

Total Fluorine Analysis to Screen for PFAS in Personal Care Products

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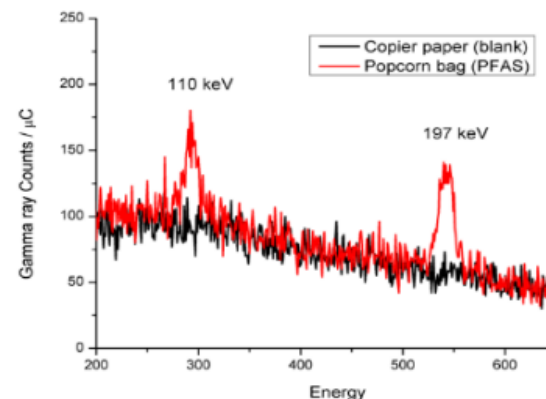
ECEC 2019
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PIGE Analysis of Fluorine



Fig. 3: PFAS-coated paper sample compared with uncoated paper. Irradiation time of 180 second with 9 nA of 3.4 MeV protons.



Spectroscopic technique
Rapid (<180 seconds)
Non-destructive



PIGE Analysis of Fluorine

Total F finds
50x – 100x
 more PFAS in
 environment
 than LC-MS/MS

Closing the Mass Balance on Fluorine on Papers and Textiles

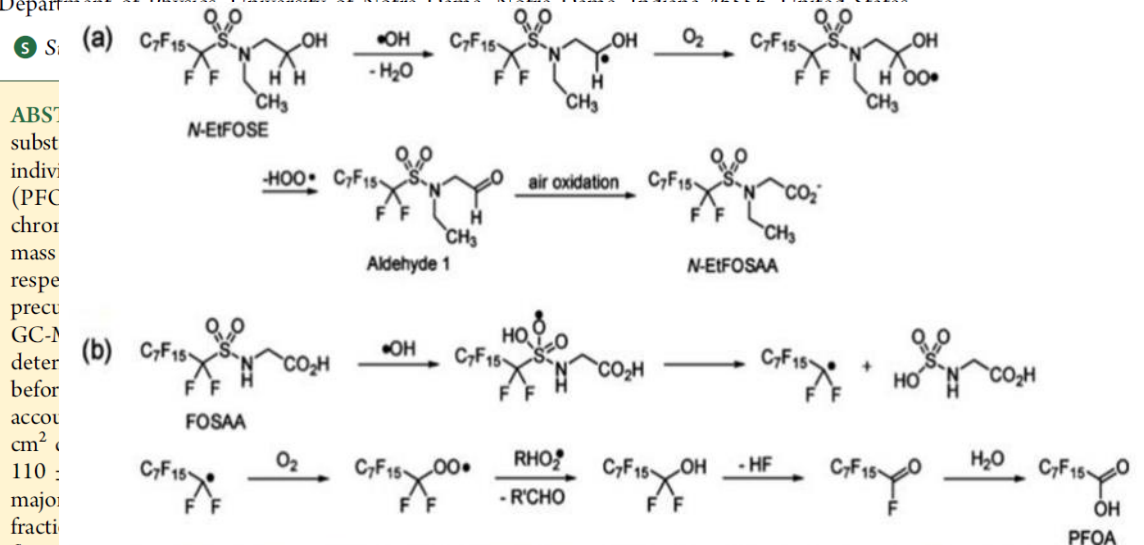
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(a) Proposed reaction mechanism for oxidation of N-EtFOSE to N-EtFOSAA via reaction with $\cdot\text{OH}$. (b) Proposed reaction mechanism for transformation of FOSAA to PFOA via reaction with $\cdot\text{OH}$.

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PIGE Analysis of Fluorine

PIGE, CIC and
NAA all agree,
TOP assay can
agree...

Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

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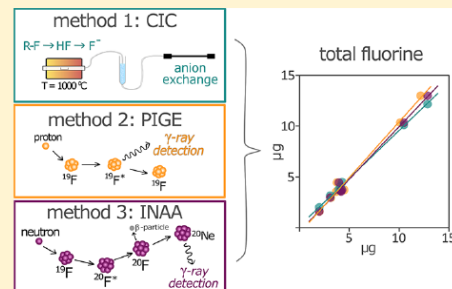
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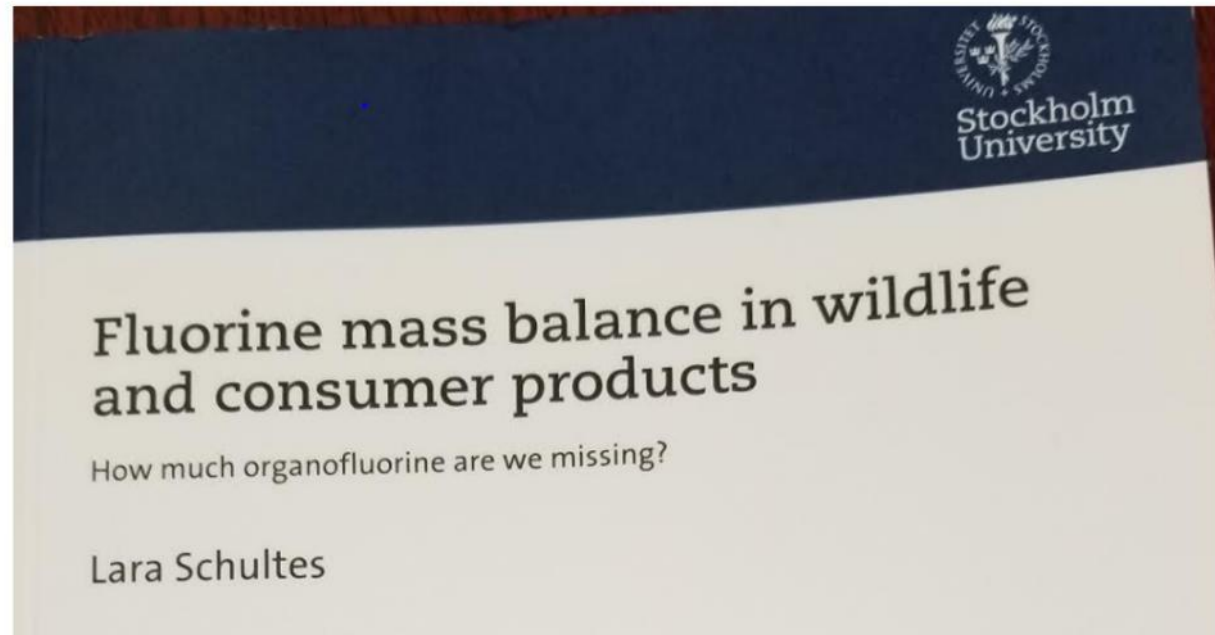
Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) represent a class of more than 4000 compounds. Their large number and structural diversity pose a considerable challenge to analytical chemists. Measurement of total fluorine in environmental samples and consumer products is therefore critical for rapidly screening for PFASs and for assessing the fraction of unexplained fluorine (i.e., fluorine mass balance). Here we compare three emerging analytical techniques for total fluorine determination: combustion ion chromatography (CIC), particle-induced γ -ray emission spectroscopy (PIGE), and instrumental neutron activation analysis (INAA). Application of each method to a certified reference material (CRM), spiked filters, and representative food packaging samples revealed good accuracy and precision. INAA and PIGE had the advantage of being nondestructive, while CIC displayed the lowest detection limits. Inconsistencies between the methods arose due to the high aluminum content in the CRM, which precluded its analysis by INAA, and sample heterogeneity (i.e., coating on the surface of the material), which resulted in higher values from the surface measurement technique PIGE compared to the values from the bulk volume techniques INAA and CIC. Comparing CIC-based extractable organic fluorine to target PFAS measurements of food packaging samples by liquid chromatography–tandem mass spectrometry revealed large amounts of unidentified organic fluorine not captured by compound-specific analysis.



Motivation: Total F Screening

- LC-MS/MS is very sensitive, but expensive
- Only sees ~1% of environmental PFAS

