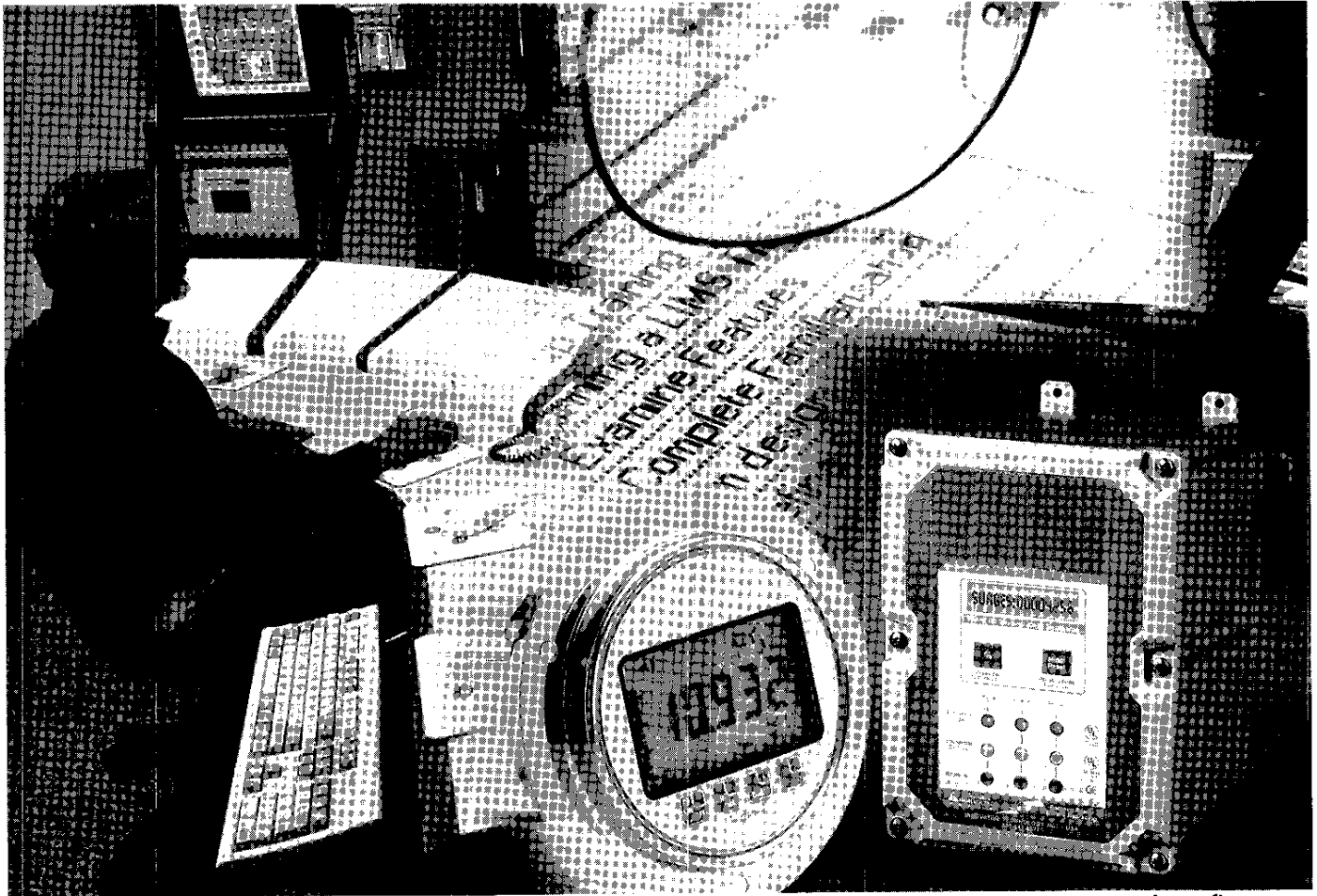


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INSTRUMENTATION

Detecting Sulfur in Diesel Fuel

By R.A. Kishore Nadkarni

Testimony heard at the just-completed US Environmental Protection Agency (EPA; Washington) public hearings confirms that diesel will remain the dominant motor fuel for bus and highway-freight-truck traffic. As Ellen Shapiro, auto fuels director for the Alliance of Automobile Manufacturers (Washington), pointed out at the Atlanta hearing, "Diesel motors will continue to do the heavy lifting that is vital to international commerce and the U.S. economy."

