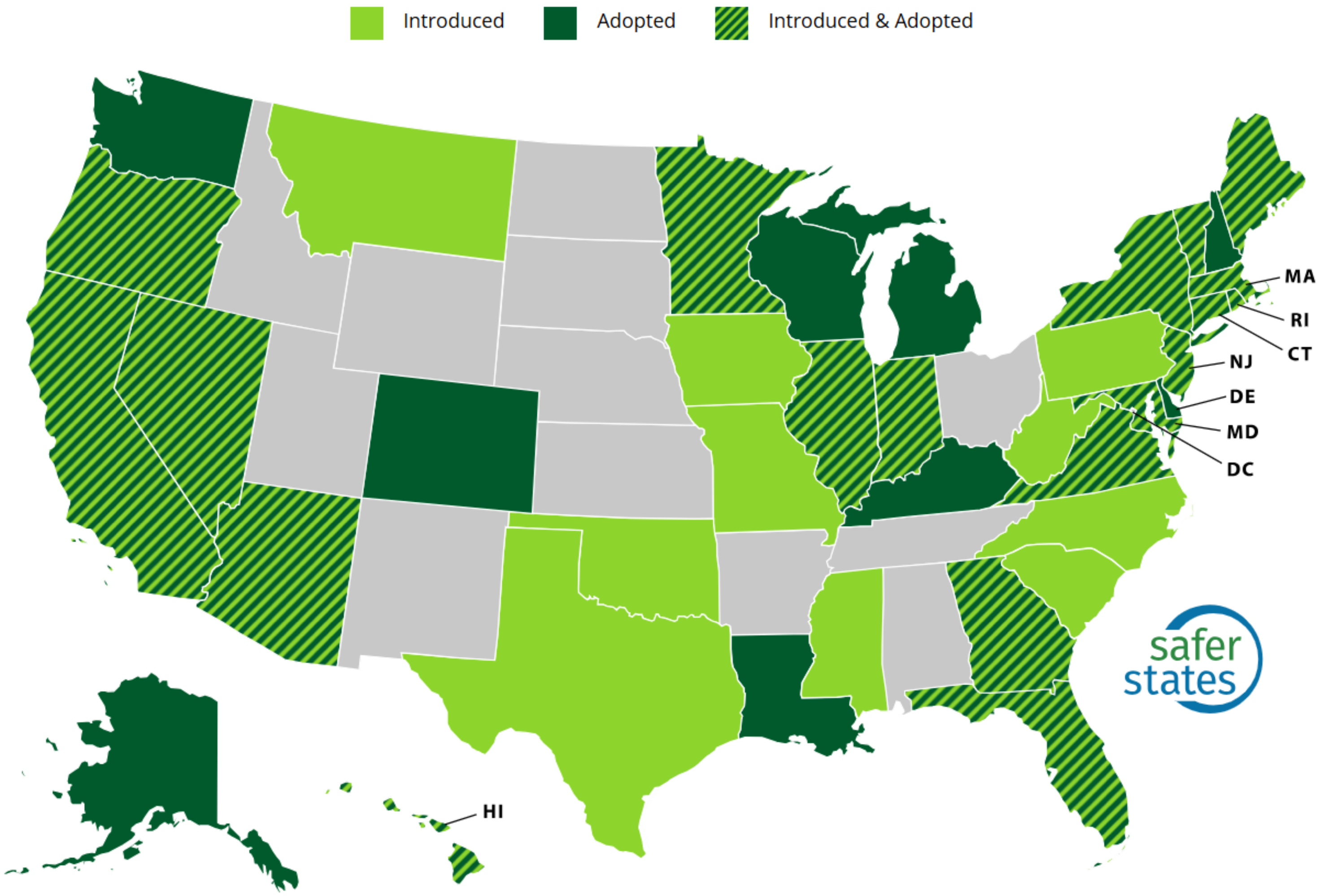
Project Rationale and Background

PFAS in consumer products

- Used in a wide variety of consumer and industrial products
- Toxic and environmentally persistent
- Contaminates wastewater and solid waste → local governments/utilities
- It is difficult for consumers, governments, and businesses to identify PFAS-containing products

Active area of policy

https://www.saferstates.org/bill-tracker/



Testing products for PFAS

- Available analytical methods are:
  - laboratory-based
  - destructive
  - time-consuming
  - (often) costly
- We had the ability to screen products:
  - in the field
  - non-destructively
  - in real-time
  - w/ a relatively low-cost investment

WHAT IF...?

