

COMPARATIVE ON-LINE ATMOSPHERIC DISTILLATION AND TOTAL SULFUR ANALYSIS METHODS IN THE GASOLINE BLENDER

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ABSTRACT

Tight blending specifications are required to make gasoline at the most reasonable cost. On-line analysis can provide crucial information to prevent giveaway and reprocessing. This paper will present a technology discussion for total sulfur analysis and determining distillation boiling points in the gasoline blender which includes:

1. How lab data and process data correlations are interpreted and best practices, including a discussion of ASTM methods
2. How tight monitoring can help the process and define the payback
3. What the issues are for transitioning to process control
4. What is known about how to optimize sampling and specific installations showing examples of good and bad practices

INTRODUCTION

One of the most critical economic issues for a petroleum refinery is selecting the optimal combinations of components to produce gasoline products. A typical refinery may have as many as 8 to 15 different hydrocarbon streams to consider as blend stocks. These may range from butane, the most volatile, to heavy naphtha- which comes from crude distillation, catalytic cracking, and thermal processing units - in addition to alkylate, polymer, and reformat. Gasoline may be blended to meet 10 to 15 different quality specifications such as vapor pressure, initial, intermediate and final boiling points, sulfur content, color, stability, aromatics content, olefin content, and octane measurements for several different portions of the blend and other local government and market requirements. The allocation of each component is critical and is important to the economics of gasoline blending.¹

This paper will describe the practical application of on-line total sulfur and boiling point analyses for process control in the gasoline blender. The calculation of economic payback used to justify on-line measurement of boiling point distribution in gasoline blending will be illustrated.

ATMOSPHERIC AND COMMON DISTILLATION METHODS AND TECHNOLOGY

There are many ASTM methods designed to determine critical boiling point profiles for petroleum products. In the gasoline blender we must comply with the ASTM D86 method which is the referee method for certification of atmospheric distillation of light and middle distillate fuels with boiling points in the range of 20°C to 400°C.

The car-starting and vapor-lock indexes have been found to be mostly affected by the front end of the Test Method D86 distillation curve (up to about 200°F (93°C)). The warm-up index is affected by the middle and to a lesser extent by the back end of the Test Method D86 curve, that is, the temperatures corresponding to the 50 to 90% off range. Hence the boiling range distribution provides fundamental information on composition.²

The Table I below lists the ASTM methods for determining the boiling point distribution of liquid petroleum fuels, some of which extend above atmospheric pressure (>1 bar).

TABLE I. BOILING POINT METHODS

ASTM METHOD	TECHNOLOGY/DESCRIPTION	APPLICATION
D3710-95 (2009)	Determination of Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography	This test method covers the determination of the boiling range distribution of gasoline and gasoline components with a final boiling point of 500°F (260°C) or lower.
D2887-08	Determination of Boiling Range Distribution of Petroleum Fractions by Gas Chromatography	The test method is applicable to petroleum products and fractions having a final boiling point of 538°C (1000°F) or lower at atmospheric pressure. It is limited to samples having a boiling range greater than 55.5°C (100°F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature.
D7345-08	Distillation of Petroleum Products at Atmospheric Pressure (Micro Distillation Method)	This test method covers a procedure for determination of the distillation characteristics of petroleum products having a boiling range between 20 to 400°C at atmospheric pressure using an automatic micro distillation apparatus. It is applicable to such products as light and middle distillates, and engine fuels containing up to 10% ethanol, and up to 20% biodiesel blends.
D86-12	Test Method for Distillation of Petroleum Products at Atmospheric Pressure	This test method covers a procedure for determination of the distillation characteristics of petroleum products having a boiling range between 20 to 400°C at atmospheric pressure and is designed for the analysis of distillate fuels and is applicable to ethanol fuel blends.

The on-line MicroDist correlates with ASTM method D7345 and uses the same technology as the portable lab Microdistillation (PMD) analyzer. The D7345 method is the method the portable lab MicroDist analyzer is based on. ASTM method D7345 is a method of atmospheric distillation and correlates to method D86. It is important to note that the recovered volume is calculated from gas flow through a calibrated capillary by measuring the differential pressure over the capillary. The volume is not measured in D7345 as it is with D86. A correlation calculation is made to D86 to translate the pressure and temperature changes in the flask to the D86 boiling point curve.

