



Sulfur

SPECIAL REPORT

Determining Trace Amounts Of Sulfur In Petroleum Products

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As refiners struggle to settle on strategies that will provide flexible and economical process investments needed to meet imminent sulfur in motor fuels regulations (Table 1), their measurement and control teams will also need to choose appropriate measurement technologies that will provide accurate and legally acceptable test data. Ironically, as sulfur content drops to very low (less than 20 ppm) levels, data that is both legally viable and accurate may not be synonymous. "At-the-gate" every-batch sampling requirements and the fact that once finalized, diesel sampling and testing requirements will likely be similar, only complicate matters further. Past measurement and control technologies must be promptly re-evaluated. As sulfur levels drop to unprecedented levels, what are the current feasible measurement technologies for the various refiner-of-the future applications?

A recent issue of *World Refining* (April 2000) discussed in detail several aspects of the many challenges facing today's refinery management team. Implicit in all future process improvement plans is the issue of economical sulfur removal and control. Sulfur is a critical element present in most of the petroleum products and lubricants either occurring naturally or in some cases, as an added product performance booster. Sulfur emissions from motor fuel products, as a result of combustion, is a major concern as fuel and vehicle become inexorably linked under Tier 2 pollution control goals.

Fortunately, a number of test methods are available for determining sulfur at various levels of concentration greater than 50 ppm (Table 2). However, as sulfur level requirements drop to less than 30 ppm, the per-

Auto Fuels: Trends and Regulations USA; California position in brackets - mg/kg (ppmw)						
<i>Some sulfur values are estimated:</i>						
Sulfur	2000	2003	2004	2005	2006	2008-10
Gasoline	250* (30)	<150** (15)	120***	90	30	<5 (<5)
Diesel	450* (500)	250 (50)	150	50	30	<10 (<5)

* 90% or less of baseline to earn credits in the ABT system

** Allotment triggers and aggressive ABT credit generation will make <30 ppmw

*** Corporate averaging or per gallon specifications begin

Table 1. In the U.S. sulfur levels in two primary motor fuels are expected to trend to near-zero levels by the end of the decade.

formance capabilities of the various technologies will require careful examination. Exacerbating the Tier 2 requirements is the knowledge that pressure from vehicle manufacturers for "near-zero" fuels will likely continue. Also co-mingling distribution issues make planning for motor fuels with sulfur levels less than 10 ppm a prudent and likely near term reality.

Over the next 2 to 4 years, sulfur in gasoline levels that are released to market, even within a close regional basis, will vary greatly based upon several factors. Participation in various sulfur allotment / credit schemes, feedstock slate commitments and investments in process improvements, will combine with small-refiner and geographic phase-in variations to produce an unprecedented dynamic for final market distributors. Refiners and downstream entities must now plan and invest in measurement and control systems that promote an optimal operation that yields a built in cushion to allow for inevitable downstream contamination. They will also need to cover their bases legally with the EPA.

Given the plethora of test methods

available for sulfur determination in petroleum products, the choice for a particular analysis would normally depend on economic considerations, the fuel matrix of interest, the sulfur concentration present and the precision of the analysis required. However, since the inception of The Clean Air Act, U.S. fuel suppliers have had to cope with federally mandated testing requirements. This pattern has continued, for example in 1997, the U.S. Environmental Protection Agency (EPA) published regulations proposing a single reference test method for determining sulfur in gasoline, reformulated gasoline (RFG) and diesel fuels, but allowed an alternate for conventional gasoline.¹

More recently, in Tier 2, a single regulatory test method was allowed with promises of a performance based measurement system (PBMS) for qualifying alternate methods.^{2,3} Other Tier 2 provisions included allowing ASTM based analysis for quality control purposes and use for tracking and control of small refiner gasoline. There were also special allowances for computer controlled blending operations that are common in most modern

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high-through put operations, as well as exceptions for producers of California (CARB) gasoline. As of this writing the EPA has not modified its sole regulatory test language and has not published its PBMS guideline.