Potential applications

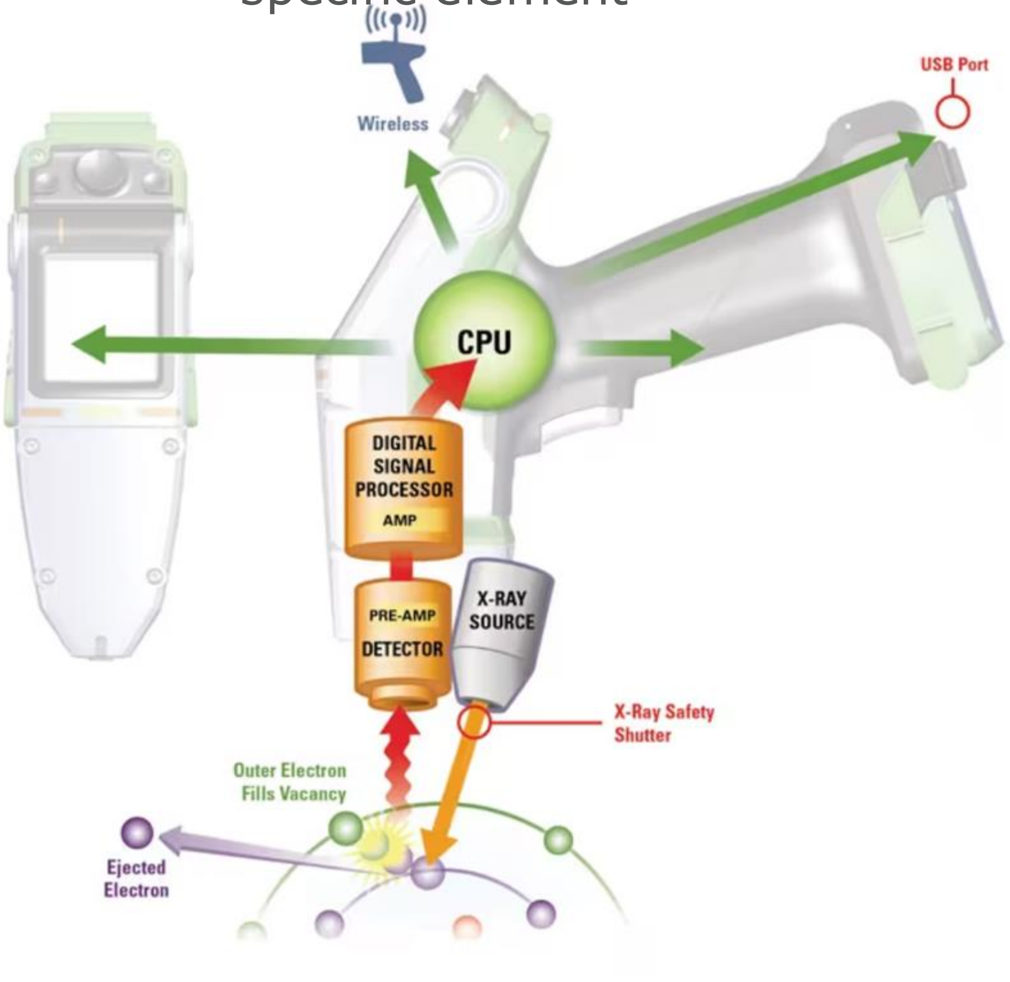
- Community testing events
- Product takeback programs
- Product replacement programs
- Supporting sustainable purchasing programs
- Prioritization within a product testing workflow
- Supporting diversion of F-containing solid waste

About XRF

XRF = X-Ray Fluorescence

Electrons are displaced from their atomic orbital positions, releasing energy that is characteristic of a specific element

- XRF measures elemental composition by detecting X-ray emission from samples
- XRF analysis is non-destructive of samples
- Handheld models



https://www.thermofisher.com/us/en/home/industrial/spectroscopy-elemental-isotope-analysis/spectroscopy-elemental-isotope-analysis-learning-center/elemental-analysis-information/xrf-technology.html

Measurement of Fluorine (F) using handheld XRF

Bruker TRACER 5g handheld XRF

- Marketed to detect light elements including F
  - More sensitive detector
  - Full control over scanning settings
  - Improved geometry between the source, sample, and detector
  - Ability to operate with helium (He) purge

Study Approach

Testing products for PFAS

Based Selections on:

- Community input
- Suspected to contain PFAS
  - Previously tested positive for PFAS
  - Product claims (e.g., "waterproof")
- Marketed as "PFAS-free", "safer alternative"
- Likelihood of human exposure from these products (e.g., sippy cups)
- High sale volumes
- Subject of existing or proposed policy
- Governmental interest/relevance (e.g., artificial turf at own parks)

Purchase or Obtained from:

- Online retailers, including Amazon and Target.
- Artificial turf, playground tile, carpet, and ski wax samples from suppliers, manufacturers, and collaborators at:
  - CA DTSC
  - Middlebury College
  - King County Parks

Community Engagement

Type of Organization	Number of Groups Engaged	Number Poll Participants
Government/Academic	6	15
Community-based organizations	9	14
Non-governmental organizations	4	6
Other community partners	6	9

Community engagement and poll participant counts

- Children's Products
- Cosmetics and Personal Care Products
- Household Products
- Clothing and Apparel
- Containers and Packaging

Products included in study

- **Children's Products**
  Pacifiers, bibs, feeding items (bowls, cups, bottles), diapers, clothing, toys, car seats, bedding, and other childcare items.
- **Household Products**
  Carpets, artificial turf and playground tiles, ski waxes, cookware and bakeware, and small kitchen appliances.
- **Packaging & Containers**
  Food-contact materials such as baking paper, sandwich bags, disposable cups, to-go boxes, candy wrappers, and popcorn bags.
- **Clothing & Apparel**
  Pants, jackets, and tops made from cotton, nylon, and polyester fabrics.
- **Cosmetics & Personal Care**
  Dental floss, deodorant, sunscreen, lip and eye makeup, and pressed foundation products.

