Determination of Sulfur in Biodiesel by X-Ray Fluorescence Spectroscopy

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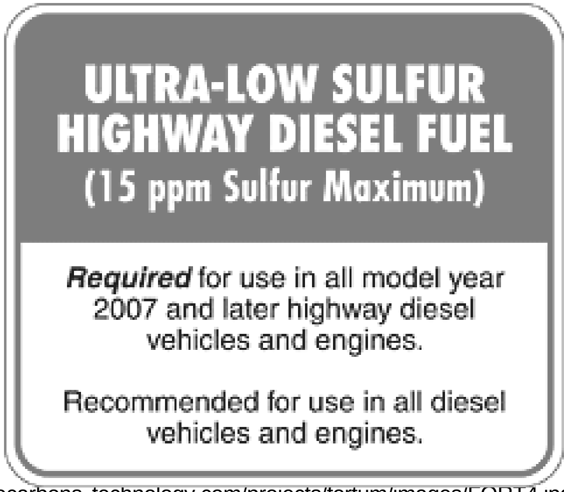


http://www.hydrocarbons-technology.com/projects/fortum/images/FORT4.jp

ASTM D 6751 – 06a
Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

Page 4

X1.5 Sulfur

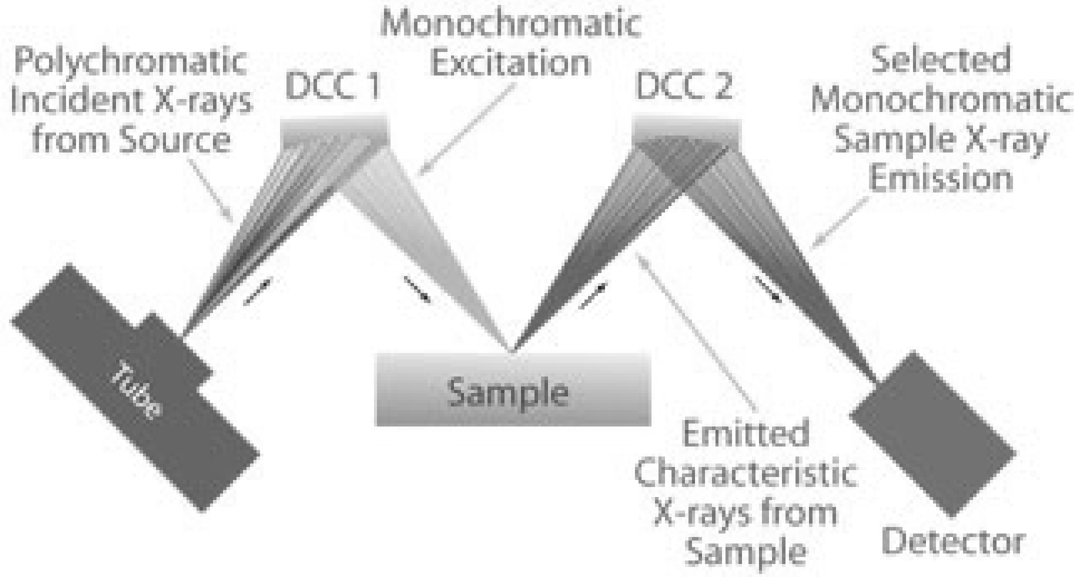
NOTE X1.1 – “Test Method D 5453 (*Ultraviolet Fluorescence*) should be used with biodiesel.”

“Biodiesel sulfur analysis … using Test Method D 2622 (*Wavelength Dispersive XRF*) yielded falsely high results due to the presence of oxygen in the biodiesel.”

This preliminary study will show that D 5453 and WD-XRF can give consistent results for sulfur in biodiesel.