Unfortunately, today's combustion technology and diesel fuel generally contribute to the emission of oxides of nitrogen (NOx) and of particulate matter (PM). Conventional wisdom holds that in order to

clean up diesel engine exhaust and to activate the best after-treatment technologies, diesel motors must combust only fuels that contain "near-zero" sulfur. Accordingly, the EPA has proposed a rule to significantly reduce the sulfur levels in highway diesel fuels by the year 2006 (1). The proposed program will bring heavy-duty diesel emissions on par with those from new cars. EPA estimates that the proposed program will result in NOx and PM emission reductions of 90% and 95%, respectively, below the current levels. To achieve these standards, the proposal calls for a 97% reduction in the sulfur content of diesel fuels.

By the EPA's own estimates, refiners will have to produce diesel at 7-ppm sulfur levels

to ensure that the sulfur standard is not exceeded during the fuel's journey to the end user. Also, for the kerosene and other additives added to diesel fuel to improve its performance, EPA is proposing to limit the sulfur content to no more than 15 ppm, the same level proposed for highway diesel fuel.

Although some of the sulfur measurement burden is handled by online instrumentation, the majority of regulatory reporting and control analysis is and will be generated by the quality control laboratory. However, the EPA has also designated only one American Society for Testing and Materials (ASTM; West Conshohocken, PA) standard test method, D 2622 (with some modifications), as the benchmark test

method for quantifying the sulfur content of diesel fuel for compliance determination. While not as controversial as the overall magnitude of the proposed mandated sulfur reduction, this lack of flexibility and capability regarding the ability to legally and accurately measure these very low sulfur concentrations is becoming a major concern for refinery measurement and control planners.

ASTM STANDARD TEST METHOD D 2622-98

The D 2622 test method is based on the technique of wavelength dispersive X-ray fluorescence spectrometry (WDXRF). As published in the *ASTM Book of Standards*, the current version (adopted in 1998) does not include test repeatability or reproducibility data for diesel fuel with a sulfur content of less than 60 ppm. As has been documented elsewhere (2, 3), D 2622 is widely used and has acceptable precision above the 50-ppm sulfur level. However, this method has very poor precision at lower sulfur levels, such as the newly proposed limits of 15 ppm in diesel. EPA has proposed two modifications to the basic D 2622 test method to improve the precision:

- Using a measurement blank closely resembling the boiling-point range and density of diesel fuel and
- Preparing calibration standards and samples in a solvent mixture of eight specified hydrocarbons and ensuring that the calibration line goes through zero.

It is also suggested that the analysis be done using only end-window XRF instruments. Without a doubt, this last requirement would pose particular difficulty for the oil industry: A large majority of the WDXRF instruments in use today are of the side-window configuration, and it may not be an easy matter to change the configuration from side window to end window.

WDXRF instruments cost upwards of \$150,000 each and usually need annual maintenance costing upwards of \$15,000. Regardless, neither the petroleum industry nor ASTM has any experience regarding the precision, either intra- or inter-laboratory, of this method when incorporating the modifi-

cations proposed by the EPA. Conversely, abundant evidence indicates that the current D 2622 test method cannot adequately meet the precision and accuracy requirements at sulfur levels of 15 ppm and below in diesel fuel.

1 COMPARISON OF SULFUR RESULTS IN GEN TC 19/WG 27 ROUND ROBIN FOR DIESELS

(All results are in ppm)

D 2622 (WDXRF)	D 4294 (EDXRF)	D 5453 (UV-FL)	D 3120 (Microcoul.)	D 1266 (Wickbold)
50	49	51	50	51
150	147	154	150	152
350	343	353	350	355
500	490	511	500	507

WDXRF results are taken as standard for comparison.

2 PRECISION OF SULFUR TEST METHODS IN GEN/TC 19/WG 27 ROUND ROBIN

(For diesel samples with sulfur levels between 10 and 500 ppm)

TEST METHOD	REPEATABILITY	REPRODUCIBILITY
D 2622 WDXRF	0.0293 X + 0.0003	0.0725 X + 0.0005
D 4294 EDXRF	Not Known	0.0289 X + 0.0016
D 5453 UV-FL	0.0285 X + 0.0002	0.1088 X + 0.0002
D 3120 Microcoul.	0.043 X + 0.0003	0.1679 X + 0.0008
D 1266 Wickbold	Not Calculated	Not Calculated

Data represent the average of duplicate results.