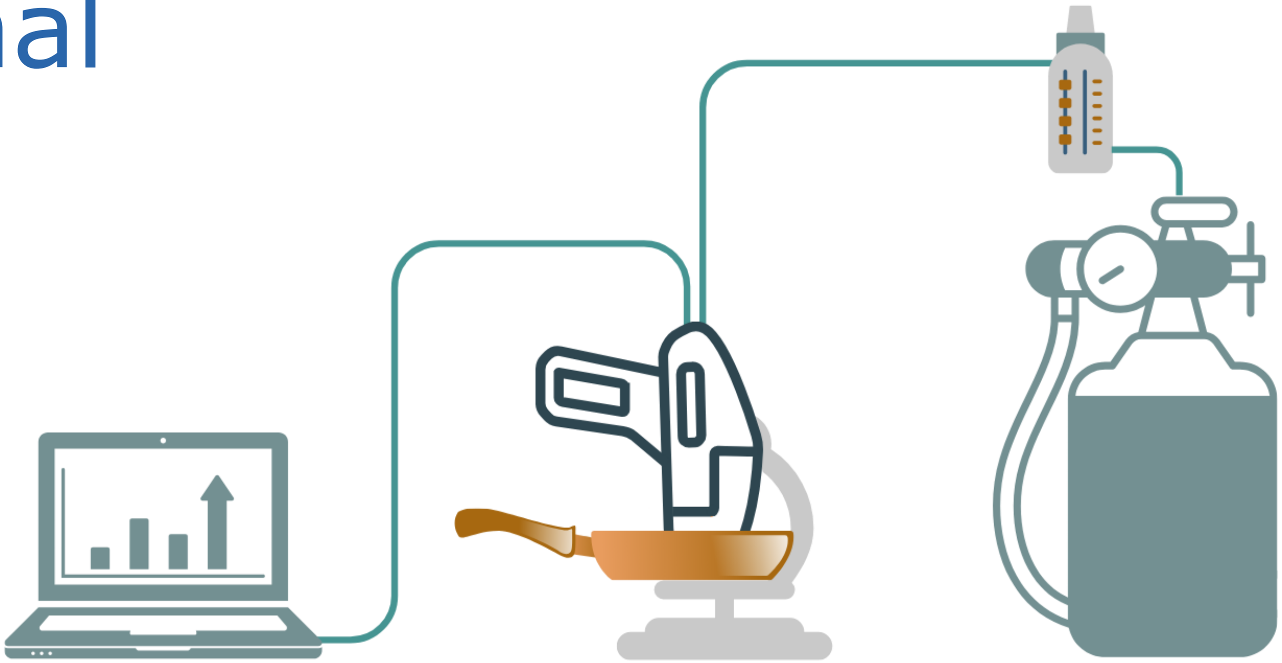
XRF protocol to maximize F signal

Helium purge of XRF chamber

Remove protective window

Optimize scanner settings

- Voltage
- Current
- Scan duration

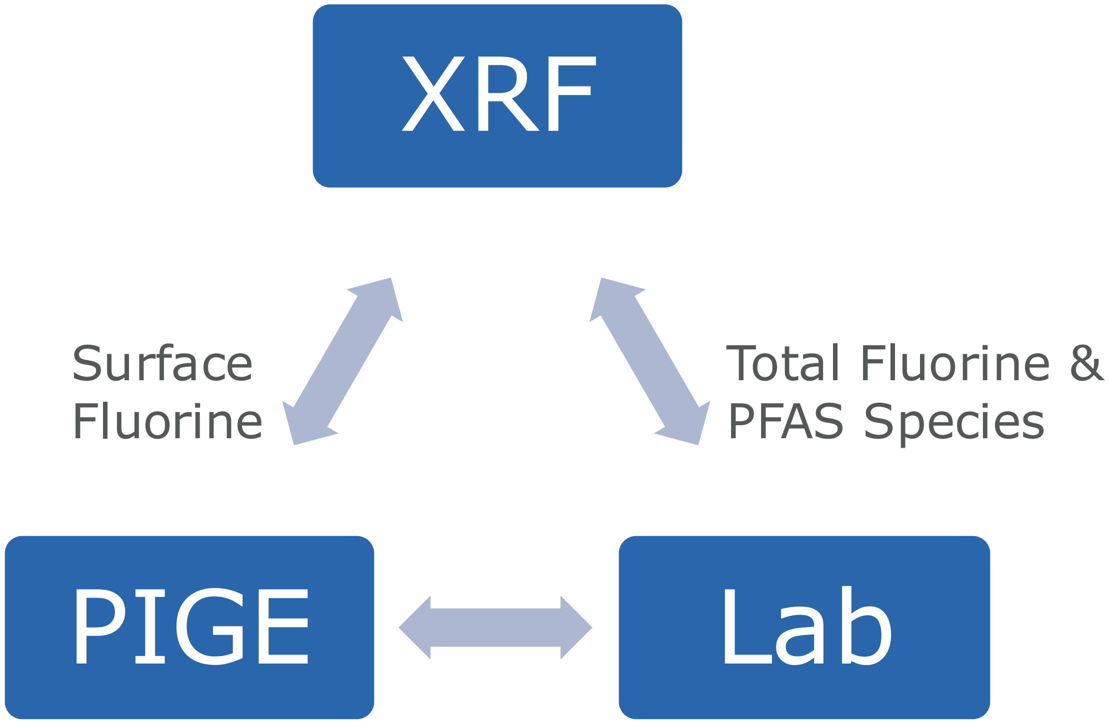


Calibration & Quantification

- **Calibration standards:**
  - Sodium fluoride (NaF) aqueous solution (NIST-traceable, Ricca)
  - Spiked onto mixed cellulose ester (MCE) filters (37 mm, 0.8 µm)
  - Concentrations: **50, 100, 200, 500, 1,000, 2,000, 5,000, 10,000 ppm**
- **Measurement:**
  - Each spiked filter scanned ≥3 times at the same spot using optimized XRF settings
  - Extracted X-ray counts from fluorine region of interest (ROI) (0.64–0.68 keV)
- **Curve fitting:**
  - Plot counts in F peak ROI vs. known concentration
  - Tested linear vs. polynomial/logarithmic models
  - Counts normalized to total X-ray counts to correct for run-to-run variability

