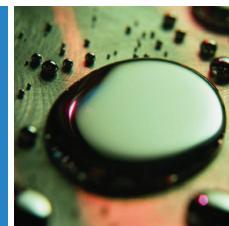


SLFA

Sulfur Monitoring in Marine Oil with the SLFA in a Growing Environmental Protection Context



Application Note

Petrochemistry
SLFA45

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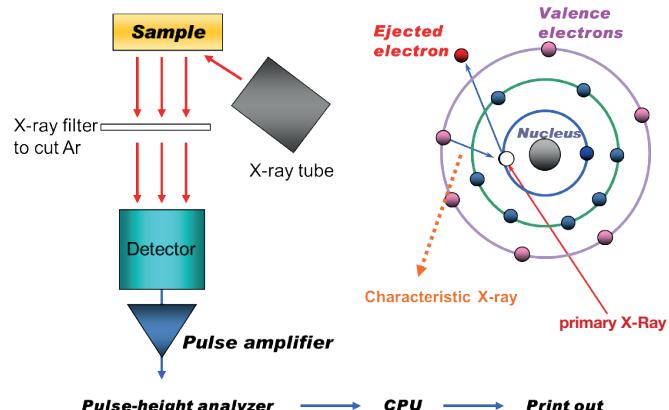
Monitoring of sulfur in petroleum products is an important topic in the current environmental protection context. Indeed, during combustion, sulfur will cause acid rain and particles emissions that induce environmental and health problems. If industries and vehicle emissions have been the main target of sulfur emission control for several decades, the new target is maritime navigation. In this domain, now, the level of sulfur is regulated by the MARPOL (International convention) Annex VI. For this specific regulation, the technique and measuring range of our SLFA series is perfectly suited to allow fast and accurate determination of sulfur in marine oil. Our compact SLFA-60 can be used on board and the SLFA-6800, with its eight position autosampler, will enhance the productivity of the control laboratories.

Keywords: EDXRF, SLFA, Sulfur in oil, Marine Oil, Marpol

Method description

EDXRF (Energy Dispersive X-Ray Fluorescence) is the regulated method for the determination of sulfur in crude oil. The principle involves the irradiation of the sample with primary X-rays that have enough energy to eject an inner electron from sulfur atoms. An outer electron will fill this vacancy and emit a characteristic secondary X-ray. A proportional counter collects the emitted X-rays to quantify the level of sulfur in crude oil.

Our SLFA series of instruments use a dedicated X-ray tube with ideal energy for sulfur excitation. They are also completely safe (close enclosure) and do not require any certification for usage.



Sample preparation

The sample preparation, simple and safe, is illustrated in the photos.

Pour 4 to 10ml of marine oil in the sample cup, cover it with a mylar film and close the assembly with an external ring, thanks to the special tool provided. That's all!

You just have to write the sample name on the back of the cell and put it into the instrument.

Measurement procedure

The operation mode cannot be more simple, as the instrument comes with multicurves precalibration. Then, simply press "start" and let the software choose the best calibration curve for your sample. The result appears real time and after the preset repetitions, the final percentage with statistic indications is printed. All the data can also be registered on an USB key.



Two other modes are available:

The administrator mode to calibrate the instrument using for instances in house references and to check the instrument parameters.

The service mode to check and control the instrument parameters during the maintenance operations.

Results

The specificity of marine oils is that they can have varying compositions depending on their origin. Indeed, as the oil is provided during the stopovers of the ships, its composition may be different from one place in the world to another.

The figure on the right shows the entire X-ray spectra of different oils measured with the MESA 50 – our multi-element EDXRF. We notice that calcium and zinc are detected in the hybrid marine fuel as vanadium and nickel are present in the residual marine fuel. However, these variations have negligible effects on the S determination with our SLFA series, due to adequate filtering of the signals.