Sulfur Determinations in Biodiesel by XRF

Instrument: XOS SINDIE 4000

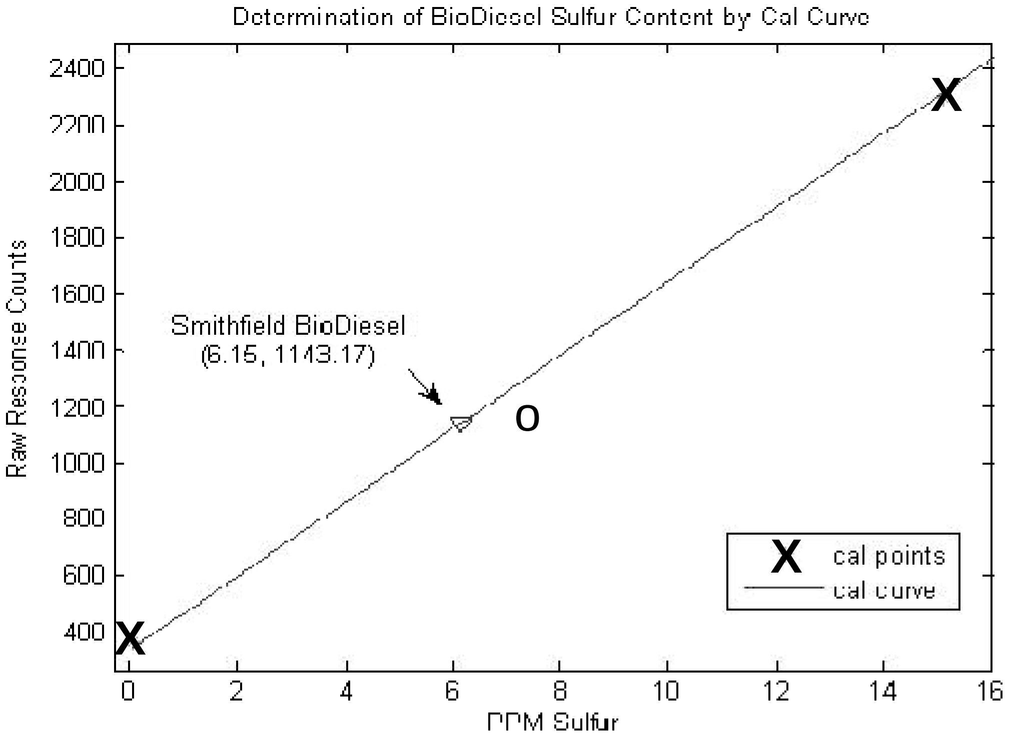


Problems with Biodiesel determinations using calibration curves:

1. Unknown sample and calibration samples must be matrix matched.
2. The C/H problem
3. The oxygen problem: biodiesel contains ≈11 % oxygen; petroleum diesel is oxygen free.
4. If biodiesel is compared to a petroleum diesel calibration curve, then the biodiesel sulfur value will be low by ≈ 20 %.

Graphical illustration of the oxygen problem in XRF:

- ? **biodiesel is approximately 11% oxygen by weight**
- ? **regular diesel standards contain negligible oxygen**



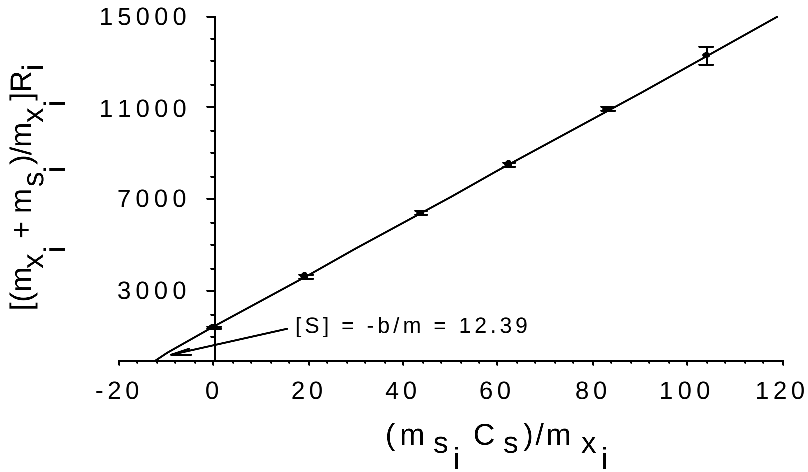
- **Calibration curve yields a bias result because of differential absorption of sulfur x-rays (interference or matrix mismatch).**

The Solutions:

? **Matrix effects can be overcome by:**

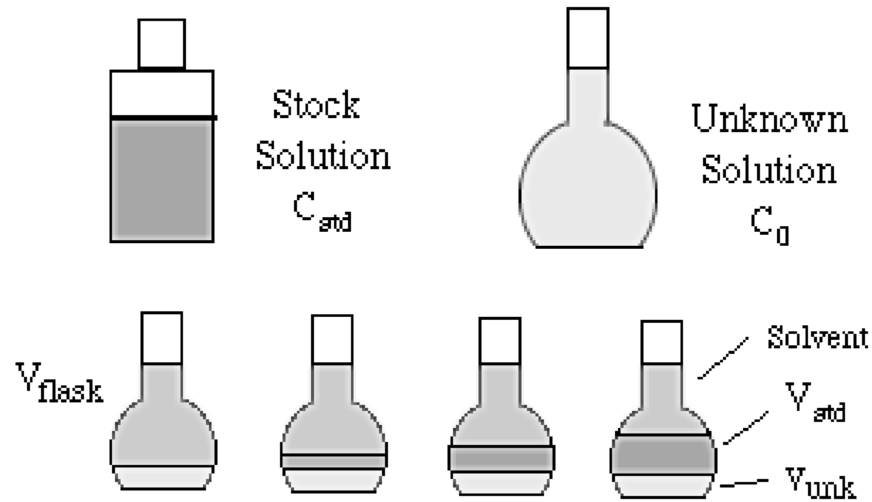
1. **Math – make corrections**
2. **Experimental design – match matrices**
3. **Gravimetric standard addition method**

systematic addition of analyte to samples; linear regression: x intercept = concentration of analyte in unspiked sample

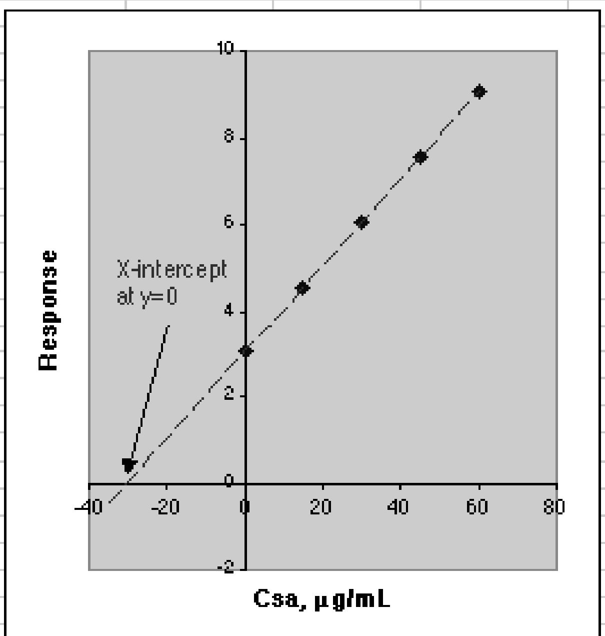


Volumetric Standard Addition Method (SAM)

T.J. Chow & T.G. Thompson
Analytical Chemistry **1951**, *27*, 18-21.



Parameters			
Cstd	150	µg/mL	
Co	153	µg/mL	
Vunk	10	mL	
Vflask	50	mL	
K	0.1	Instrument senstitivity	
Calculated			
Vstd	Cunk (not known)	Csa	Response
0	30.6	0	3.06
5	30.6	15	4.56
10	30.6	30	6.06
15	30.6	45	7.56
20	30.6	60	9.06
for y=mx+b, LLS gives us			
Slope	0.100	m	
Intercept	3.060	b	
X-intercept	-30.60	-b/m	
Co	153	-Xint*Vflask/Vunk	



Graphics from
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Department of Chemistry
California State University, Fresno

Experimental Approach

? NIST diesel SRM 2723a (11 ± 1.1 ppm sulfur) and CRM LGC10 (11 ± 0.9 ppm sulfur) as control “unknowns”

  ? calibration curve and standard addition with diesel SRM 2770

? various biodiesels

  ? designer diesel SRM calibration curve and standard addition with high concentration sulfur (SRM 1624d)

? Are there significant differences?