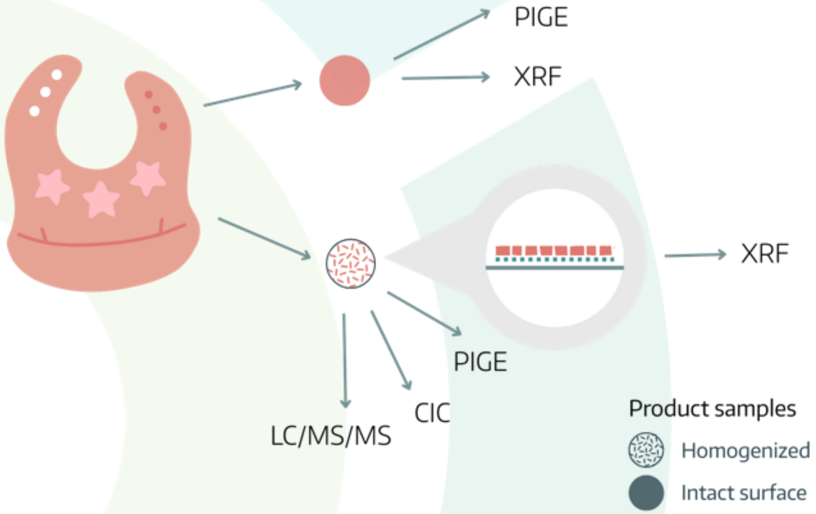
Analytical Approaches

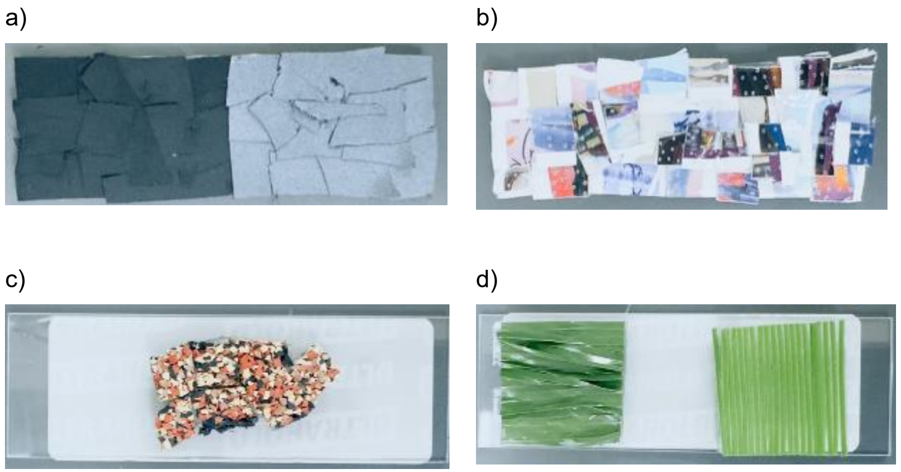
- **Handheld XRF (Bruker TRACER 5g)**
- **PIGE (Particle-Induced Gamma-ray Emission)**
  - Gold standard for surface fluorine
- **CIC (Combustion Ion Chromatography)**
  - Gold standard for total fluorine.
- **LC/MS-MS**
  - Gold standard for quantifying individual PFAS species



Sample Preparation

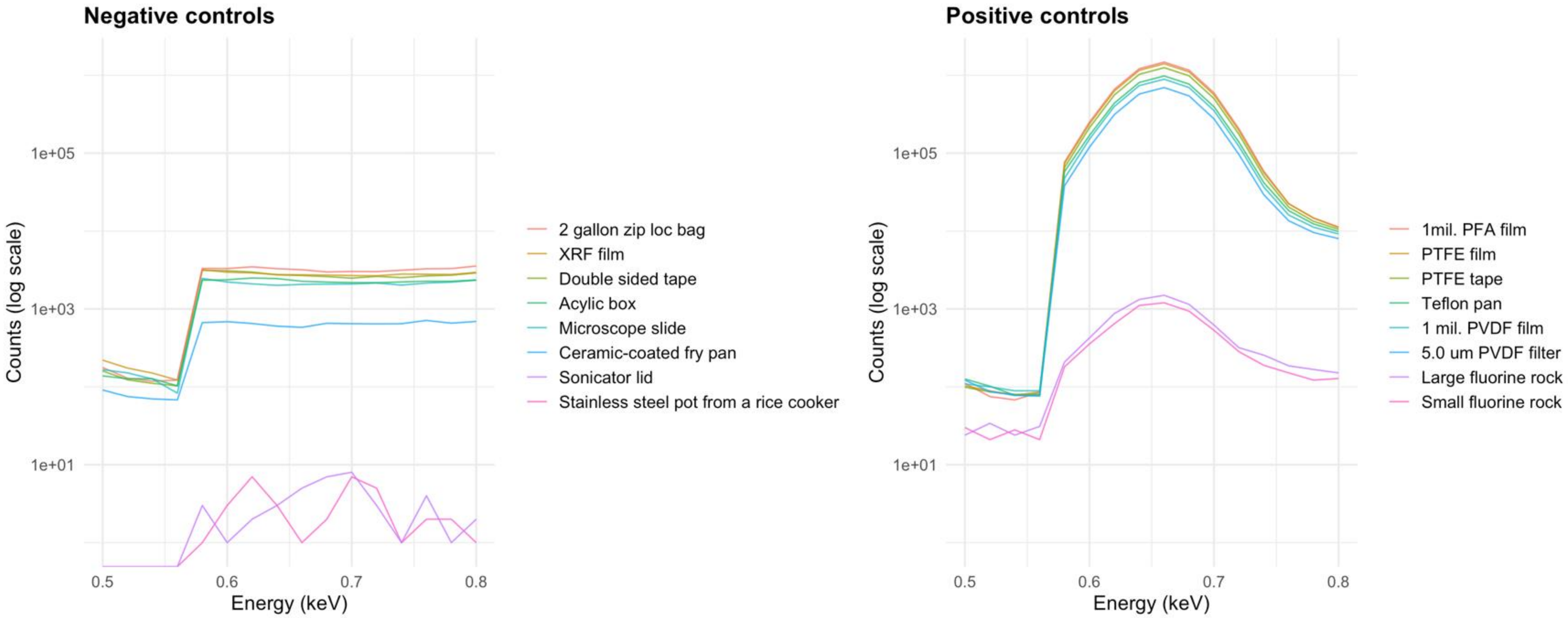
- Samples prepared as **intact** or "**homogenized**" (which I will now call **"processed"**)
- Processed samples mounted on microscope slides for XRF testing.