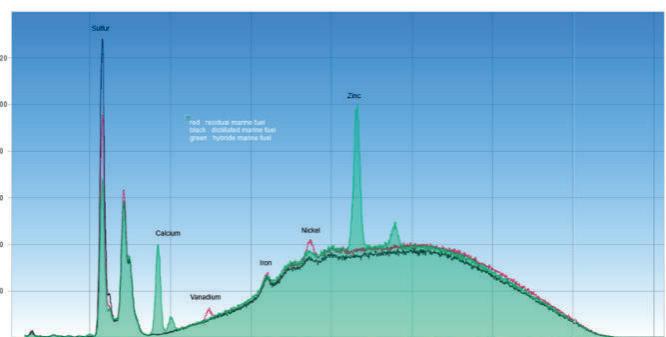
Compliant with the following regulations:

ASTM D4294

ISO 8754

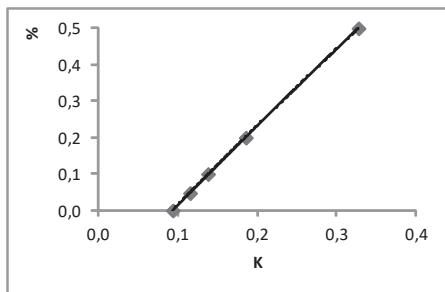
JIS K2541/B7995

EDXRF is sensitive to the matrix effect. Hence, the built-in default calibration curves need to be adapted to all kinds of marine fuel. The series of CRMs of residual oils standards from JSS are very well adapted to the application. With these 8 standards set from 0 to 4%, the instrument will cover the full range of S concentration needed for marine oil. To get the best accuracy, two calibration curves are set up for low and high S – and the software automatically chooses the suitable one.



An example of the low level sulfur calibration curve is presented in the next figure, illustrating the sensitivity of the instrument and the linearity of the measurement in the covered range.

% = B * K + C			
B =	2,14777		
C =	-0,20006		
Range :	0,0000-0,5000%		
STD DEV :	0,0024		
STD #	%	K	SUB
1	0,0000	0,09401	(-0,0019)
2	0,0478	0,11564	(-0,0005)
3	0,1000	0,1382	(-0,0032)
4	0,2000	0,18564	(-0,0013)
5	0,5000	0,32717	(-0,0026)



Different bunker fuels were tested using the SLFA-60 pre-calibrated as described above. The results were compared to a contract lab values and show great consistency regardless of the range.

Bunker fuel type*	Horiba value	Contract lab value	Difference	Remarks
Distillated Marine Bunker Fuel and Hydrid Bunker Fuel				
sample 1	0,018	<0,03		curve low
sample 2 - Hybrid	0,072	0,078	-0,006	curve low
sample 3	0,095	0,099	-0,004	curve low
sample 4	0,66	0,69	-0,03	curve high
sample 5 - Hybrid	1,47	1,46	0,01	curve high
Residual Marine Bunker Fuel				
sample 6	2,93	2,94	-0,01	curve high
sample 7	0,74	0,72	0,02	curve high
sample 8	3,20	3,10	0,10	curve high
sample 9	3,33	3,36	-0,03	curve high
sample 10	1,62	1,56	0,06	curve high
QC sample	1,07	1,04	0,03	curve high

* Samples kindly provided by Naias Labs.

As a reminder, the main specifications of the SLFA-60 are a measurement range from 0 to 10%, with a repeatability of 15ppm or less on a 1% sulfur sample, and a lower detection limit of 20ppm where the SLFA 6800, using a more intense X-ray tube, has a repeatability of 5ppm for 1% sulfur and a detection limit of 5ppm.

Conclusion

The SLFA-60 and the SLFA-6800 are the ideal tools for sulfur determination in marine oils.

The SLFA-60's simplicity allows anyone to get the result in few minutes. Furthermore, its small size, light weight without utilities required, like a gas cylinder, make it ideal for on board usage, in a tanker, for example.

The SLFA-6800 is ideal for contract laboratories with its 8 position autosampler.

These instruments benefit from HORIBA's lengthy experience and customer feedback in the application domain.