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Petroleum and Beyond XRF Analysis of Alternative Energy Sources

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Introduction

Natural Resources Canada, CanmetENERGY

Canadian leader in clean energy research and technology development. With a vast scientific staff and over 100 years of experience ,CanmetENERGY is Canada's knowledge centre for scientific expertise on clean energy technologies.

Introduction

Characterization Laboratory

- We are a team of chemists and technologists providing routine and specialized analytical services and expert advice to both internal and external clients involved with energy technologies

Introduction

Kids say the funniest things…

> My children think I have the best job in the world! They think that my XRF Spectrometer is an oversized XBOX. They say,' Mom's going to go to work to play with her XBOX'. .. I was about to say it's not an XBOX… but then I thought, X-ray BOX...hmm they could be right and I definitely have fun with it!

Anything to link the generations and maybe new XRF users

Fossil Fuels

- Through extensive research done by the scientific community on how to extract the raw fuel and make it into a viable source for our daily use , we have obtained a lot of knowledge on this fuel type and are able to characterize its properties reasonably well

- One method of analysis that has proven to be an excellent and versatile technique for the determination of the elemental composition of both liquid and solid fuels is:

XRF Spectrometry

Fossil Fuels - Liquid

Liquid Petroleum Fuels

- Gasoline
- Diesel
- Residual oil
- No.6 Fuel Oil

PETROLEUM- LIQUID FUELS

- Sulfur in oils –ASTM D2622
  - Fast and efficient method that does not destroy the sample
  - The main drawback is sample size, requiring at least 10 mls. This proved to be problematic for some of our clients performing research at a bench scale. Spacers used to reduce sample size.
  - Able to get as low as 10 ppm ,which for most of our clients was sufficient.

Petroleum – Liquid Fuels

– Trace elements in oil

- An in-house method was developed so that the analysis could be carried out by the fused bead method on the WD-XRF
- This method was very time consuming

Fossil Fuels

- Solid Fuels
  - Coal
  - Coke
  - Petroleum Coke
  - Ash deposits

Fossil Fuels-Solid Fuels

- Analyse fuels for major and minor components as per ASTM D4326
- Trace elements are also included in the suite
- All samples prepared in a Lithium Borate flux
- Despite the fact that many of the samples differ somewhat we are able to cover everything with the quantitative method set-up on the WD-XRF