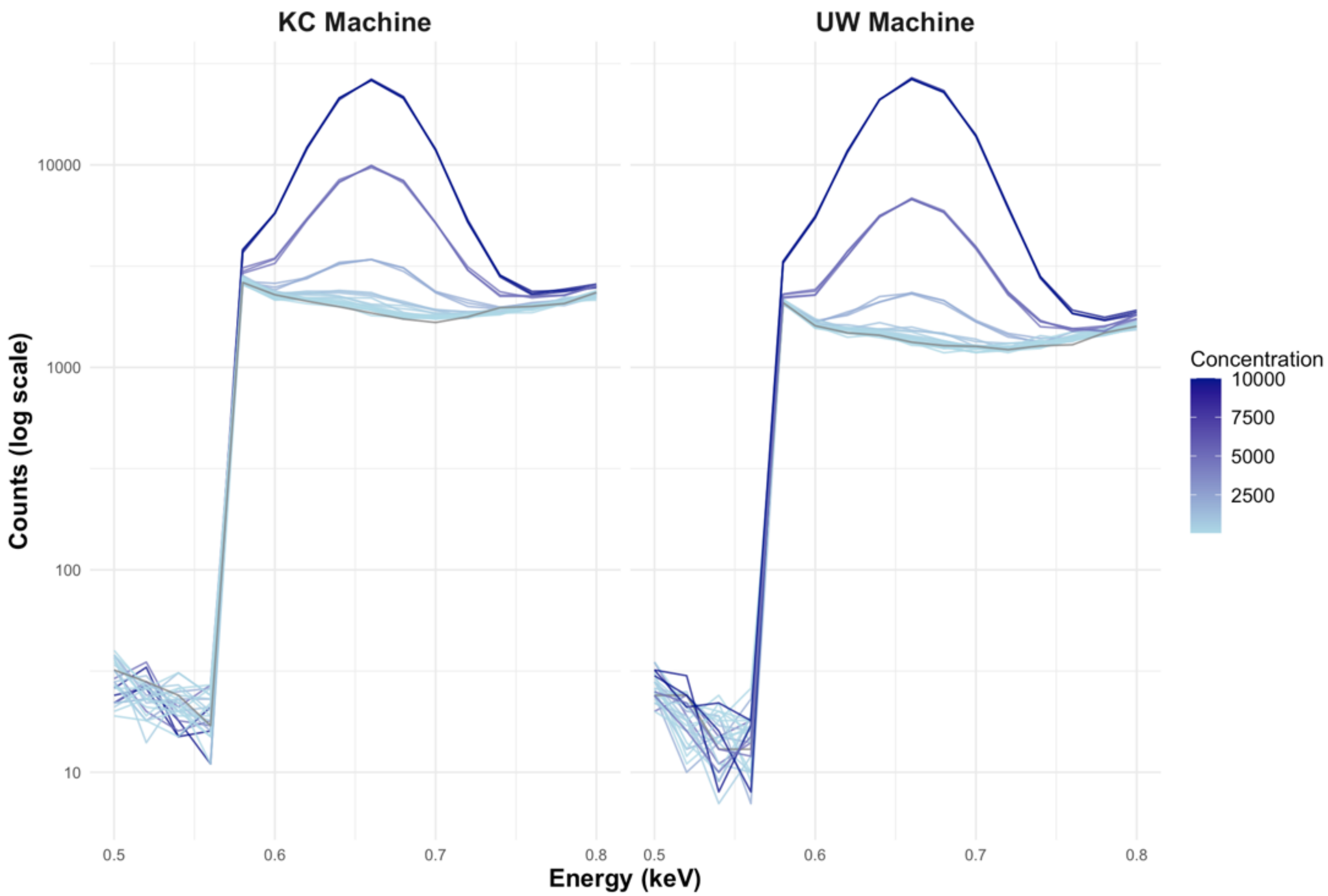
Processed samples of:
a) nylon jacket, showing two surface types.
b) adhesive bandage, showing one surface type.
c) playground tile made of rubber, showing one surface type
d) artificial turf, showing two surface types.

SPECTRA from Negative & Positive Controls



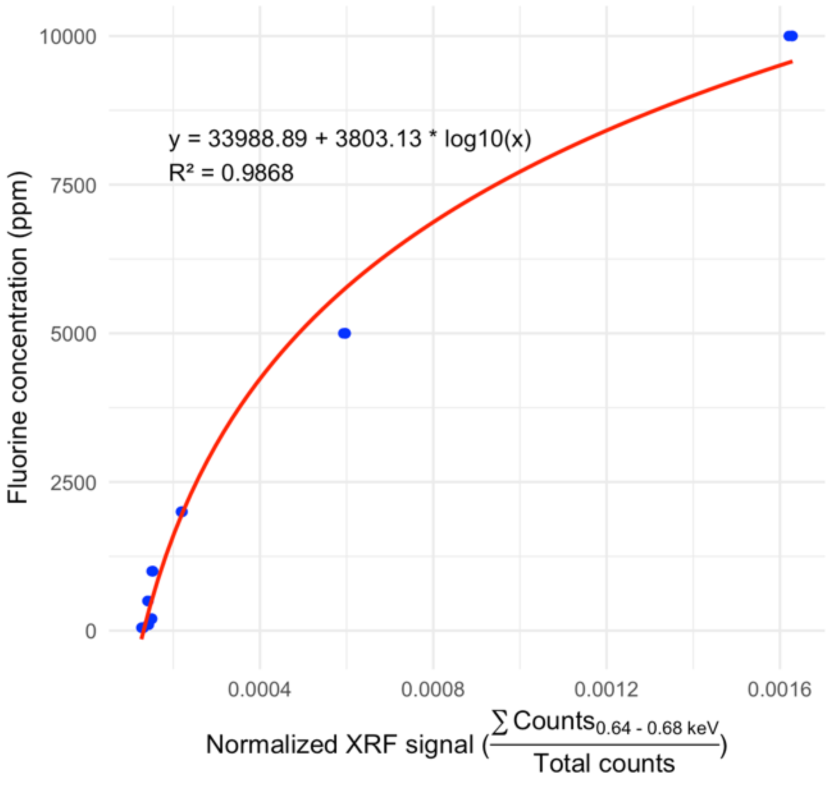
XRF spectrum from different objects known to contain fluorine (right, positive controls) and known not to contain fluorine (left, negative controls)