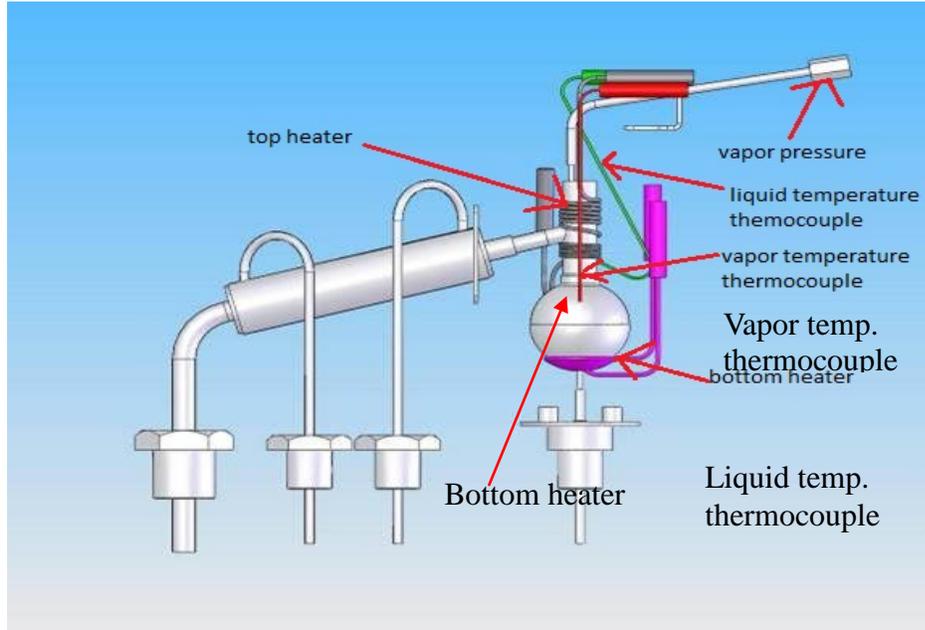


FIGURE 1 MICRODISTILLATION TECHNOLOGY

The D7345 method utilizes a smaller volume flask for 10 ml. of sample which is one-tenth the volume of a standard D86 instrument, therefore the distillation time is faster and averages 10 minutes for gasoline. This is less than a third of the time for a standard D86 method and matches most fast simulated distillation methods. The boiling point curve is directly correlated to the D86 curve and requires no software change because of fuel sample change. The same instrument can detect any of the Group 1-4 fuel types by doing a test distillation in which the new heating profile is set up automatically causing minimal delay in the next analysis. The method is highly precise for determining gasoline boiling point data and field tests have proven the 50% point to be well within the D86 method limits resulting in better tracking of blending changes caused by component changes since it measures the change in pressure and temperature in the flask and does not require correlation software. A nitrogen pressure circuit is connected to the analysis flask and controls the filling and exhausting of the flask. This system minimizes failure of mechanical parts. A nitrogen generator option prevents the need for an external nitrogen source (since it filters the nitrogen from air) and produces a very low flow to keep the nitrogen circuit filled. So there is only one utility gas required- instrument air for the generator and actuators and compressed air for the purge. The boiling flask is self-cleaning and is self-contained and insulated inside a small purged enclosure. The system automatically detects vapor pressure changes and will run a higher heating cycle to clean out any particulates or soot that may build up. This preventive action makes sure the distillation runs smoothly without error in the results due to build-up.

TOTAL SULFUR METHODS AND TECHNOLOGY

Because of the harmful effects of sulfur emissions from motor vehicles, a number of government regulatory agencies, principally in North America and Europe, have been vigorously controlling and gradually reducing the sulfur content of the fuels used in automobiles, aviation, marine vessels, off-road vehicles, power generating utilities, and home heating.

The total sulfur methods for liquid petroleum fuels are listed in the following table. The on-line instruments either correlate to the laboratory methods or have their own associated method.

TABLE II. TOTAL SULFUR METHODS

ASTM METHOD	TECHNOLOGY/DESCRIPTION	APPLICATION
D5453-12	Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	Applicable fuels are naphthas, distillates, engine oil, ethanol, Fatty Acid Methyl Ester (FAME), and engine fuels such as gasoline, oxygen-enriched diesel, biodiesel, diesel/biodiesel blends, and jet fuel. Samples containing 1.0 to 8000 mg/kg total sulfur can be analyzed.
D2622-10	Determination of Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry	Applicable to petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol and biodiesel. The range of this test method is between the PLOQ value of 3 mg/kg total sulfur and 4.6 wt.% total sulfur.
D3120-08	Determination of Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry	This test method covers the determination of sulfur concentration in the range from 3.0 to 1000 mg/kg in light liquid hydrocarbons and fuels with oxygenates boiling in the range from 26 to 274°C (80 to 525°F).
D4294-10	Determination of Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry	Applicable fuels include diesel fuel, jet fuel, kerosene, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel, and similar petroleum products. Oxygenated fuels have different precisions. The scope of measurement is 17 mg/kg to 4.6 mass %.
D6920-07	Standard Test Method for Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection	This test method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C. This test method is applicable to naphthas, distillates, and motor fuels such as gasolines, reformulated gasolines, gasohols, diesels and biodiesels containing