While most refiners and importers are formulating the plans needed to meet requirements for reducing sulfur levels in all motor fuels, a debate about the appropriate test methods for measuring the new very low levels of sulfur has sprung up. During the mid-1990s, when producers of gasoline for the California market were faced with similar challenges a group of refiners (Western States Petroleum Association or WSPA) petitioned the California Air Resources Board (CARB) for more flexible and economical sulfur test methods. In short, what WSPA and CARB needed were economical test methods that could measure very low levels of sulfur, while giving the same (equivalent) results as found when using the regulatory method D 2622 (x-ray fluorescence). Various laboratory studies and cooperative multi-laboratory testing revealed that D 5453 (combustion fluorescence) was such a sulfur test method. D 4045 (combustion rateometric lead acetate) was also allowed for less than 10 ppm levels.⁴

Meanwhile, the analytical community has been busily working on several fronts. In an effort to inform itself and decision-makers of all stripes as to the latest developments for the measurement of sulfur at very low levels, several studies have been completed or are on going. It is illuminating to look at three major bodies of work, two of

Modern ASTM Laboratory Methods		
Test Method ASTM#	Name	Estimated limit of quantitation in multi-lab round robin situations in (mg/kg)
D1266-98 Annex A1	Lamp Method with extended procedure	10-20
D 2622-98 gasoline	WDXRF (gasoline and diesel precision data are separ- ated in the method)	10-15
D2622-98 diesel		10-15
D 3120-96	Oxidative Microcoulometry	10-20
D 4045-96	Hydrogenolysis and Rateometric Colorimetry	1
D 5453-93	UV Fluorescence	1
D 6334-98	WDXRF (gasoline only)	15
D 4294-98	EDXRF (gasoline and diesel)	150
D 6445-99	EDXRF (gasoline only)	48

Table 2. Listing of most modern total sulfur test methods and estimates of their limit of quantitation based on recent round robin studies and ASTM crosscheck program activity.



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all-terrain sulfur analyzer.

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- Free from matrix effects — saves money by analyzing multiple streams
- Optimizes batch averaging
- Highly reliable/maintenance-free over long periods
- Add total nitrogen analysis (ASTM D4629)
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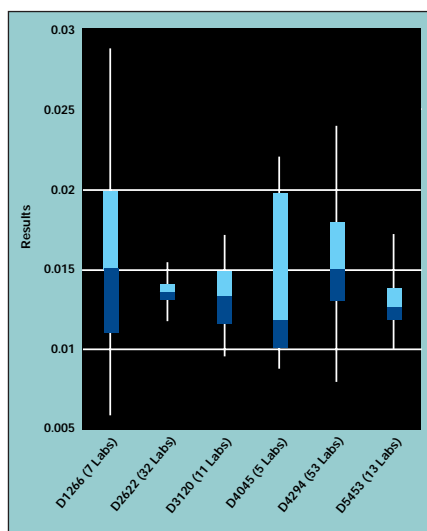


Figure 1. Graphic summary of motor gasoline ASTM crosscheck program activity, August 1999.

which were done specifically to review the analytical performance of the major consensus test methods used in the petroleum products testing laboratories for low concentrations of sulfur.

ASTM Research Report, D.02 - 1456 In a very thorough research study done at SWRI in San Antonio, Texas, three sulfur methods were compared for fitness for use.⁵ The three test methods examined were ASTM D 2622 wavelength dispersive X-ray fluorescence, D 4294 energy dispersive X-ray fluorescence, and D 5453 combustion UV-fluorescence methods for the analysis of fuels at < 500 mg/kg sulfur level. All three methods were found to be equivalent for measurements in the 150 to 500 mg/kg range. D 5453 and D 2622 demonstrated equivalent fitness for use down to 20 mg/kg. Strong evidence was found that D 5453 can be fit-for-use in multi-laboratory situations down to the 1 mg/kg sulfur level. D 2622 was not found viable at < 10 mg/kg levels.

To analyze for sulfur compound bias, a single iso-octane matrix was used to minimize well-known carbon/hydrogen ratio interference in the XRF test methods. All three test methods were then evaluated for any bias with respect to 24 commonly occurring organo-sulfur compounds. No bias was detected and the accuracy was within the precision limits for each of the test methods. Of these three test methods, the best low-level precision and accuracy was found in D 2622 and D 5453. Of these two, D 5453 was found to generate better data in the low (< 50 mg/kg) sulfur regime. In fact, this work also suggests that the

ASTM Cross-Check Program 1-9 mg/kg sulfur						
	D5453			D 2622		
Sample	Conc.*	SD*	RSD%	Conc.*	SD*	RSD%
RFG 9810	2.5	1.0	40	6.5	5.5	85
RFG 9907	2.2	1.0	40	6.0	5.5	85
JF 9711	3.5	1.8	51	13.9	13.3	96
RFG 9806	4.5	1.4	31	9.0	7.1	79
RFG 9706	5.0	1.5	30	7.4	5.2	70
RFG 9712	5.0	1.0	20	8.8	5.3	60
RFG 9612	8.7	1.9	22	12.2	5.7	47

*ppmw - rounded

Table 3. ASTM crosscheck program results for samples found to contain less than 10 mg/kg sulfur.