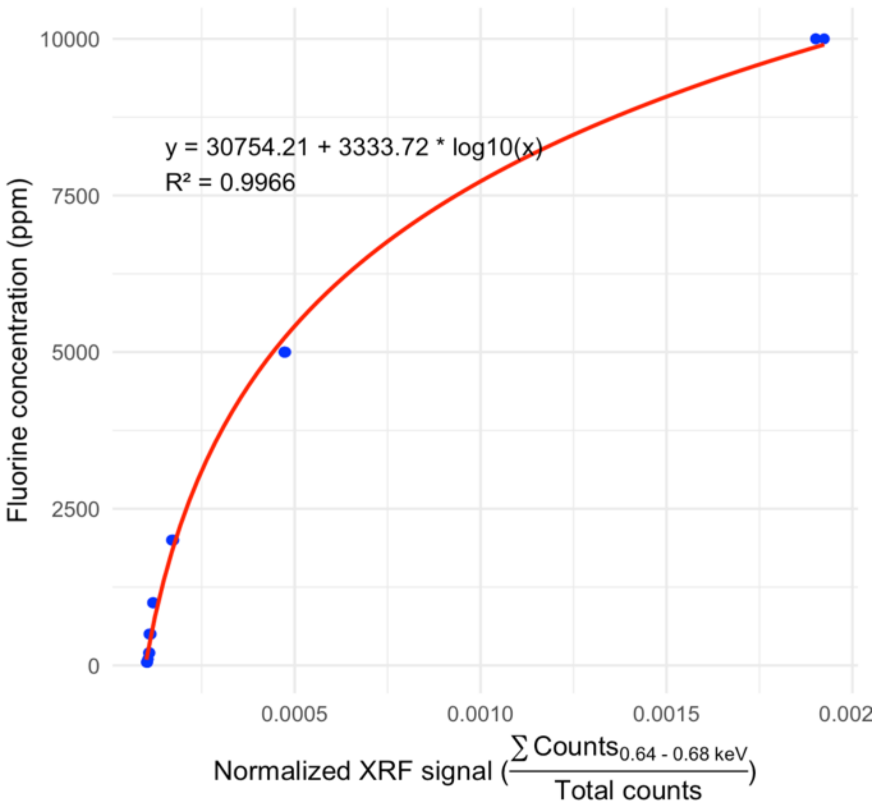
Spectra Across Different Fluorine Levels



XRF spectrum from different levels of fluorine concentrations using the 2 handheld XRF machines

Preliminary Calibration Curves of Handheld XRF



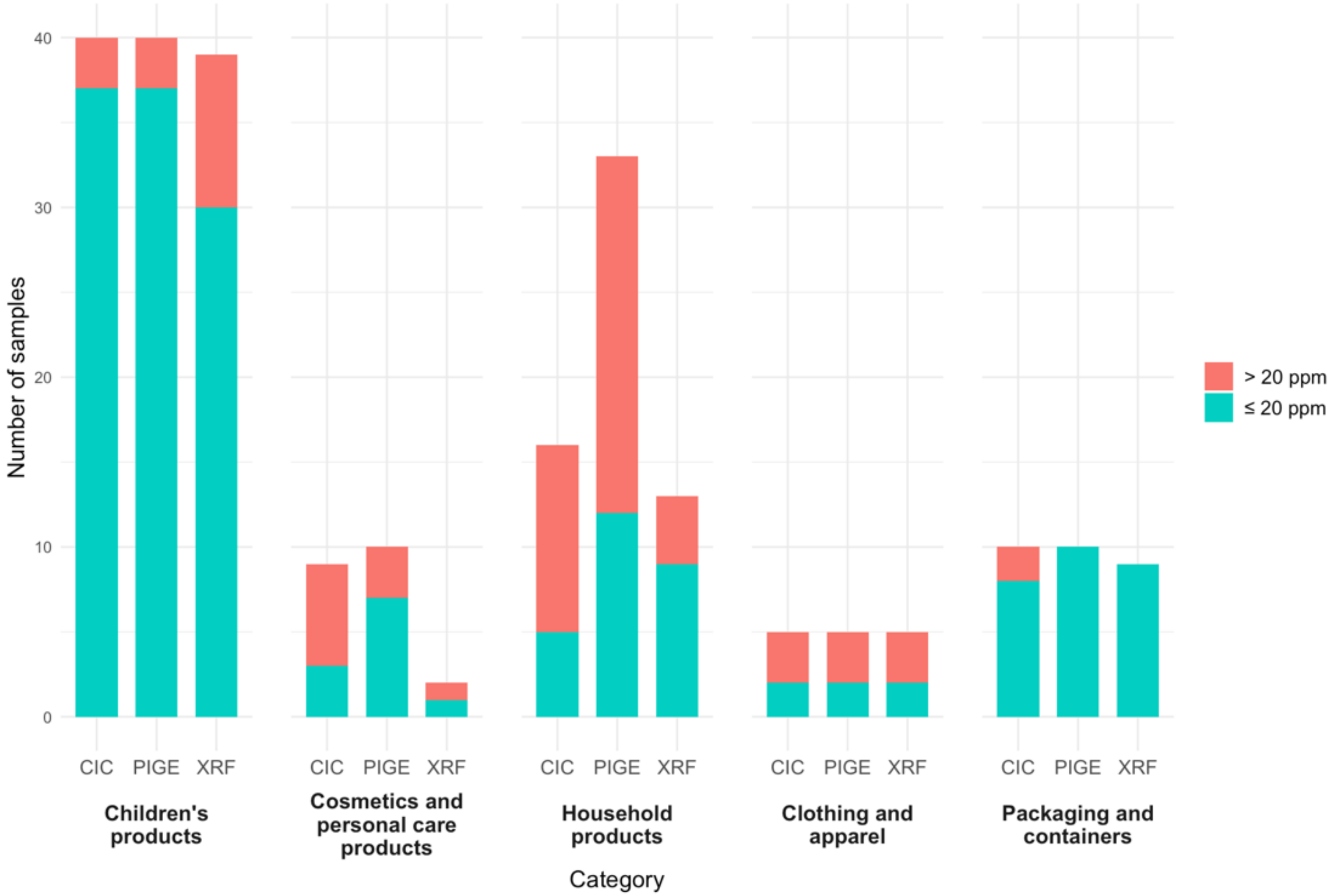


- Have tried many different fitting strategies and results don’t change

XRF detector response at different levels of fluorine concentration for each of the two handheld XRFs (King County machine left and UW machine right)