		approximately 1 to 100 mg/kg total sulfur in gasoline type products, and approximately 1 to 40 mg/kg sulfur in diesel type products.
D7041-04 (2010)	Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Online Gas Chromatography with Flame Photometric Detection	Applicable fuels are liquid hydrocarbons with a final boiling point less than 450°C. This test method is applicable for total sulfur levels from 0.5 to 100 mg S/kg.
D7039-07	Determination of Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry	Applicable fuels are single phase gasolines, diesel fuels, and refinery process streams used to blend gasoline and diesel, at concentrations from 2 mg/kg to 500 mg/kg. Gasolines with oxygenates require matrix matching of calibration samples.

In this paper, the performance of the D5453 total sulfur analyzers in the gasoline blending application will be discussed. The sample combustion and UV detection process used in the on-line total sulfur analyzers are designed to provide accurate measurement of sulfur in liquid or gas hydrocarbon streams. Total sulfur detection is accomplished through pyro-fluorescence which involves heating the sample to over 1000°C in the presence of excess of oxygen and exposing the combusted material to UV light for detection. The UV light is absorbed, which produces a specific wavelength of light from the sulfur components that is detected by the photomultiplier tube inside the sulfur detector. The signal produced by the photomultiplier tube is sent for processing and is recorded as 4-20 ma analog outputs. Because a filter lens allows only the appropriate wavelength of light to reach the photomultiplier tube (PMT), the current produced by the PMT is proportional to the amount of SO₂ being fluoresced. The effluent of the sulfur chamber is then vented.

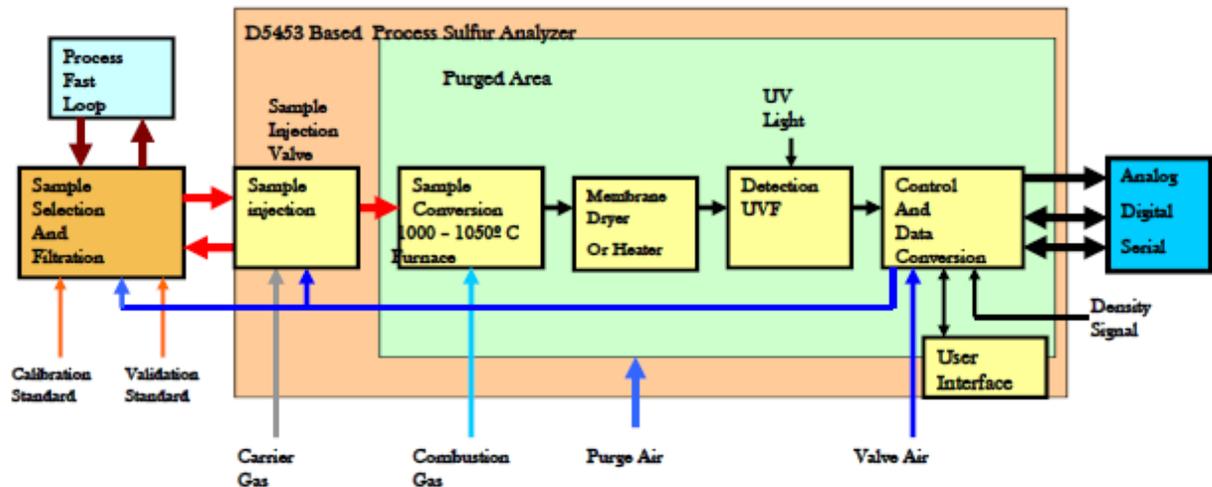


FIGURE 2 D5453 PROCESS ANALYZER TECHNOLOGY

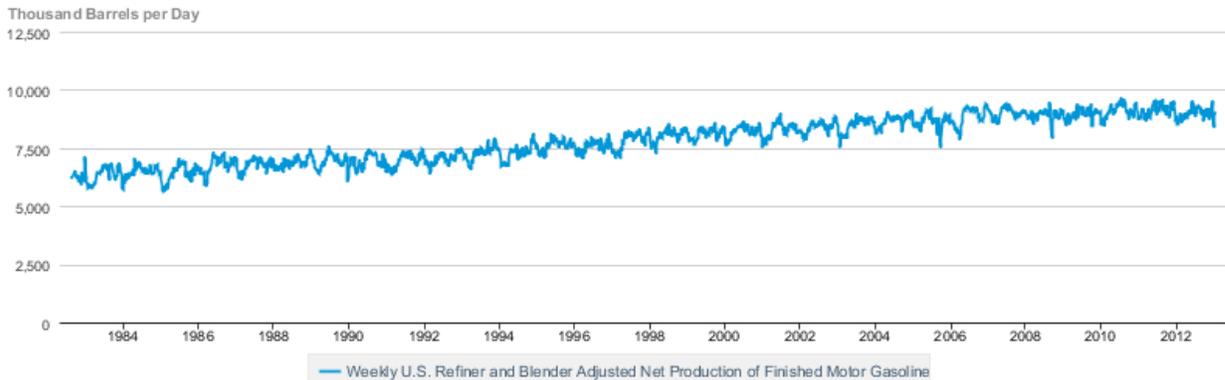
PROCESS AND LABORATORY CORRELATION- THE PAYBACK