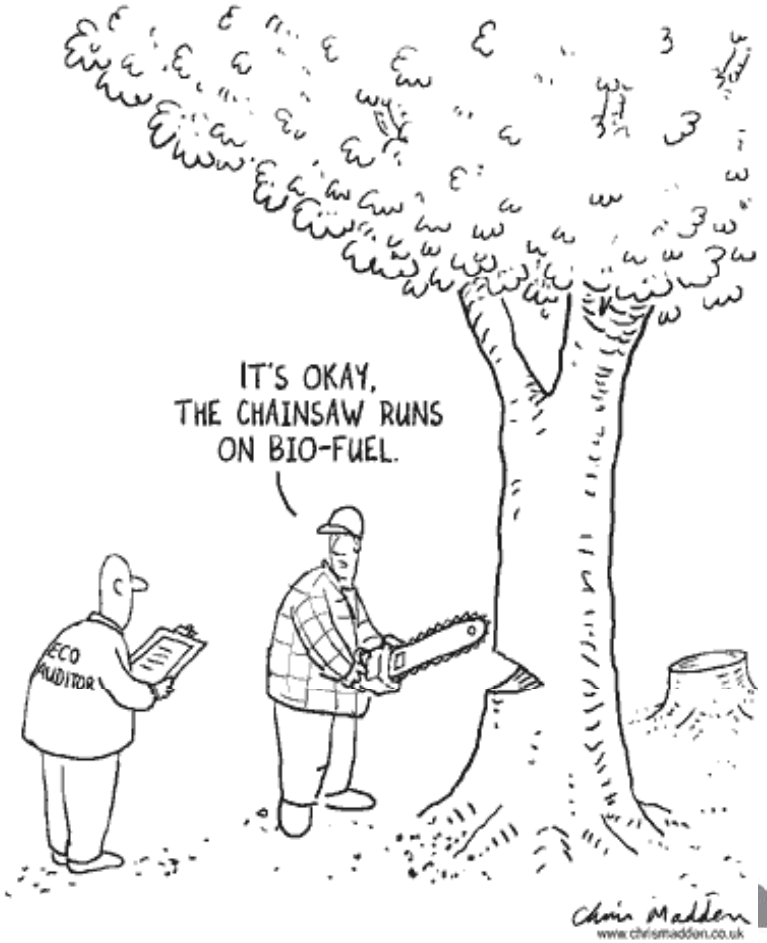
Co-firing coals with petroleum cokes

- Petroleum cokes are abundant,possess a high calorific value and low ash content
- Contains a high level of vanadium; environmental and health concerns
- Successful speciation of vanadium using XRF and XRD

Fossil Fuels

- Still continues to be the bulk of our analysis
- Benefit: a lot of literature and certified standards available
- Co-firing coals with biomass is becoming popular

Alternative Energy Sources



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Alternative Energy Sources
Solid Fuels

- During the early 2000's research into the combustion of biomass started to increase
- Depending upon the source of the biomass feedstock, samples started exhibiting with high levels of
  - Potassium
  - Phosphorous
  - Manganese

Alternative Energy Sources

- Some sources:
  - Wood
  - Miscanthus
  - Hay
  - Corn husks
  - Switchgrass
- And the list goes on, if you can burn it our scientists will try it

Alternative Energy Sources

- The quantitative curves were definitely not calibrated to the levels that the biomass samples were presenting
- Excellent correlation between the quantitative method and semi-quant program. Calibrations extrapolated extremely well out to the high levels.
- Extreme variances were seen , this was dependent upon the feedstock
- Use a reduced temperature of 550 C to ash biomass samples prior to fusion

Alternative Energy Sources

- No major issues with the analysis of biomass samples using WD-XRF. Samples fuse well and the Quantitative curves and Semi-Quant program work well
- Drawback: Limited literature available; even though biomass differ significantly than fossil fuels, still a lot of reference to these methods for analysis. Hard to purchase standards for elemental composition.
- Biomass proficiency program allows us to monitor our performance, and to date we have been very successful

Alternative Energy Sources
Bio-Fuels

Sulfur content:

- XRF has been tried for this determination however, due to the presence of highly oxygenated compounds, has proven to be problematic. Results are typically lower.
- Looking into trying to matrix match the fuels as closely as possible

Alternative Energy Sources

- Restaurant Grease
- Tire Pyrolysis Oils
- Pyrolysis Oils
- Used lubricants
- Municipal Solids Waste

Alternative Energy Sources

Restaurant Grease to Bio-diesel and Supercetane

(Supercetane is created through a process (CETC-OTTAWA) which produces a middle distillate with a high cetane number.)

- Monitored various parameters including sulfur in these products
- Sulfur was analysed using XRF- ASTM D2622 used as the reference method
- Sulfur levels very low, usually near the 10 ppm level

Alternative Energy Sources

- **Used lubricants to diesel**
  - A technology designed and created by scientists at CETC-OTTAWA, known as the ROBYS SYSTEM converts used lubricants into a diesel fuel
  - XRF was used to monitor the sulfur content in the process using ASTM D2622

Alternative Energy Sources

Tire Pyrolysis Oils

- Major use for tire pyrolysis oils will be for a diesel-like product
- Characterized tire pyrolysis oils for a variety of parameters
  - Analysed oils by XRF using the SINDIE-S stand alone unit as well as the WD-XRF to determine sulfur content

Alternative Energy Sources

Pyrolysis Oils

- Residual wood and agricultural feedstocks are converted into pyrolysis oils through a proprietary process
  - XRF used to monitor sulfur content
  - Trace element analysis were performed by both WD-XRF and ICP

Alternative Energy Sources

Indeed a larger footprint is being left for the next generations to come – our waste

Research has provided a possible answer to our municipal waste dilemma

Refuse Derived Fuel

One persons's garbage is another's fuel

Alternative Energy Sources

- Refuse Derived Fuels
  - –Using plasma, Municipal waste is converted:
    - to a slag used as construction aggregates
    - to a high quality syngas used to deliver power to the grid

  By-products from the process of the breakdown of RDF started showing up in the lab about five years ago