3 REPRODUCIBILITY OF TEST METHODS USED IN THE GEN ROUND ROBIN FOR DIESEL SAMPLES

SULFUR LEVEL (PPM)	D 2622 (WDXRF)	D 4294 (EDXRF)	D 5453 (UV-FL)	D 3120 (MICROCOUL.)	D 1266 (WICKBOLD)
50	9	37	7	16	17
350	330	350	40	67	74

ASTM RESEARCH REPORT D02.1456

In a detailed research study conducted by Southwest Research Institute (SwRI; San Antonio), three dominant sulfur test methods were compared for fitness of use (4). The three ASTM sulfur test methods examined were D 2622 WDXRF, D 4294 energy-dispersive XRF (EDXRF), and D 5453 combustion ultraviolet (UV)-fluorescence for measurements in the range of 0- to 500-ppm sulfur. While both D 2622 and D 5453 test methods demonstrated an equivalent fitness for use down to 20 ppm, only the D 5453 test method was found fit for use down to 1 ppm. Thus, for the new stringent low-

sulfur content fuel requirements, X-ray methods D 2622 and D 4294 may no longer be useful. While D 2622 had the lowest standard deviation across the higher concentration ranges, test method D 5453 had the best standard deviation at sulfur levels below 50 ppm.

The bias of these three test methods was also studied at 10- to 200-ppm sulfur levels by the use of a single iso-octane matrix for gravimetrically prepared samples containing 24 organo-sulfur compounds expected to be present in gasoline and diesel fuels. No bias (i.e., accuracy within the precision limits for each test method) was found in any of the three methods.

Additionally, the study aimed to identify the best low-level precision and accuracy capabilities in test methods D 2622 and D 5453. Of these two, the D 5453 method had better data at the lowest sulfur levels (below 30 ppm). In fuel samples containing less than 10-ppm sulfur, D 5453 demonstrated no difficulty in handling the analysis. Thus, the D 2622 test method was at its limit of detection at 10-ppm sulfur, and D 4294 capability is ensured only above the 50-ppm sulfur level. Again, D 5453 was reliable at sulfur levels as low as 1 ppm.

Overall, this study found strong evidence that D 5453, not D 2622, could be routinely applied to the determination of sulfur in liquid hydrocarbons at levels below 10 ppm. This conclusion is consistent with most petroleum-industry laboratory experience.

EUROPEAN ROUND ROBIN

The newly proposed EN 228 and EN 590 regulations require 350-ppm sulfur in current diesel products and 50-ppm sulfur for the year 2005. Some countries, such as Germany, have expedited these time frames by providing tax incentives that reward 10-ppm-sulfur motor fuels. To ascertain testing capabilities at these levels, a very large round robin was recently completed in Europe, under the Center for European Normalization (CEN) Technical Committee (TC) 19 Working Group (WG) 27. Sixty-nine laboratories from nine countries participated in the determination of sul-

fur at levels between 5 and 500 ppm in eight gasoline and seven diesel samples using five test methods: D 3622 WDXRF, D 4294 EDXRF, D 5453 combustion UV-fluorescence, D 3120 combustion microcoulometry, and D 1266 Wickbold combustion (5).

At most sulfur levels tested, all five test methods produced essentially equivalent results (Table 1, P. 11), but the precision of different test methods varied considerably (Tables 2 and 3, P. 11). For sulfur concentrations below 30 ppm, the best reproducibility and accuracy were obtained using the D 2622 and D 5453 test methods. Of these, the D 5453 method was considered suitable for determination of sulfur at and below the 10-ppm level required in the future European diesel fuels.

The recommendations of this CFN round robin are consistent with the conclusions of the SwRI study, in short, that test method D 5453 is the most suitable test method for determining the level of sulfur in diesel (or gasoline) products containing 10-ppm sulfur or less.

ASTM INTER-LABORATORY CROSS-CHECK PROGRAM

For the last decade, ASTM Committee D02 on Petroleum Products and Lubricants, through its Coordinating Subcommittee (CS) 92, has conducted a voluntary proficiency testing program (6). One of the products analyzed in this program is # 2 diesel fuel; 260 laboratories worldwide were involved. The most commonly used test methods for sulfur determination in these cross-checks are D 4294 EDXRF, D 2622 WDXRF, and D 5453 UV-fluorescence, in that order. Based on five recent cross-check rounds, on the average, the three methods were used by 147, 64, and 19 laboratories, respectively. Three other test methods—D 129 bomb combustion (nine laboratories), D 1266 Wickbold (three or four laboratories), and D 4045 hydrogenolysis and rateometric colorimetry (three or four laboratories)—were used to a much lower extent.