Refinery optimization objectives change daily based on economically available feedstocks and their qualities, product markets & accessibility, product specifications, and seasonality impacting both specifications & demands. Optimization efforts require the refiner to work closer to product specification limits.

The largest concentration of refining capacity is in North America (in fact, the United States), accounting for about one-quarter of the crude oil distillation capacity worldwide. Asia and Europe follow as refining centers. North America (again, the United States) has by far the largest concentration of downstream capacity – the processing units necessary to maximize output of gasoline. The gasoline emphasis of course mirrors the demand and hence refinery output in the different regions, since no other global region uses as much of its oil in the form of gasoline as North America.

The production of finished gasoline in the US is not declining.³ At the end of January 2013, U.S. production was more than 9,000,000 barrels per day.

Weekly U.S. Refiner and Blender Adjusted Net Production of Finished Motor Gasoline



 Source: U.S. Energy Information Administration

FIGURE 3 GASOLINE PRODUCTION VOLUME BY YEAR

The goal of gasoline blending is to blend as economically as possible to reduce the octane usage and achieve the desirable boiling point target. Octane rating is measured relative to a mixture of 2,2,4-Trimethylpentane (an isomer of octane) and n-heptane. It is estimated that consistent octane giveaway of 0.1 octane numbers can cost a refinery several millions of dollars a year.⁴

The important target point in the gasoline specification is the boiling point temperature at the 50% (T50) recovered volume which is controlled by the octane addition. Both butane and natural gasoline will raise the T50 point. The target is 150°F (after ethanol addition). Anything above 150°F will cost money to the refinery and result in giveaway of expensive products. The goal

here is to get the lab and process analyzer to agree as close as possible. Since the laboratory D86 method is the certification test requirement, the process analyzer must correlate as close as possible. At a large refinery with 400,000 barrel per day crude throughput, 1°F closer to the lab T50 value in winter gasoline blending is conservatively worth \$310,000 per month. The return is also higher in the winter since more butane is added to meet the RVP requirements. Butane is a cheaper blending component than most of the other ingredients. That makes fall and winter gasoline cheaper to produce. According to ASTM D86, the reproducibility requirements show that the difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material would exceed the following only in one case in twenty.⁵ For groups 1-3 fuel types in which gasoline fits, the following precision (reproducibility) is noted in the ASTM D86-12 method:

- IBP: $R = 0.0595(E + 51.19)$, valid range: 20 – 70°C
- E10: $R = 3.20$, valid range: 35 – 95°C
- E50: $R = 1.88$, valid range: 65 – 220°C
- E90: $R = 0.019(E + 59.77)$, valid range: 110 – 245°C
- FBP: $R = 6.78$ valid range, 135 – 260°C