Alternative Energy Sources

- **A new challenge**!
  - Elemental composition was being requested – XRF took on the challenge
  - Various sample types were submitted to our lab
  - Very little literature available for the analysis of the by-products of refuse derived fuels

Alternative Energy Sources

- And so began our journey
  - Some of the samples, during the ashing process formed a vitrified product with our ashing crucibles
  - Stopped the pre-ashing and just started adding directly to the flux
  - This worked and has continued to work, for most samples
  - Sample preparation for the bulk of their samples has been resolved

Alternative Energy Sources

- Use a combination of quantitative method and semi-quantitative program to ensure that all the major and minor components are being identified as well as to determine presence of trace metals not in the normal suite
- To date a standardized method for the analysis of RDF for the characterization of the elemental composition does not exist
- Identifiable trends have been observed
- The most colorful fused beads have been derived from the products of RDF

XRF ANALYSIS

- XRF, for our applications, has been found to be very versatile and repeatable. We are able to apply the XRF technique to most liquid samples and to all of our solid samples

XRD DATA
Comparison of Fossil Fuels-Ash Basis

Petroleum Coke		
SiO2	Wt%	42.26
Al2O3	Wt%	14.39
Fe2O3	Wt%	9.21
TiO2	Wt%	0.61
P2O5	Wt%	0.1
CaO	Wt%	4.11
MgO	Wt%	1.32
SO3	Wt%	1.85
Na2O	Wt%	1.1
K2O	Wt%	1.71
V2O5	Wt%	20.26
NiO	Wt%	2.56
Ba	ppm	1460
Sr	ppm	662
Mn	ppm	338
Cr	ppm	NR
Cu	ppm	205
Zn	ppm	270
LOI	Wt%	0.21

coal		
SiO2	Wt%	51.79
Al2O3	Wt%	29.69
Fe2O3	Wt%	7.57
TiO2	Wt%	1.47
P2O5	Wt%	0.72
CaO	Wt%	2.43
MgO	Wt%	0.85
SO3	Wt%	1.16
Na2O	Wt%	0.54
K2O	Wt%	1.55
V2O5	Wt%	0.071
NiO	Wt%	0.022
BaO	Wt%	0.203
SrO	Wt%	0.165
MnO	Wt%	0.092
Cr2O3	Wt%	0.04
LOI	Wt%	1.65

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XRF DATA-BIOMASS
ASH BASIS

		WOOD	*MISCANTHUS*	*BEANS*
SiO2	Wt%	0.945	33.8	3.286
Al2O3	Wt%	0.454	0.27	0.734
Fe2O3	Wt%	0.171	0.5	0.595
TiO2	Wt%	0.037	0	0.038
P2O5	Wt%	8.43	5.25	27.764
CaO	Wt%	32.78	16.27	5.48
MgO	Wt%	6.41	3.06	7.008
SO3	Wt%	2.57	3.77	5.714
Na2O	Wt%	0.03	0.163	0.108
K2O	Wt%	21.17	25.89	39.816
Ba	ppm	736	332	176
Sr	ppm	837	101	62
V	ppm	0	12	28
Ni	ppm	22	8	30
Mn	ppm	866	2328	366
Cr	ppm	0	5	15
Cu	ppm	46	35	306
Zn	ppm	1521	519	946
LOI	Wt%	26.6	10.69	5.54

XRF ANALYSIS – ON THE HORIZON

- For many of our liquid samples , particularly the alternative fuels, method development will be undertaken in the area of trace metal analysis
- For problematic RDF related samples, work is being done to combine SEM/EDX and WD-XRF
- Work on refining method for the analysis of highly oxygenated samples
- Method development on XRF analysis of solid fuels on ground samples and to determine the level of quantitation. This may allow us to analyse samples that have exhibited issues with fusion

XRF analysis

Some very wise men once gave me the following advice

- –Make sure your calibrations lines are straight
- –Prepare your samples well, if your sample prep fails then all fails

I have been trying to live by these two rules

Conclusion

- At the end of the day this is truly what we as scientists are trying to achieve, little by little. Maybe with time we will eliminate most of the footprint

Thank you everyone very much
for your time!

Please feel free to ask questions