Testing the Limits

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We are at the dawn of the new age of sulphur limits in automotive fuels. So-called zero sulphur fuels (less than 10 mg/kg) were first available in the European Union in 2005 and will be mandatory by 2009. In the USA during 2006 there will be a nationwide transition of most diesel fuel from low sulphur to ultra low sulphur (ULS) diesel (less than 15 mg/kg) as a precursor to new 2007 diesel engines and vehicles. New stringent fuel specifications result in a need for improved testing methods and this article updates a previous one, “Chasing the Limits” from February/March 2004. That article described how the new Oxford Instruments Twin-XULS sulphur analyser with a Low Background Proportional Counter has low spectral background giving the improved limit of detection necessary to measure accurately the new low sulphur limits. Since then the new technology has become the only bench-top XRF technique possessing all three of an Energy Institute IP method, an ASTM method and a performance statement from the United States Environmental Protection Agency (USEPA). Thus, bench-top EDXRF retains its reputation of being "the most cost effective, simplest, and most reliable method of doing product release 24 hours a day".

To achieve this wide-ranging acceptability required an intensive program of work only made possible by the willingness of instrument users in committing their time for interlaboratory studies. No matter what a manufacturer may claim, only real data produced by real users is acceptable for setting performance standards. It is also desirable that although a manufacturer may fund and be involved in a study that the management of that study is under an independent body.

An interlaboratory precision study under the leadership of the Energy Institute involved eight laboratories in Europe, the Middle East and USA, testing nineteen samples of diesel including biodiesel and gasoline including CARB gasoline. Acquisition and distribution of samples, preparation of protocol and reporting forms and collection and collation of data were the responsibility of Intertek Testing Services. There were two versions of the draft method, one in IP format and one in ASTM format. The data was statistically analysed by both the Energy Institute and ASTM because they use slightly different criteria. As a result, in the summer of 2005, the Energy Institute issued the new test method IP531 and ASTM issued its version as D7212 in February 2006. These methods cover diesel fuel and gasoline up to 50 mg/kg sulphur.

In Europe and under ISO requirements, any test method listed in a specification has to meet a performance requirement that says that two times its reproducibility (R) must not exceed the specification level. This is colloquially known as the 2R rule and thus for the new European specification of 10 mg/kg a test method must have a reproducibility not exceeding 5 mg/kg. Reproducibility is the difference between two single and independent test results obtained by different operators working in different laboratories on identical test material that, in the long run, in the normal and correct operation of the test method, is exceeded by only one case in twenty.

However, the USEPA decided on a more stringent requirement that effectively reduces the uncertainty of measurement to 2 mg/kg since this was the tolerance allowed by the new regulations for ultra low sulphur diesel. They consider two types of methods, which are either those issued by voluntary consensus standards bodies (VCSB) such as ASTM, or those from a non-VCSB source. Whichever method is in use it must meet performance criteria given in regulations 40 CFR 80.584 & 80.585 and each laboratory has to qualify each individual method it uses. For a VCSB method, the qualification is valid whilst the instrument remains in the same laboratory. It is valid for five years with a non-VCSB method unless it gains VCSB acceptance. USEPA takes the view that this approach allows for greater flexibility in instrument selection and encourages the development and use of better instrumentation.

Qualification comprises precision and accuracy tests. Precision involves repeat tests over at least twenty days using a diesel fuel with between 5 and 15 mg/kg sulphur and achieving a standard deviation less than 0.72 mg/kg sulphur. Accuracy comes from the average of ten measurements on two commercially available gravimetric sulphur standards, one between 1 and 10 mg/kg sulphur and the other between 10 and 20 mg/kg sulphur. Both mean values shall be within 0.54 mg/kg of their respective accepted reference values.

During 2005, the USEPA organised their own interlaboratory study specifically for ULS diesel with the stipulation that every participating laboratory must qualify its methods. In the study, there were 129 laboratories with 149 instruments covering six methods of which six used the new Oxford Instruments Twin-XULS. Each participant received five fuel samples in July and August 2005 with one of the samples supplied blind in both months. Another of the samples in both months was the gravimetric standard NIST SRM 1616b (kerosene with 8.41 mg/kg sulphur). Each laboratory measured every sample in triplicate.

Following all this work through 2005 there are now clear performance statements for the new technology obtained from carefully controlled interlaboratory precision studies. The two new standard test methods have precision statements that cover diesel fuel and gasoline up to 50 mg/kg.

For the Energy Institute IP531 method, there are global precision statements that are:

IP531 repeatability for the range 2 to 50 mg/kg = 2.0 mg/kg
IP531 reproducibility for the range 2 to 50 mg/kg = 5.0 mg/kg

With ASTM’s data treatment, the figures for D7212 are slightly different as shown in Table 1 ASTM D7212 Precision. In due course the Energy Institute will amend IP531 using this later data.

Table 1 ASTM D7212 Precision

S mg/kg	r mg/kg	R mg/kg
8	2.0	4.6
10	2.0	4.7
15	2.1	4.9
20	2.2	5.1
25	2.2	5.2
30	2.3	5.3
35	2.3	5.4
40	2.3	5.4
45	2.4	5.5

EPA’s data covers just ULS diesel and usually restricting the scope of a method will produce tighter precision. Adding the stringent prequalification stage also tends to improve precision and accuracy so overall, the EPA precision is much better than the IP and ASTM method precisions. There was a requirement for each laboratory to use two calibration methods, which were the one employed “normal” calibration standards (“In-House”), and an alternative one prepared using four NIST SRMs. However, the new method D7212 specifies the use of eight calibration standards prepared from very pure base oil and an accurately known primary standard. Therefore, using only four SRM’s does not comply with the method as written so the data below excludes that from the alternative calibration. Table 2 EPA Reproducibility at 15 mg/kg shows comparison data from the four methods used in the interlaboratory precision study. D2622 is the original ASTM wavelength dispersive XRF method for sulphur and D7039 is the newer monochromatic wavelength dispersive XRF method. D5453 is the ultraviolet fluorescence method. Originally, the laboratories using Oxford Instruments Twin-XULS instruments in the EPA study appeared as using a “non-VCSB” method listed as “EDXRF” but now that is becoming ASTM D7212 they gain the full status of a “VCSB” method.

Table 2 EPA Reproducibility at 15 mg/kg

EPA RR Results	Method	R @15 mg/kg mg/kg
In-House Calibration	D2622	2.71
– ASTM Robust Outlier	D7212	1.94
Determination	D5453	2.68
	D7039	2.25

Clearly, the new methodology implemented by the Oxford Instruments Twin-XULS has proved itself for the new low sulphur limits and it offers the performance that the industry needs. Already the method has gained acceptability as both Energy Institute and ASTM methods and the EPA study shows it can match other methods for the new stringent demands of the transition to ULS diesel starting in 2006.Clearly, the new methodology implemented by the Oxford Instruments Twin-XULS has proved itself for the new low sulphur limits and it offers the performance that the industry needs. Already the method has gained acceptability as both Energy Institute and ASTM methods and the EPA study shows it can match other methods for the new stringent demands of the transition to ULS diesel starting in 2006.