

S2 RANGER

ANALYSIS OF SULPHUR IN PETROCHEMICAL PRODUCTS – THE S2 RANGER FULFILLS THE ASTM D6445 AND ASTM D4294 / IP 336 / ISO 8754 STANDARDS

Introduction

The use and composition of fuels derived from petrochemical products are continually being updated to reflect changes in attitude towards environmental and public health issues. In most nations legislation is in place to control, or reduce, the effects that some components of fuels have upon both micro and macro-ecosystems. Diesel and gasoline are the two fuels that are most affected but there are increasing controls over marine fuels, crude oils and recycled fuels used in domestic heating systems.

Sulphur levels in fuel are constantly being forced down with the result that, in Europe, the maximum permitted Sulphur concentration will be 50 mg/kg by 2005. Many national governments also offer tax incentives to companies that produce fuels with even lower limits.

To support petrochemists in their goals of conforming to increasingly demanding norms, Bruker AXS has introduced the benchtop S2 RANGER EDX spectrometer. This lab report outlines method



details and performance data to show that the S2 RANGER is the ideal partner for the analysis of Sulphur in petrochemical products.

Sulphur Analysis

In relation to the quantity of sample throughput, Sulphur is the most analyzed element by benchtop XRF spectrometers in petrochemical laboratories. There are two key standards that are routinely used in order to determine Sulphur levels: ASTM D6445 (The analysis of Sulphur in Gasoline by Energy-dispersive X-ray fluorescence spectrometry) and ASTM D4294 / IP 336 / ISO 8754 (The analysis of Sulphur in Petroleum and Petroleum products by Energy-dispersive X-ray fluorescence spectrometry).

ASTM D6445

This test method covers the measurement of Sulphur in unleaded gasoline and gasoline-oxygenate blends and covers a Sulphur concentration range from 48 to 1000 mg/kg. Following this method the S2 RANGER was calibrated using a set of seven certified reference gasolines. The samples were prepared by simply pouring them into a plastic liquid cell fitted with a polycarbonate film (Figure 1).



Figure 1: Disposable liquid cups for XRF analysis of liquid fuels

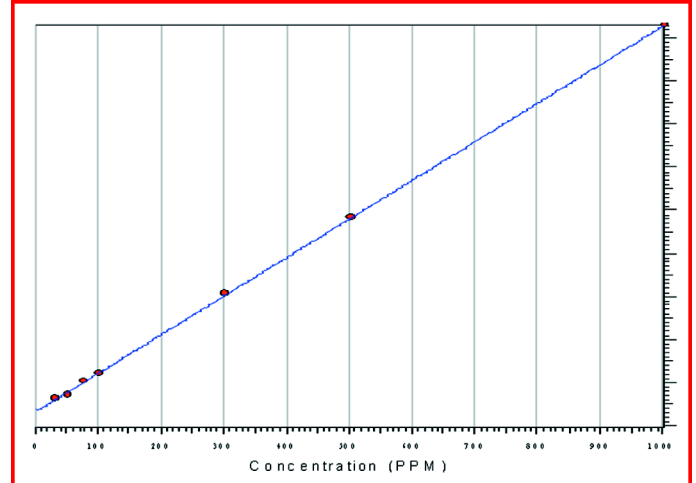


Figure 2. Calibration plot for Sulphur in Gasoline (according to ASTM D6445)

Figure 2 shows the calibration curve for this method. The seven reference materials gave a standard error of regression of 3.2mg/kg. The lower limit of detection for Sulphur was calculated to be 3.5mg/kg (3 sigma). This is based on 200 seconds analysis time.

In order to comply with the terms of this test method a precision trial had to be carried out. A 100mg/kg test sample was measured twenty times. The method stipulates that for this sample the difference between two successive measurements can exceed 19.7mg/kg only one time in twenty. The results of the precision trial are given in Table 1.

D6445 100mg/kg Test Sample			
Minimum Measured Value	97mg/kg	Permitted difference between 2 measurements	19.7mg/kg
Maximum Measured Value	104mg/kg		
Mean Value	100.6mg/kg	Maximum difference between 2 measurements	6.8mg/kg
Standard Deviation (1σ)	2.1mg/kg		
Relative Standard Deviation	2.1 %	Method Status	PASS

Table 1: Precision Trial according to ASTM D6445

ASTM D4294 / IP 336 / ISO 8754

This test method covers the measurement of Sulphur in hydrocarbons such as naphthas, distillates, fuel oils, residues, lubricating base oils and unleaded gasoline. It has been adopted by ASTM, IP and ISO and has been allocated individual method numbers by these organisations. The test method is applicable to products having sulphur contents in the range 0.015% (m/m) to 5.00% (m/m). In practice this concentration range is split into two – 0.015 to 0.1% and 0.1 to 5.00%.

To test the low range method, seven light mineral oil standards were measured to produce a calibration with the range 0.01 to 0.1%. The standards gave a standard error of regression of

0.0007%. The lower limit of detection for Sulphur was calculated to be 3.4mg/kg (3 sigma). This is based on 200 seconds analysis time.

For the high range method, eight crude oil standards were measured to produce a calibration with the range 0.1 to 5.00%. The standards gave a standard error of regression of 0.009 %.

Similar precision criteria to those described to D6445 also apply to D4294. For both the mineral and crude oil methods, twenty repeat measurements were done. The data is shown in Table 2. It is clearly demonstrated that the S2 RANGER again exceeds the performance criteria demanded by these norms.

Repeat Number	D4294 Low Range S Conc. % (m/m)	D4294 High Range S Conc. % (m/m)	Repeat Number	D4294 Low Range S Conc. % (m/m)	D4294 High Range S Conc. % (m/m)
1	0.031	1.00	14	0.032	1.01
2	0.030	1.00	15	0.031	1.02
3	0.031	1.00	16	0.031	1.02
4	0.031	1.00	17	0.032	1.00
5	0.032	1.01	18	0.032	1.01
6	0.031	1.01	19	0.032	1.01
7	0.030	1.01	20	0.033	1.00
8	0.032	1.02	Mean	0.031	1.009
9	0.031	1.00	Standard Deviation (1σ)	0.0008	0.008
10	0.032	1.00	Relative Standard Deviation	2.41	0.806
11	0.031	1.02	Permitted difference between 2 measurements	0.006	0.034
12	0.032	1.02	Maximum difference between 2 measurements	0.002	0.023
13	0.032	1.01	Method Status	PASS	PASS

Table 2: Precision Trial according to ASTM D4294 (low and high ranges).

Conclusion

For many years X-ray fluorescence (XRF) has been at the forefront of petrochemical analysis, routinely measuring both Lead and Sulphur from low limits of detection to major concentrations. XRF has worked in tandem with international standard test methods, or 'norms', to enable analysts around the globe produce consistent and comparative data. To support petrochemists in their goals of conforming to increasingly demanding norms, Bruker AXS has introduced the S2 RANGER.

This lab report shows that the S2 RANGER exceeds the performance criteria demanded by the the ASTM D6445, ASTM D4294 / IP 336 / ISO 8754 standard test methods. The demonstrated analytical performance coupled with an intuitive touch-screen interface, compact all-in-one design and Bruker AXS' global support network makes the S2 RANGER the instrument of choice for the analysis of Sulphur in petrochemical products.

Remark: The given results are typical values and depend strongly on the reference material used, the specimen preparation, and the measuring parameters (such as irradiated area, excitation, etc.), and may be improved by optimizing single measuring parameters.

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