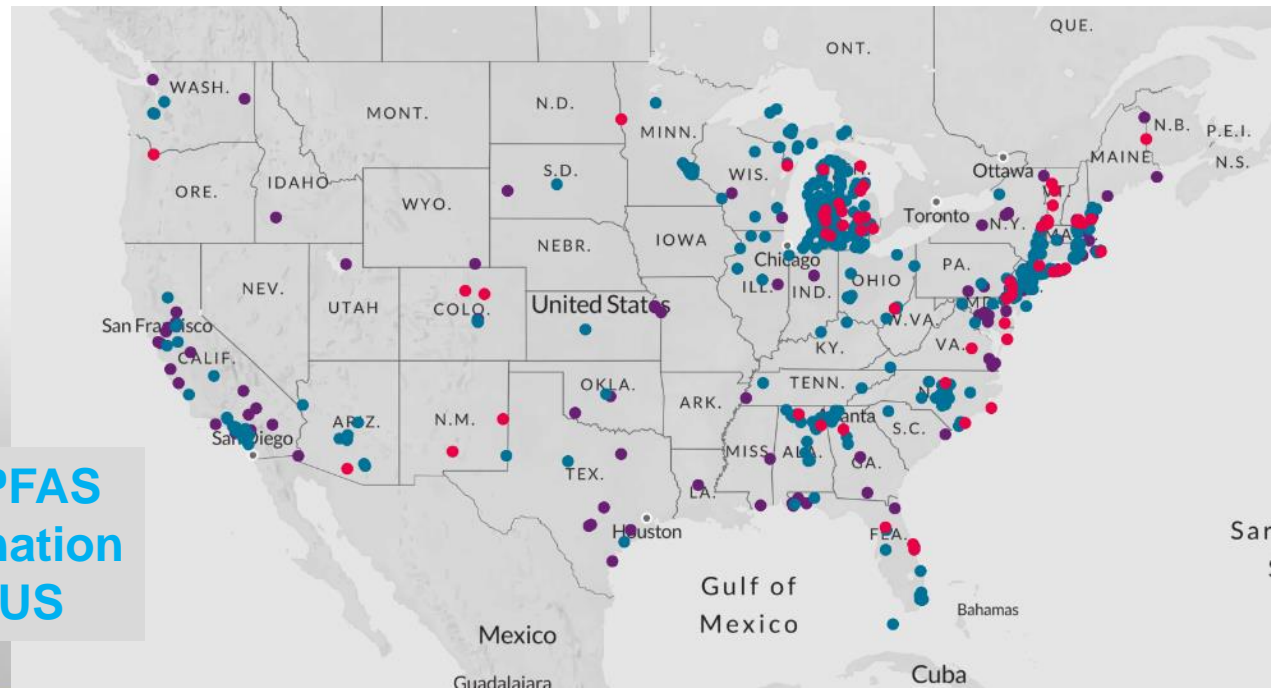


Doctoral Thesis in Applied Environmental Science at Stockholm University, Sweden 2019



Motivation: Total F Screening

- LC-MS/MS is very sensitive, but expensive
- Total F is complementary screening tool:
e.g. Groundwater



**EWG: PFAS
contamination
in the US**



Motivation: Total F Screening

- LC-MS/MS is very sensitive, but expensive
- Total F is complementary screening tool:
e.g. Food packaging paper



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Fluorinated Compounds in U.S. Fast Food Packaging

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Researchers found fluorina
third of the fast food packe
according to a report [cnn.i](#)



RETWEETS 237 LIKES 205



Researchers find "another reason" to
avoid fast food: Chemicals in the packaging



Researchers find 'another reason' to avoid fast food: Chemi
Substances with links to health problems have been found in wr
containers, where they can leach into food.

washingtonpost.com



The Nasty Ingredient in Fast-Food Wrappers
[mojo.ly/2jCPzA4](#)



RETWEETS 19 LIKES 22



Motivation: Total F Screening

- LC-MS/MS is very sensitive, but expensive
- Total F is complementary screening tool:
 - e.g. Great Lakes Fish Study
 - Textiles: Firefighters PPE & AFFF
 - Remediation Efficiency
 - Landfill Fate and Transport
 - New uses of PFAS...



Personal Care Products

- Largely unregulated by federal government

The **Cosmetic Ingredient Review (CIR)**, based in [Washington, D.C.](#), assesses and reviews the safety of ingredients in cosmetics and publishes the results in peer-reviewed scientific literature. The company was established in 1976 by the [Personal Care Products Council](#) (then called the Cosmetic, Toiletry, and Fragrance Association)

Overall funding for CIR comes from the cosmetic industry's main trade association, the Personal Care Products Council.^[1]

As of 2013, the [European Union](#) bans nearly 1,400 chemicals from personal care products because they are carcinogenic, mutagenic, or toxic to reproduction. In the United States, CIR has found only eleven chemicals to be "unsafe for use in cosmetics".^[1]



Personal Care Products

Environmental
Science
Processes & Impacts



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Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: implications for environmental emissions and human exposure†

Lara Schultes, *^a Robin Vestergren,^{*b} Kristina Volkova,^c Emelie Westberg, ^b Therese Jacobson^c and Jonathan P. Benskin *^a

Included 31 Creams, Pencils, Powders, Foundations, Shaving creams.... (39 PFAS)



Personal Care Products

PFAS found:

PTFE

Polyperfluoromethylisopropyl ether

Trifluoroacetyl tripeptide-2

Ammonium C6-16 perfluoroalkylethyl phosphate

C9-15 fluoroalcohol phosphate

Polyperfluoroethoxymethoxy difluoroethyl PEG phosphate

Perfluorooctyl triethoxysilane

Trifluoropropyl demethiconol



Personal Care Products

Our Study: **235 cosmetics**

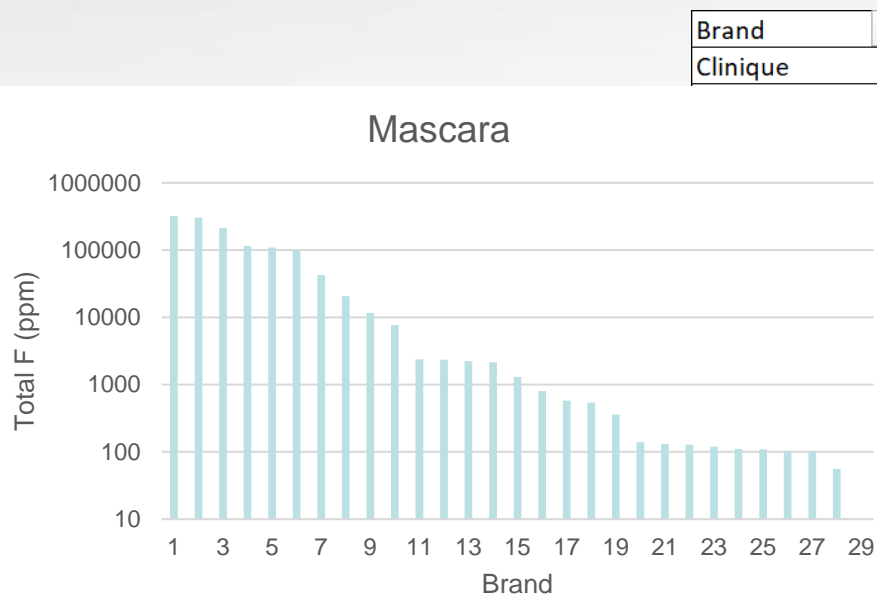
mascaras,
eye-makeup,
liquid lipsticks,
cream lipsticks,
face makeup, and
skin care.

category	number of samples tested	number of brands tested	Avg: 54% % with F
mascaras	29	19	79
eye makeup	48	14	56
lipsticks	56	26	70
face makeup	59	21	51
other	43	11	26

Table 1: Percentages of Personal Care Products Containing Fluorine



Personal Care Products



Brand	Product	Ta-Normalized Count
Clinique	High Impact Mascara	679812
Clinique	Lash Sensational H2O Proof Mascara	643403.0
Clinique	Suptuous Extreme Waterproof Mascara	453392
Clinique	Lights, Camera, Splashes Waterproof Mascara	243740.7
Clinique	Lash Blast Waterproof (Black)	230082.8
Clinique	Better Than Sex Waterproof Mascara	206537.8
Clinique	The Super Sizer Waterproof Mascara	89589.0
Clinique	Megaprotein Mascara Hydrofuge	43458.1
Clinique	In Extreme Dimension 3D Lash Mascara	24344
Clinique	Lashblast 24 HR Mascara (Discontinued)	16089.5
Clinique	Drama Lash Maximum Volumizing Mascara	4873.0
Clinique	Clump Crusher Mascara (Waterproof)	4826.9
Clinique	Cannonball Waterproof Mascara	4585.5
Clinique	Perversion Mascara	4396.5
Clinique	Outrageous Volume Dramatic Volume Mascara (Black)	2608.3
Clinique	Pro Mascara	1554.4
PUR	Volume Vixen 4 in 1 Mascara	1078.5
Physicians Formula	Organic Wear Mascara	998.6
Perricone	No Makeup Mascara	615.025
PUR	Fully Charged Mascara	152.872
Tarte	Lights Camera Lashes Mascara	137.265
Butter London	Stroke of Wow Mascara	130.781
Julep	With a Twist Mascara	111.559
Urban Decay	Subversion Thicker, Longer, Stronger Lash Primer	92.7
Benefit	Bad Gal Bang Mascara	90.2082
Juice Beauty	Phyto Pigments Ultra Natural Mascara	78.5246
PUR	Big Look H2O Proof Mascara	75.6
Juice Beauty	Ultra-Natural Black Mascara	-21.9
PUR	Big Look Mascara	-210.8



Personal Care Products

Next Steps:

- Identify specific PFAS analytes
- F in 92% of waterproof mascaras
- F in 89% of liquid lipsticks
- Publish – increase market pressure



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