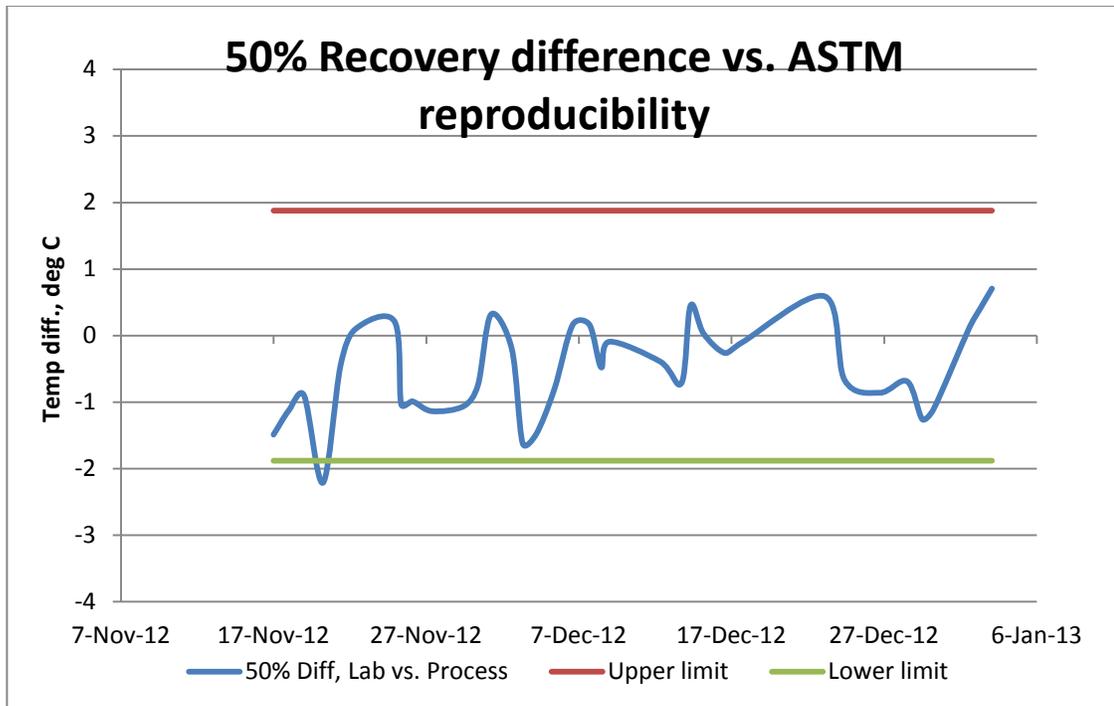


FIGURE 4 50% BOILING POINT, DIFFERENCE LAB VS. PROCESS VS. ASTM

Figure 4 shows good reproducibility of the on-line MicroDist physical distillation analyzer to the laboratory D86 analyzer since the difference in the two measurements falls within the 1.88°C

reproducibility as stated in the method. The 50% recovery point is the tightest control point used in the gasoline specification so good reproducibility means there is good 24/7 process on-line monitoring.

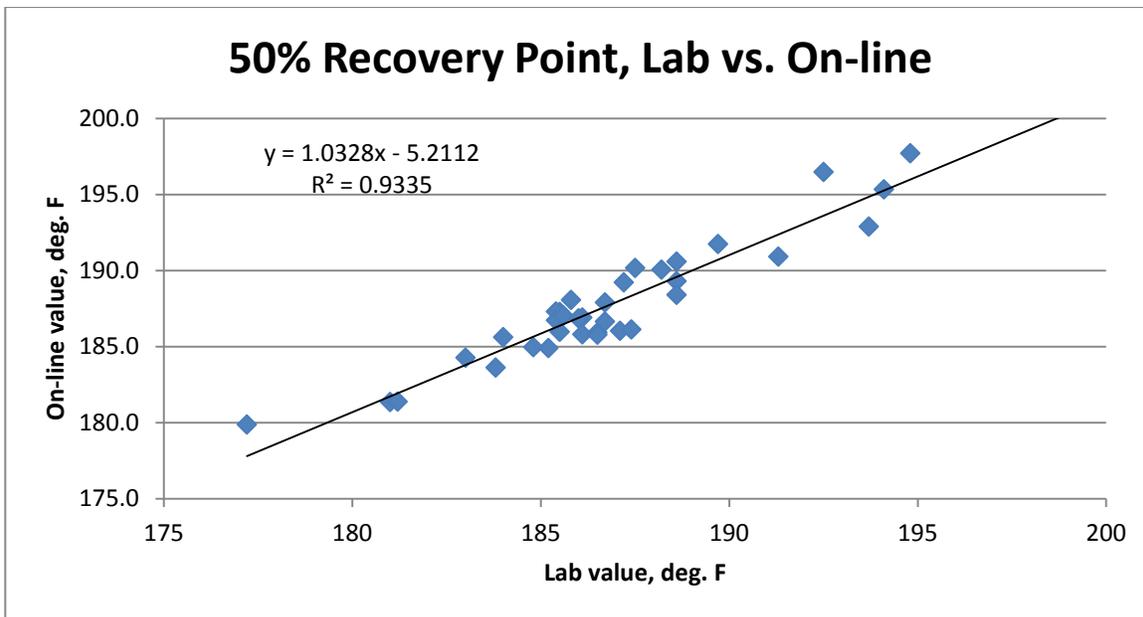


FIGURE 5 50% BOILING POINT, LAB VS. ON-LINE REPRODUCIBILITY

Figure 5 shows the 93% regression analysis of the lab and process values at the 50% recovery point, showing good correlation of the data, resulting in good process control for the gasoline production

The calculation of profitability in the gasoline blender for a boiling point analyzer is displayed in Table 3.

* This calculation is conservative and will double for every degree closer to the 50% recovery point as compared to the lab data. This calculation would be better shown by tracking the trend result over time with the different blends and estimating a long-term return on investment on final product.