Preliminary Results

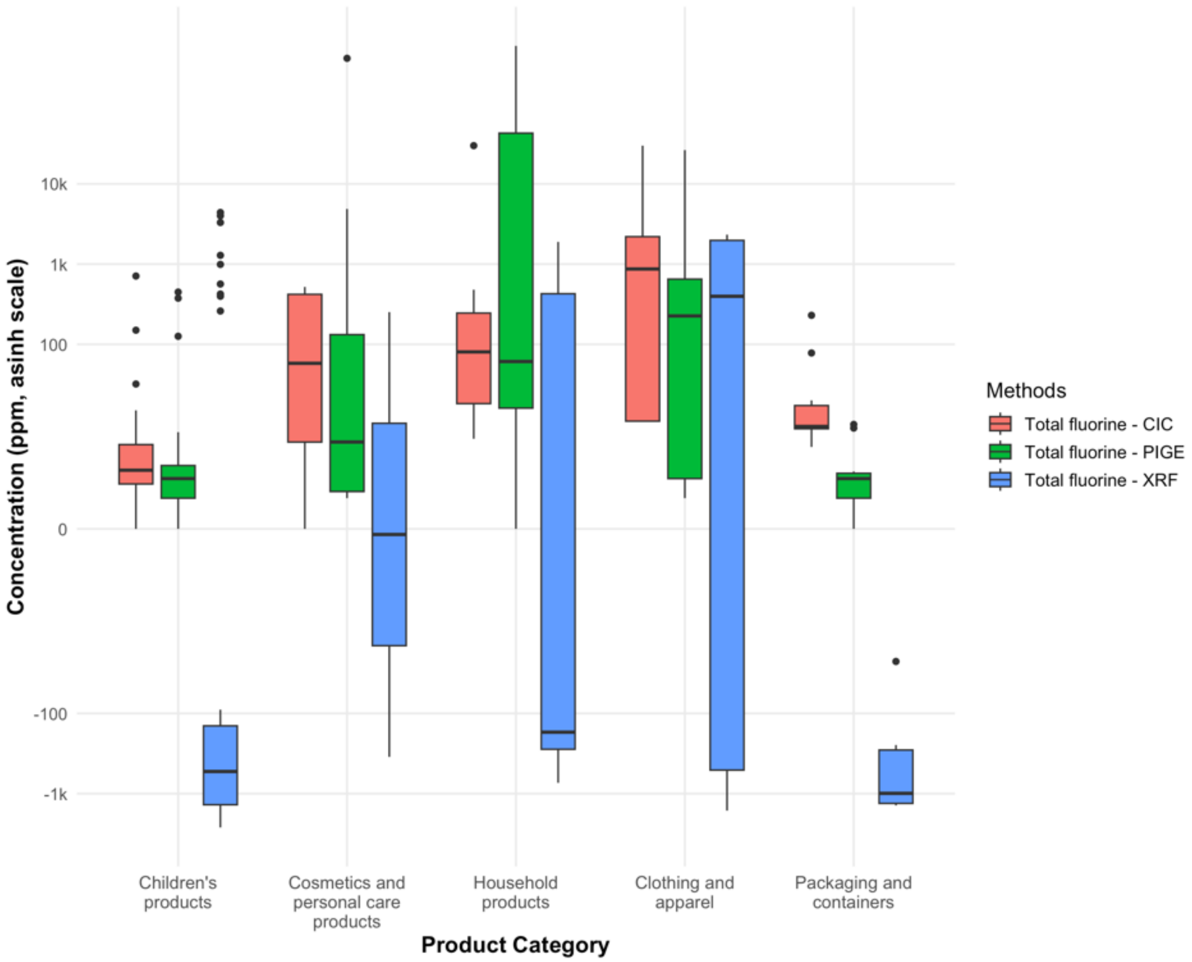
Comparing XRF with other methods



Proportion of fluorine detection by different methods and by product category

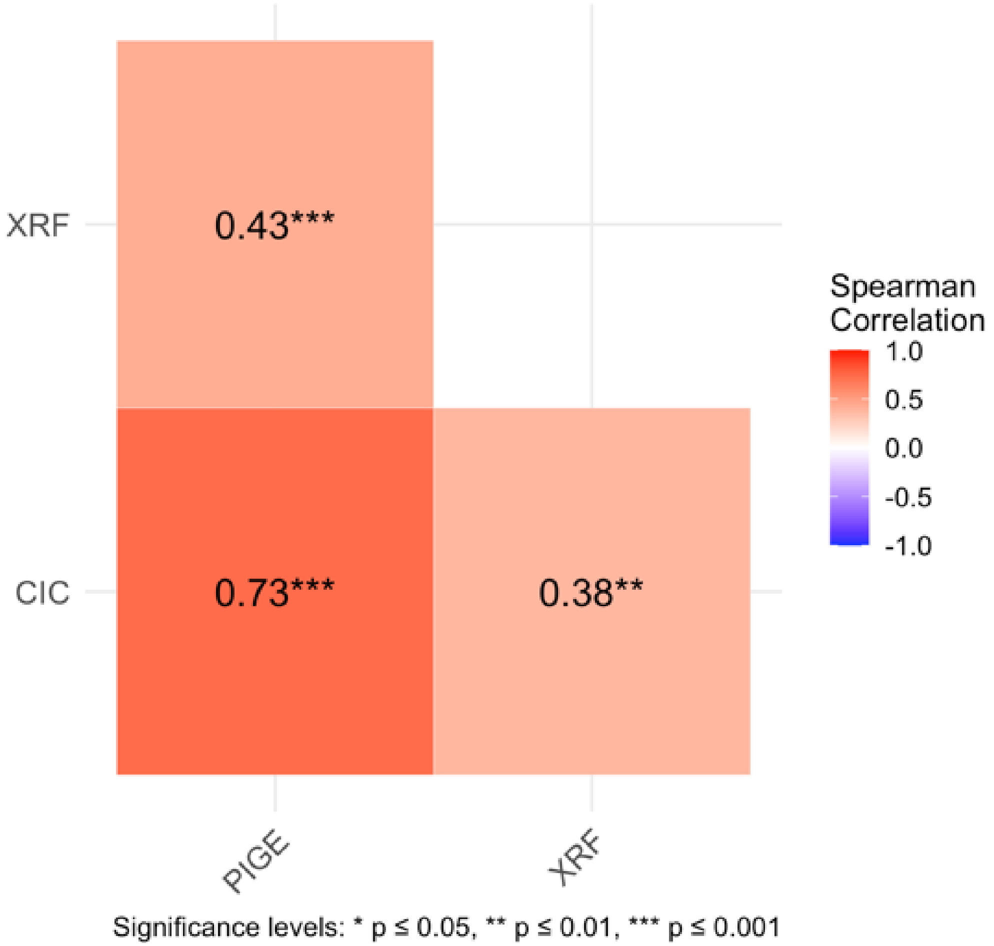
- Applied a 20 ppm threshold for "detection"
- *How many samples exceeded 20 ppm?*
  - CIC: 25/80 (31%) positive
  - PIGE: 30/98 (31%) positive
  - XRF: 17/68 (25%) positive
- Focus on 67 processed samples with XRF, PIGE, and CIC measurements