D 5453 test method can be routinely used for determining sulfur in liquid hydrocarbons at levels less than 1 mg/kg.

Center for European Normalization Cross Check WG 27 Round Robin Exercise.

In a just completed very large round robin in Europe, 69 laboratories from nine countries participated in the determination of sulfur at levels between 5.0 and 500 mg/kg. Eight gasoline and 7 diesel samples were measured using principally five test methods: WDXRF (D 2622), EDXRF (D 4294), combustion-UV-fluorescence (D 5453), microcoulometry (D 3120) and Wickbold combustion (D 1266). At most levels tested, all five test methods were found to produce essentially equivalent results, but the precision of different methods varied considerably.⁶

For less than 30 ppm sulfur concentrations, the best reproducibility and accuracy was obtained for WDXRF and UV-fluorescence methods with many of the conclusions of ASTM RR-D.02-1456 regarding UV fluorescence performance at very low levels being confirmed. As Work Group 27 wraps up this phase of its work, the final outcome of this European round robin and its effect on European sulfur in motor fuel law is unknown. However, the combustion UV-fluorescence method was considered suitable for determining sulfur at and below the 10 mg/kg content required in future fuels for Europe, while continued work on the WDXRF method is required for these very low sulfur levels.

ASTM Interlaboratory Cross Check Program

For nearly a decade, ASTM D02 Committee on Petroleum Products and Lubricants through its coordinating subcommittee 92

has instituted a voluntary proficiency testing program.⁷ Eleven types of products are analyzed mostly thrice a year by about 1,300 laboratories worldwide. A survey among these laboratories, conducted in August 1999, showed that the most commonly used test methods for determining low levels of sulfur in motor gasoline, #2 diesel fuel, reformulated gasoline and aviation turbine fuel were ASTM D 2622 WDXRF, D 4294 EDXRF and D 5453 UV-fluorescence. Other test methods such as D 1266 lamp, D 3120 microcoulometry, D 4045 hydrogenolysis rateometric colorimetry and D 6344 WDXRF were used to a much lesser extent.⁸

There is a vast amount of data available through these ASTM crosschecks. One consideration when viewing this data is that overall there can appear to be good agreement between the mean results obtained by alternate methods for a particular product. However, sometimes there is considerable difference between the precision obtained by the individual test methods. This point is vividly illustrated in the Box and Whisker graph plotted for motor gasoline in Figure 1.

Even though sulfur results by each method shown in Figure 1 were reasonably close, the range of results by each method and thus the reproducibility of the analyses widely varied from unacceptable to very precise. Thus, great care must be exercised in making decisions regarding the product quality among buyers and sellers, and by the regulatory agencies. The precision of the analysis is perhaps even more important than the average values in case of dispute.

The ASTM CS 92 crosscheck data clearly indicate that for gasoline samples below 10 mg/kg level, D 2622 has extremely poor precision. At around 30 mg/kg level, D 2622 has improved reproducibility, but D 5453 has still superior reproducibility (Tables

ASTM Cross-Check Program 10-30 mg/kg sulfur						
Sample	D5453			D 2622		
	Conc.*	SD*	RSD%	Conc.*	SD*	RSD%
MG 9612	10	2	20	14	10	71
RFG 9807	11	2	18	13	6	46
RFG 9709	13	3	23	14	6	43
RFG 9910	17	2	12	18	6	33
RFG 9609	14	3	21	15	6	40
RFG 9906	14	2	14	17	6	35
RFG 9703	27	5	19	28	6	22
RFG 9901	29	2	7	30	7	23
RFG 9803	30	4	13	34	10	29
RFG 9904	23	2	9	24	8	33

*ppmw - rounded

Table 4. ASTM crosscheck program results for samples found to contain less than 10-30 mg/kg sulfur.

