Determination of Light Elements by XRF

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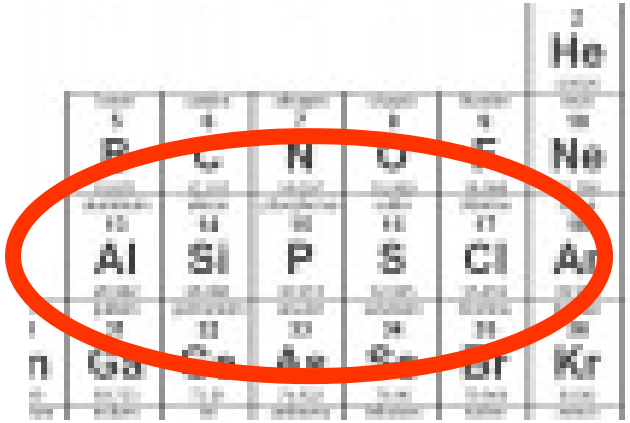
Which Elements will I discuss



- Silicon, Phosphorous, Sulfur, Chlorine
- Accurate Measurement Important to
  - Fuels performance
  - Various Issues in refining
- Analytically challenging
  - Difficult or impossible by ICP-OES
  - Can achieve low ppm level quantitation by XRF

General Issues and Limitations of ICP/ICP-MS

Organic Matrix

- Easy sample prep but
- Organics raise background and hurt detection limits
- Require dilution, at least 5x1 to achieve viscosity match
- Volatile components give false positive results
- Suspended solids can partition in spray chamber

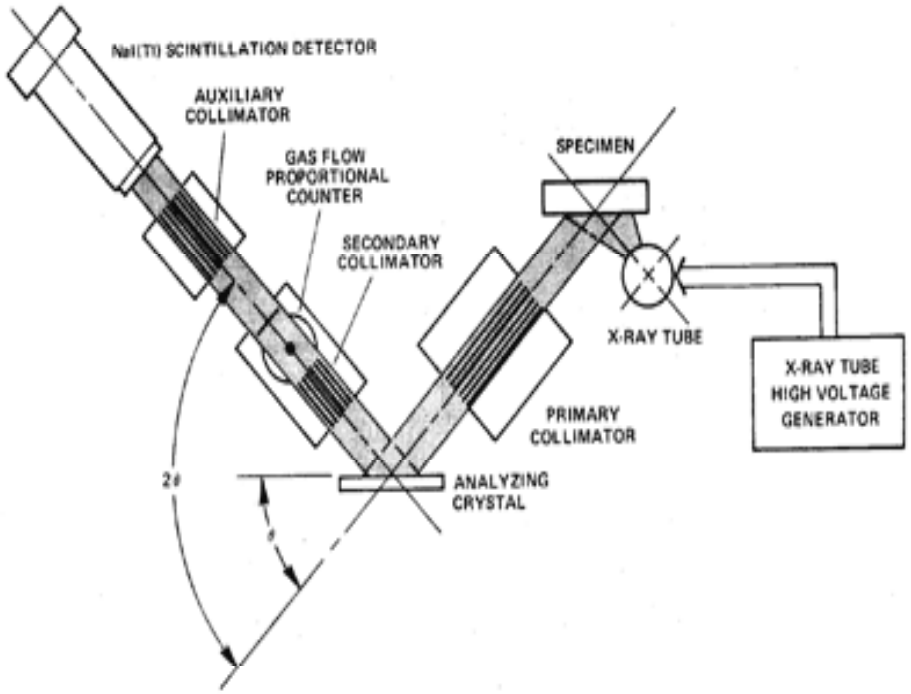
Aqueous matrix

- Requires digestion of organics
- Lose volatile elements with most digestions
- Significant dilution factors on sealed digestion
- Digestions are involved procedures

Element Specific Issues in ICP-OES

- Si Issues
  - .03 ppm detection limit
  - Volatile siloxanes impair quantitation
  - Inorganic silicates separate in ICP spray chamber
- P Issues
  - .5 ppm practical detection limit after dilution
  - Requires sealed digestions
  - Interferences in ICP-MS
- S Issues
  - Poor detection limits, 3-5 ppm
- Cl Issues
  - Requires specialized ICP
  - Very poor detection limits, 100’s of ppm

Basic Issues for WD-XRF Trace Analysis



Standard WD Instrument

- Excitation source
- Film choice
- Analyzer Crystal
- Analysis Time
- Dealing with Interferences and matrix effects

Common XRF Excitation Sources

Rh, Pd, Ag
general sources, broad excitation
light elements rely on La line not Ka line