Fluorine Concentrations Distributions



- XRF estimates have higher variability and many negative values
- Quantitative estimate results should be treated as preliminary and needing further adjustments

Rank-order correlations across methods

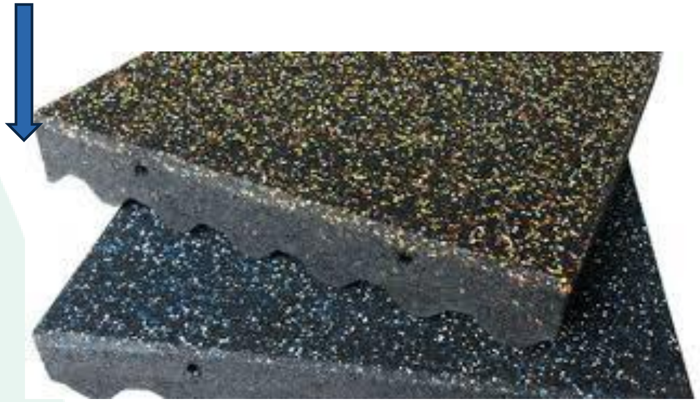


- XRF moderately correlated with PIGE & CIC in terms of rank order

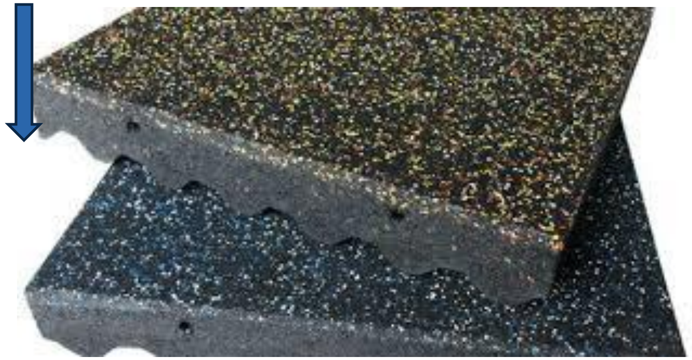
Comparing Handheld XRF With Other Methods For Fluorine Detection

XRF
X-Rays
penetrate ~ 1
micron

PIGE
Gamma-Rays
penetrate ~ 250
micron



CIC
Analyzes a processed
portion of the coating
(top layer of the
product when possible)



Agreement across three methods (processed samples)

XRF Detect	PIGE Detect	CIC Detect	# of Samples	% of Samples	PIGE Concentration Mean (Range)	CIC Concentration Mean (Range)
No	No	No	40	60.6	2.1 (0–9)	6.0 (0.4–20)
No	No	Yes	4	6.1	12.1 (2.5–20)	143 (78–230)
No	Yes	Yes	6	9.1	64.8 (23–126)	222 (32–480)
Yes	No	No	8	12.1	2.2 (1–7)	4.2 (0.4–8.8)
Yes	No	Yes	1	1.5	13 (13–13)	57 (57–57)
Yes	Yes	Yes	7	10.6	4,043 (26–26,405)	4,927 (76–30,000)

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Agreement statistics (processed samples)

Comparison	Sensitivity	Specificity	Accuracy	Cohen's Kappa
XRF vs. PIGE	53.8%	81.8%	76.5%	0.32
XRF vs. CIC	44.4%	83.3%	72.7%	0.29

When was agreement better/worse?

Sample	N	# of detects (PIGE)	# of XRF detects	False Pos	False Neg	Sensitivity	Specificity	Median ppm (Range)
All homgenized	68	13	7	10	6	0.54	0.82	2 (0 - 26405)
>200 ppm	5	5	5	0	0	1.00	NA	448 (226 - 26405)
20 - 200 ppm	8	8	2	0	6	0.25	NA	62.5 (23 - 170)
<20 ppm	54	0	0	10	0	NA	0.81	2 (0 - 16)
Dead time % <30	25	5	4	2	1	0.80	0.90	2 (0 - 26405)
Dead time % >30	43	8	3	8	5	0.38	0.77	2 (0 - 376)
Plastic	14	2	0	0	2	0.00	1.00	1.5 (0 - 89)
Rubber	14	3	1	4	2	0.33	0.64	4 (1 - 26)
Fabric	33	7	6	6	1	0.86	0.77	2 (0 - 26405)
Cookware***	17	14	11	0	3	0.79	1.00	16802.5 (1 - 525914)

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When was agreement better/worse?

XRF better detected F when:

- F concentrations were high
- Deadtime % was low
- Scanning certain matrices (metal, fabrics)

Limitations

- Calibration/quantitation
  - High variability
  - Many (highly) negative values
  - Quantitative estimates do not match other methods
- High number of F-free products
  - Limits ability to assess detection capacity
- Current protocol may be difficult to deploy
  - Need to rigorously assess performance of intact samples
  - Need to explore opportunities to make easier for field use

Current/future planned work

- Improving quantitation performance (in the service of better classification performance)
    - Additional F standards
        - Plaster of Paris
        - Resin
- Focused product sampling
    - Cookware, children’s products, carpet
- Optimization for field deployment
    - Shorter scan times
    - Whether He purge is needed for products with very high surface F (e.g., non-stick cookware, legacy apparel)
    - Software to automate quantitation

Concluding remarks

- Evidence that handheld XRF can detect high levels of fluorine at the surface of products
- Further performance and optimization research is warranted to identify limits of use
- May be useful for specific products and applications

Community-guided research explores new tool to spot signs of PFAS in everyday products

New pilot project explores how a portable tool—and community input—can help identify toxic "forever chemicals" in the products we use every day

https://kingcounty.gov/en/dept/dnrp/waste-services/hazardous-waste-program/news-events/news/2025-08-21-pfas-research-xrf

Questions?

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