Another important issue to discuss with lab and process correlation techniques is the method correlation and bias of different ASTM methods. It is normally not recommended to use a different method for on-line analysis since the correlation to the laboratory method would result in another bias calculation that may be difficult to compare. The following data shows two different total sulfur ASTM methods (D5453 and D7041) and their correlation to the referee laboratory method (D5453). Total sulfur analysis in both these cases is quite consistent and well maintained in both the field and laboratory testing. Good sampling and testing practices also contribute to good correlation between the laboratory and corresponding on-line analysis.

TABLE III. ECONOMICS OF BOILING POINT ANALYZER IN GASOLINE BLENDER

Investment	
Boiling Point Analyzer and Sample System with Installation costs, including shelter, total per system	\$350,000
Economics	
Incremental analyzer earnings \$/year	
400,000 barrel/day refinery (1 °F closer results to 50% recovery point)	\$300,000/month x 12 months= \$3,600,000
Analyzer Maintenance \$/year	\$14,160
Net analyzer earnings \$/year	\$3,585,840
Before tax payout, years	0.10 (pay off in 36 days or about 5 weeks)*

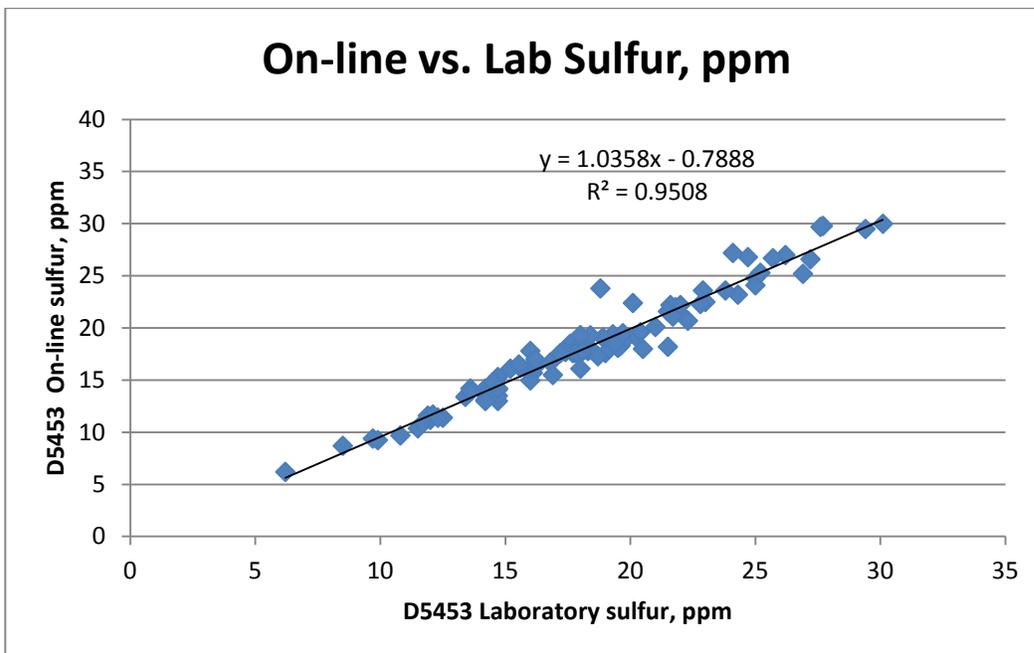


FIGURE 6 ONE YEAR DATA, D5453

Figure 6 shows the linear regression coefficient of the Antek D5453 on-line analyzer verses the Antek D5453 laboratory analyzer over the period of a year. The values are within 95% agreement which is an indicator of consistent data.