Rh typical, best for S, P, not as good for Cl

Pd, Ag better for Cl but lose performance for S, P

Cr specific for light elements

My instrument uses Rhodium

- Rh x-ray tube lines
  - Ka 20.2 keV
  - La 2.7 keV
- Pd x-ray tube
  - Ka 21.2 keV
  - La 2.8 keV
- Ag x-ray tube
  - 22.2 keV
  - 3.0 keV
- Cr
  - Ka 5.4 keV

Ka energies

- Si 1.7 keV
- P 2.0 keV
- S 2.3 keV
- Cl 2.6 keV

Film Choices for naphtha/gasoline

- Key factors
  - Stability, stability, stability
    - Leaking film is a big problem
    - Naphtha and gasoline are potent solvents
  - Contaminants
    - Can’t do trace measurements against high backgrounds
  - Transparency and Thickness
    - Weak x-rays don’t penetrate thick films

Stability Test and Comparison

- Screening Test:
  - Single cup for several hours
  - No wrinkling, weeping, or breakage
- Formal Stability Test
  - Ten sample cups
  - Elevated so film is not supported
  - % failures at 2 hours, 24 hours

Stability Tests with Gasoline

Film	Thickness	Screening	% of 10 for Two Hour	% of 10 for > 24 Hour
Polypropylene	All	Fail		
Polycarbonate	All	Fail		
Mylar	6.0	Fail		
Etnom	1.5	Fail		
Etnom	3.0	Pass	100%	100%
Prolene	3.0	Fail		
Prolene	4.0	Fail		
Kapton	7.0	Pass	100%	100%
Mylar/prolene	4.5	Pass	100%	100%

Film Backgrounds By Element

Film	Si	P	S	Cl
Etnom 3.0	1.509	.255	.029 2.44	1.238
Prolene 4.0	.1625	.06	.01533 8.95	.941
Kapton	.1910	2.24	.019 5.59	.934
Mylar 2.5	.1304	.08	.014 4.63	.836
Mylar/prolene	.226	.39	.023 7.42	.796

Measurement taken on nanopure water sample, 8g sample
Upper taken on 28 mm mask, lower 34 mm mask
All in kcps

Signal Response by Film for Silicon (counts/ppm, Rh excitation)

Film	Thickness	Si
Etnom	3.0	9.8
Kapton	7.0	4.6
Mylar/prolene	6.5	7.8
Mylar	2.5	10.2

Mylar is best but does not have sufficient solvent resistance
Etnom is excellent but has a high silicon background
Kapton has half the signal response due to thickness and composition
Mylar/Prolene is my current choice for silicon but watch out for lot variation in silicon background

Analyzer Crystal Comparison

Crystal	Si	P	S	Cl
Ge		x	x	X
Curved Ge		XX	XX	
InSb	XX			
PET				
OVO 55				

Preferred Options for Light Elements

	Si	P	S	Cl
Best Film	Mylar/prolene	ETNOM	ETNOM	ETNOM
Best Crystal	InSb	Curved Ge	Curved Ge	Curved Ge
Excitation	Rh	Rh	Rh	Rh (Cr)
Mask	34	34	34	34

One method will not give best results for all elements
Cannot keep sample in instrument long enough for trace measurements on Everything (ten minutes analysis is goal)

Matricies and Interferences

- C,H Matrix
  - Gasoline, naphtha
    - mixed aromatic/aliphatic
    - PX matrix or PX/mineral oil matrix
  - Diesel, Jet,
    - highly aliphatic
    - Mineral oil matrix
- Sulfur varies widely
  - Diesel typically 6 ppm
  - Coker naphtha, hundreds ppm
- O content varies from zero to few percent
  - Very low in refinery streams and diesel
  - Blended gasoline can have 6-10% Ethanol
  - Biofuels oxygen content depends on oil

Basic Calibration Strategy

- Pick hydrocarbon matrix
  - Aromatic/aliphatic (mixture of paraxylene/mineral oil)
  - Aliphatic (mineral oil)
- Add oxygenate to matrix at approximate level
- Measure Element of choice at background and peak with 5 minute counting maximum
- Measure S only at peak with 30 second max.
- Improve accuracy by standard addition if warranted

Limits of Detection and Quantitation

Element	Detection Limit (3x background)	Quantitation Limit	Monochromatic XRF Detection Limit
Si	0.2	3	?
P	0.4	1	?
S	0.2	1	0.1
Cl	1	5	0.1

Conclusions

- WD-XRF provides relatively simple method for trace determination of light elements
- Critical factors are
  - Excitation wavelength
  - Crystal choice
  - Film choice
- Low ppm analyses can be achieved for all elements if these are optimized
- With Silicon contamination is very critical
  - Silicon oil contaminates most lab plastic and nitrile gloves
  - Dust contains significant silicon content