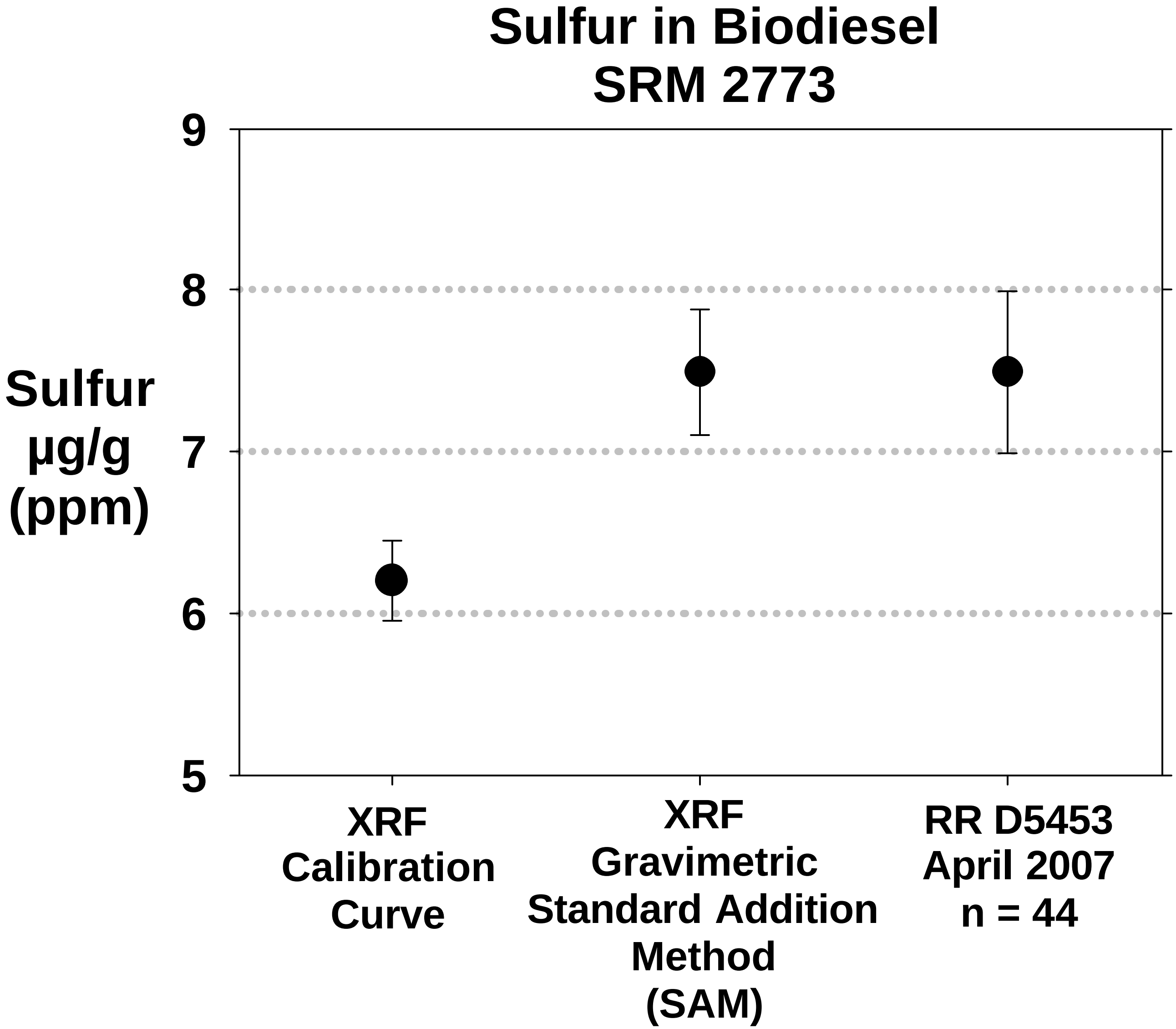
Results by the Two Methods

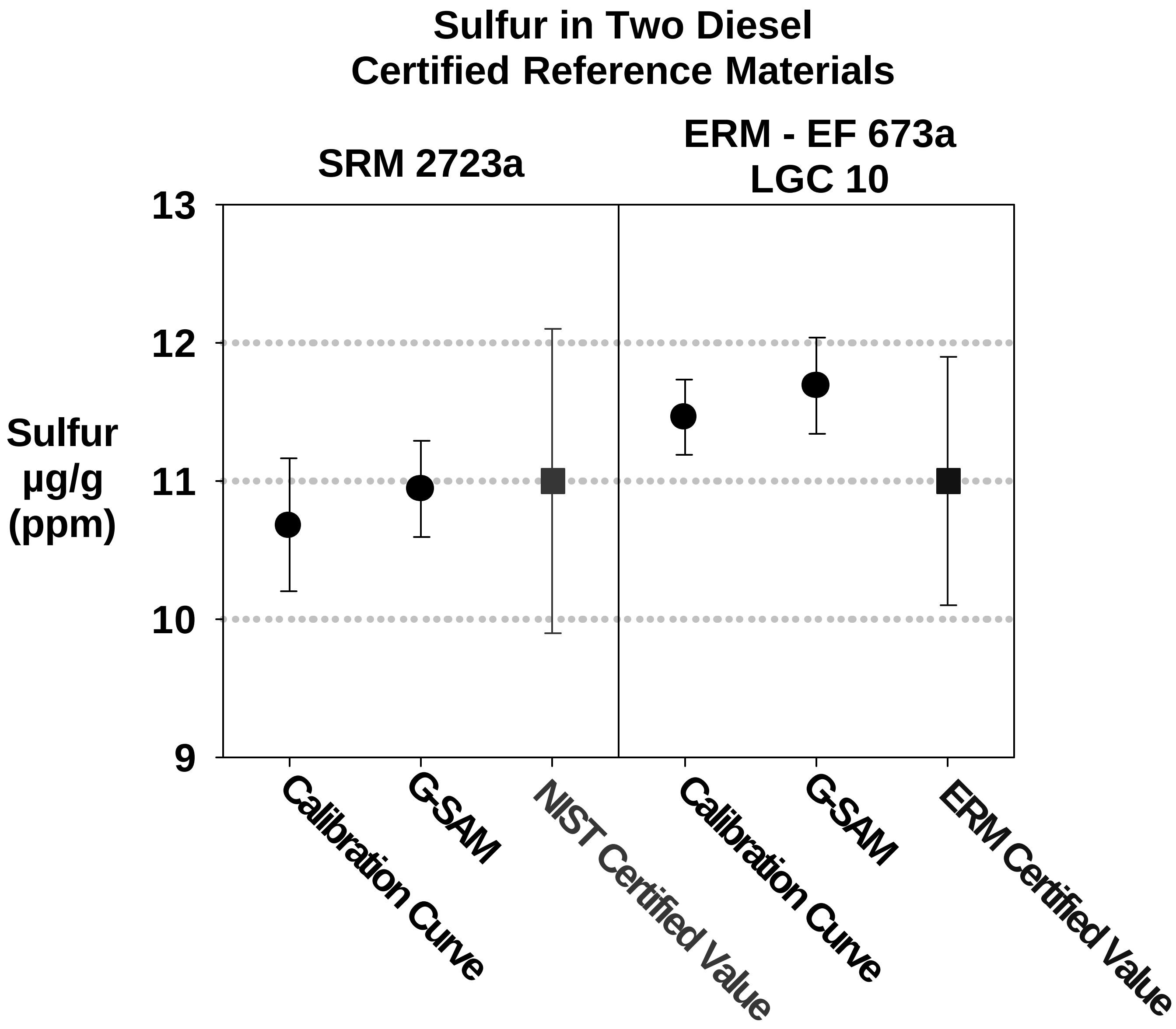
Sample	Calibration Curve (ppm)	Standard Addition Method (SAM) (ppm)	Relative Difference %
Petroleum Diesel Samples			
SRM 2723a	10.68 ± 0.48	10.94 ± 0.35	- 2.4 %
LGC 10	11.46 ± 0.27	11.69 ± 0.35	- 2.0 %
Biodiesel Samples			
SRM 2773	6.16 ± 0.10	7.51 ± 0.37	- 18 %
NREL 52537	2.86 ± 0.22	3.59 ± 0.26	- 20 %
NREL 52533	9.78 ± 0.29	12.29 ± 0.13	- 20 %

Results by the Two Methods compared to Certified Values

Sample	Calibration Curve (ppm)	Standard Addition Method (SAM) (ppm)	Certified Values (ppm)
Petroleum Diesel Samples			
SRM 2723a	10.68 ± 0.48	10.94 ± 0.35	11.0 ± 1.1
LGC 10	11.46 ± 0.27	11.69 ± 0.35	11.0 ± 0.9
Biodiesel Sample			
SRM 2773	6.16 ± 0.10	7.51 ± 0.37	7.49 ± 0.50

Round Robin Data D 5453 April 2007
N = 44; 95 % CI


Sulfur in Biodiesel
SRM 2773
9
8
7
6
5
Sulfur
µg/g
(ppm)
XRF
Calibration
Curve
XRF
Gravimetric
Standard Addition
Method
(SAM)
RR D5453
April 2007
n = 44



Sulfur in Two Diesel
Certified Reference Materials
SRM 2723a
ERM - EF 673a
LGC 10
Sulfur
µg/g
(ppm)
13
12
11
10
9
Calibration Curve
G-SAM
NIST Certified Value
Calibration Curve
G-SAM
ERM Certified Value

Summary

- ? Biodiesel XRF problem: matrix effects – Oxygen and Carbon
- ? A Solution: gravimetric standard addition method (G-SAM)
- ? Statistical analysis of uncertainties is complex.
- ? The XRF method is very precise; uncertainty is less than 1 ppm in the 6 to 10 ppm range.
- ? The XRF method using G-SAM is accurate - uncertainties overlap certified values.
- ? For B5 and B20 it may be possible to use blending to construct calibration curves.