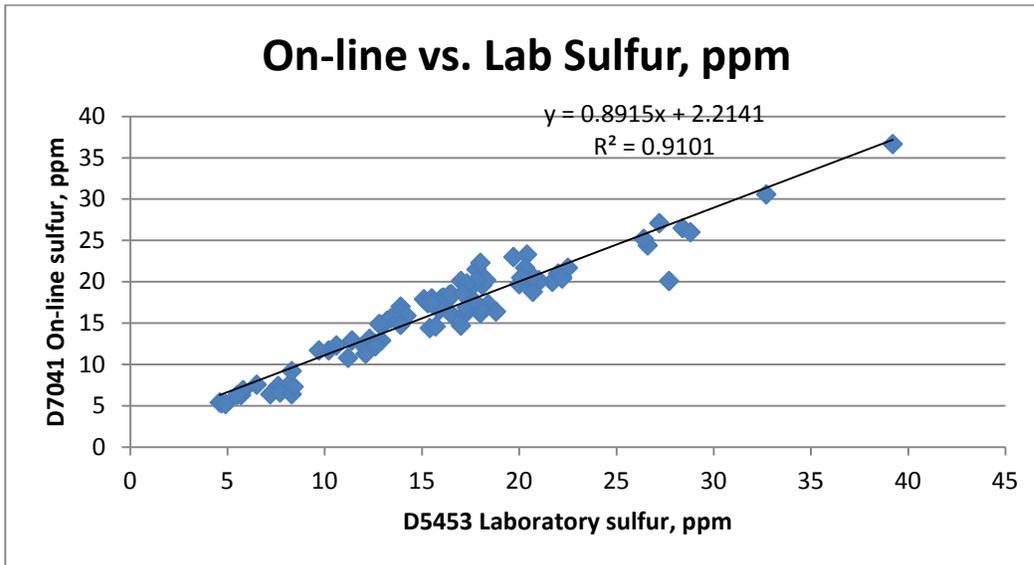


FIGURE 7 90 DAYS DATA, D5453 AND D7041 ON-LINE

Figure 7 shows cross comparison of ASTM methods – laboratory D5453 compared to on-line D7041 using a flame photometric detector. The regression analysis for 90 days of data shows 91 percent correlation so these two methods have good correlation. Over a longer period of time this analysis may average a closer number. It is still accepted standard practice to perform this correlation with instruments utilizing the same ASTM test method. With proper sample handling, calibration, and bias calculation, the issues of cross-correlation of methods can be minimized.

TRANSITIONING TO PROCESS CONTROL

Everyone likes getting systems that work. The phrase “Get it and forget it” is a common goal in the industry, but seldom achieved. Another question to consider is how to justify transitioning a measurement from the lab to the process and then using that data for certification or control? Can a measure in dollars be put on the delay in getting a lab analysis required to control your process? What is a two hour delay to get a boiling point reading or a sulfur result worth? Are the reject ratios of your product high enough to justify getting a process analyzer? Of course all these answers depend on the throughput of the refinery and the value that online certification can bring by needing fewer laboratory tests and/or reducing the turn-around time for sample results.

If a refinery normally makes a certification test three times in 24 hours, and could eliminate the requirement of two of those tests, there is a significant opportunity for cost savings. For instance, manpower could be dedicated to another critical test requirement since a faster on-line analysis does not require a technician to stand over an analyzer waiting on results. Furthermore, a 10 minute analysis for on-line D86 versus 40 minutes for laboratory D86 boiling point analysis can result in significant savings since any transgressions that may occur in the process during the time waiting for the laboratory results will be tracked by the process analyzer and operator adjustments can be made quickly. (See Figure 8, continuous on-line sulfur tracking) The laboratory may not even detect the sulfur excursion to make the proper adjustment. Figure 9 shows that within 2 sample injections, a significant step change is noted (in less than 5 minutes), demonstrating the sensitivity of this method for tracking quick changes in the process.