4 ANALYSIS OF DIESEL SAMPLES IN ASTM CS 92 CROSS-CHECKS

SAMPLE	D 129 (Bomb)	D 1266 (Wickbold)	D 2622 (WDXRF)	D 4045 (Microcoul.)	D 4294 (EDXRF)	D 5453 (UV-FL.)
DL 9810 X	534	500	440	*	456	440
SD	25	120	20	*	37	33
%RSD	4.7	24	4.6	*	8.1	7.5
N	9	4	63	2	145	16
DL 9902 X	614	*	466	421	487	471
SD	222	*	19	152	27	55
%RSD	36	*	4.1	36	5.5	11.7
N	10	1	64	4	142	20
DL 9906 X	2830	3100	3124	3059	3141	3133
SD	840	50	94	262	117	254
%RSD	30	1.6	3.0	8.6	3.7	8.2
N	9	5	4	3	136	17
DL 9910 X	290	29	69.1	*	91	55
SD	270	38	6.1	*	31	17
%RSD	93	131	8.8	*	34	31
N	9	3	58	4	137	24
DL 0002 X	540	360	419	*	436	423
SD	260	90	15	*	34	45
%RSD	48	25	3.6	*	7.8	10.6
N	10	5	70	3	158	20

ABBREVIATIONS: X, mean value (ppm); SD, standard deviation (ppm); %RSD, relative standard deviation (%); N, number of valid results; *, insufficient data for statistical calculations

It is instructive to review the data generated in these cross-checks to assess the real-world capabilities of these test methods for low-sulfur content determination. Table 4 summarizes the data obtained in the last five CS 92 cross-checks using these six test methods to test # 2 diesel fuel.

The data clearly show that the D 129 bomb and D 1266 Wickbold test methods are unsuitable for this analysis. The reproducibility of the D 129 method results varies from 30% to 93% relative standard deviation (or %RSD), and reproducibility of the D 1266 method ranges from 2 %RSD to 131 %RSD. In some cases the values obtained by these two methods are also biased compared with those obtained by other test methods. The other three main test methods (D 4045 is used very infrequently) produce essentially similar mean values.

At the sulfur concentration range of these five samples (60–460 ppm), the precision of D 2622 results was superior to that of the D 4294 and D 5453 test methods. Unfortunately, the sulfur level of interest in the recently proposed EPA diesel regulations is far below the levels in these cross-checks. If analytical experience in low-sulfur gasoline and European-grade diesel is

any indication, at 15 ppm and below, the D 5453 method appears to be best suited for obtaining optimum precision and sulfur measurement accuracy.

At the moment, petroleum-industry laboratories have no experience to determine whether the D 2622 modifications from by EPA will produce adequately accurate and precise results. It is hoped that the ASTM D02 Subcommittee 3 on Elemental Analysis will initiate an industry cross-check later this year to validate the modified method. Based on the SwRI, CFN, and ASTM CS 92 cross-checks discussed above, petroleum-industry control and measurement teams must carefully examine various sulfur test method capabilities as they begin their journey toward the production of

near-zero-sulfur fuels.

References

1. U.S. Environmental Protection Agency, Federal Register, 40 CFR Parts 80, 85, and 86 (May 17, 2000).
2. R.A. Nadkarni, "Determination of Trace Amounts of Sulfur in Petroleum Products: The State of the Art," World Refining, Vol. 10, No. 5 (June 2000).
3. R.A. Nadkarni, "Determination of Sulfur in Petroleum Products and Lubricants: A Critical Review of Test Performance," American Laboratory (submitted for publication).
4. K. Kohl, "ASTM D 5453: Fitness for Use Study," ASTM Research Report RR-02-1456 (1999).
5. P. Littarelli, "Round Robin Exercise for Sulfur Methods for EN 228 and EN 590 Fuel Specifications," CEN/TC 19/AVC 27 (April 2000).
6. W.J. Bover, "Tackling Interlaboratory Variability for the Global Marketplace," ASTM Standardization News, p. 56 (June 1994).



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