3 and 4). A graphic summary is presented in Figures 2 and 3.

At sulfur levels over and above 50 mg/kg, however, based on the ASTM cross-checks conducted between June 1996 through December 1998, both D 2622 and D 5453 methods produce equivalent results in RFG, motor gasoline, diesel and jet fuel samples (Figure 4). D 5453 inter-lab precision at levels greater than about 250 mg/kg is generally acceptable, but can be inferior to D 2622.

Based on the precision of analysis, D 5453 appears to be superior to D 2622 at < 50 mg/kg sulfur levels and equivalent above this level for the critical sulfur measurements of the coming decade. Thus, there is no technical reason why D 5453 should not be designated as a primary or alternate regulatory method of analysis for sulfur in gasoline type products. Incidentally, the cost of instrumentation and maintenance for D 5453 equipment is considerably lower than that needed for D 2622 equipment. Similar arguments may eventually be formulated for other ASTM test methods, depending on regulatory targets and the materials to be analyzed.

Over a dozen test methods are currently available for determining sulfur in petroleum products and lubricants. Each method has its advantages and drawbacks. It is also known that certain individual labs have demonstrated impressive measurement capabilities for individual methods. For now however, in all states except California, the use of a single method for regulatory reporting purposes is required. Accordingly the EPA has allowed the following, "We believe that any imprecision of sulfur values derived from analysis using ASTM D 2622

will, over the course of numerous batches, average out to near zero."⁹

An intelligent choice must be made based on the method's accuracy and precision before deciding which method to use for a particular product. Since the method precision is often dependent on the sulfur concentration level and the product matrix, this can be a critical decision for measurement and control managers. Arbitrarily using a method without these considerations can only result in producing data without much reliability, which does not help in settling disputes either in commercial transactions or in regulatory affairs. ■

The Author

Kishore Nadkarni is chairman of ASTM D02.03 sub-committee for elemental analysis and ISO/TC 28. He has over 20 years experience as lab head and worldwide analytical leader for Exxon R&E and Chemical Company. Mr. Nadkarni is also chairman and vice-chairman for several other ASTM sub-committees, including CS-92 on Inter-laboratory Cross-check programs and CS-93 on International Activities and Standards. He completed a doctorate in analytical chemistry from the University of Bombay and post-doctorate studies at the University of Kentucky, Lexington, Kentucky.

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2. Environmental Protection Agency, Federal Register 64 (92), 40 CFR Parts 80, 85 and 86, Page 26055, May 13, 1999.

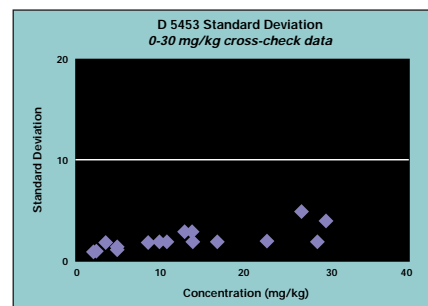


Figure 2. Graphic summary of ASTM cross-check data shown in Tables 3 and 4 for the combustion fluorescence test method D5453.

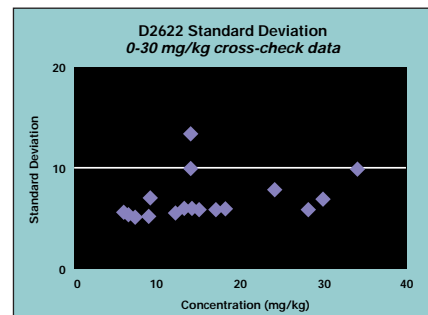


Figure 3. Graphic summary of ASTM cross-check data shown in Tables 3 and 4 for the WDXRF test method D 2622.

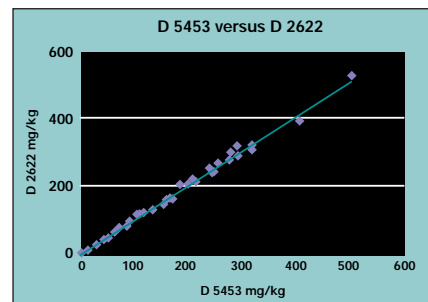


Figure 4. Graphic summary of ASTM cross-check data comparing D 5453 and D 2622 for sulfur levels up to 500 mg/kg.

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