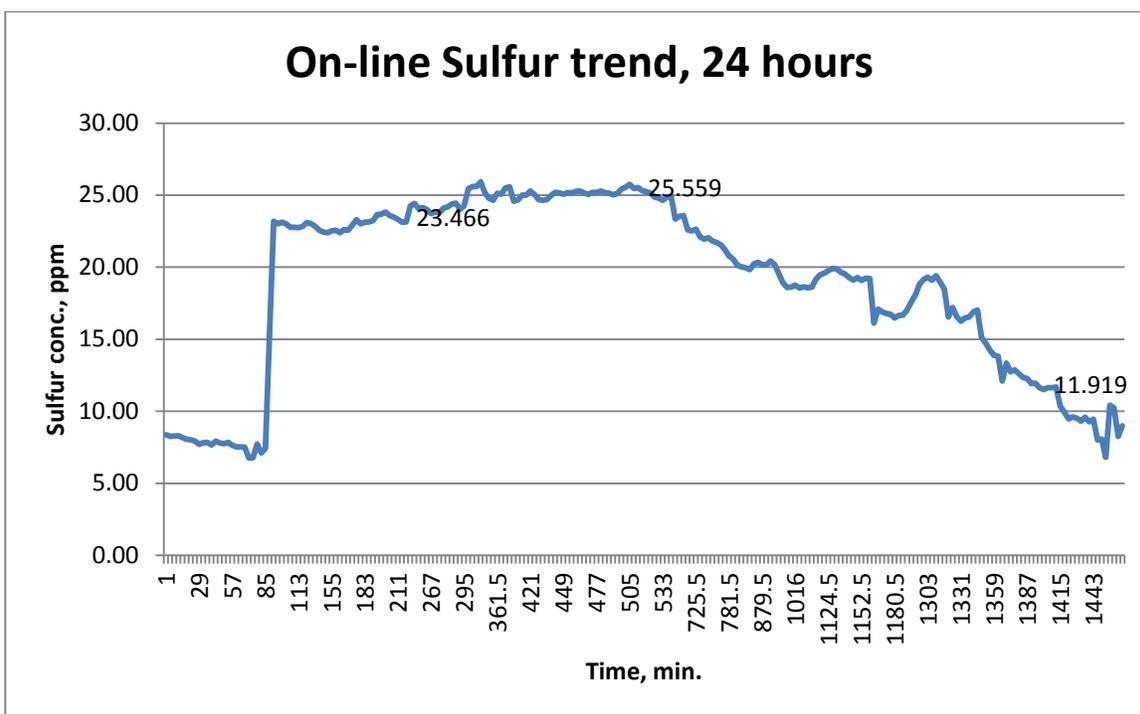
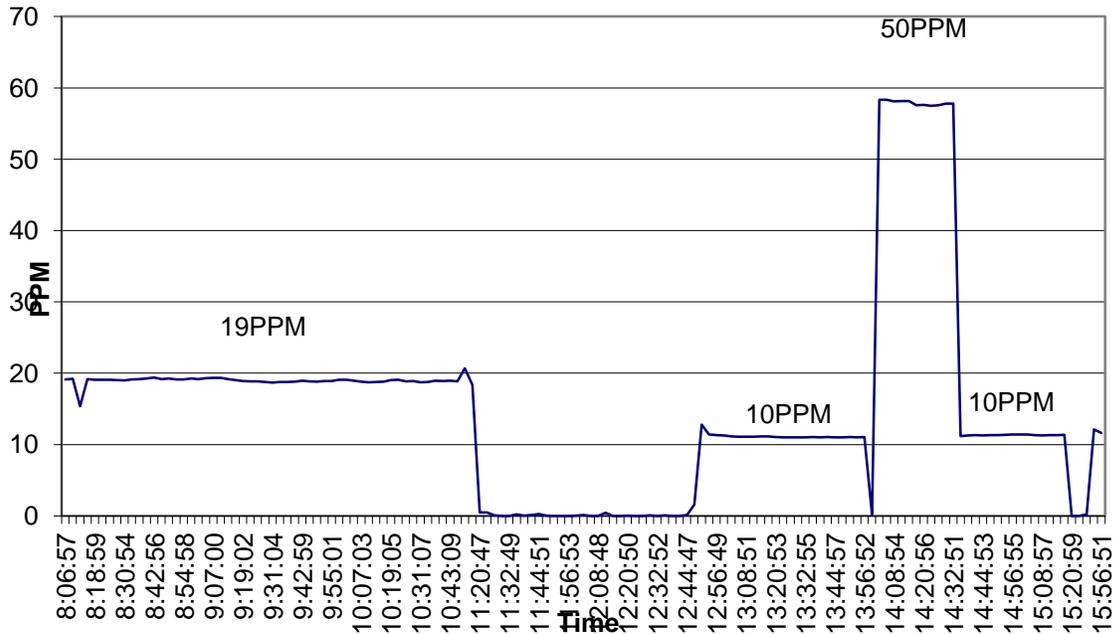


FIGURE 8 CONTINUOUS ON-LINE SULFUR TRACKING

Competition and new measurement advances have encouraged technology advances and led to improved performance and cost improvements. Critical evaluation of sample system design for specific installations and applications is required and not always available. Most sample systems are designed based on duplicating previous projects with new features added but without proper evaluation. And in many cases it is trial and error to make the system work properly since it is application dependent.

The most critical time in the life of a process analyzer is start-up. The confidence level in an analyzer is determined by the operators and the analyzer engineers. If the first weeks and months do not go well, the acceptance of the analyzer can be difficult.



**FIGURE 9 TOTAL SULFUR 0-50 PPM STEP CHANGE
OPTIMIZING THE INSTALLATION AND SAMPLING SYSTEM**

Sample transport is the least understood area of science of on-line analyzers.

While there are detailed specifications for shelters and analyzers, not very much of the technical specifications for analyzers describe sample systems. It gets treated as an art form, designed and handled differently by everyone who builds one. A poorly designed sample system and installation mistakes will result in poor performance.⁶

Figure 10 shows the regression coefficient (R^2) which is a predictor of good correlation of values. Note that with poor cooling in the on-line MicroDist, the correlation is 89% with the D7345 micro-distillation method compared to the D86 lab method. Figure 5 shows the correlation coefficient in a system with good cooling. The precision has increased to 95% as compared to the lab method. So cooling of the sample is important if using a method that calculates initial boiling point and front end boiling points which are more volatile in gasoline applications. The sample must be cooled 15 degrees C below initial boiling point to establish good precision.

Physical property analyzers require high sample flow and return rates which require the proper drain, line size, and sample recovery system to handle the flow and volume output. The design of the filtration system is important to prevent back pressure and low sample flow rates. A self-cleaning system is optimal for longer intervals between change-out.

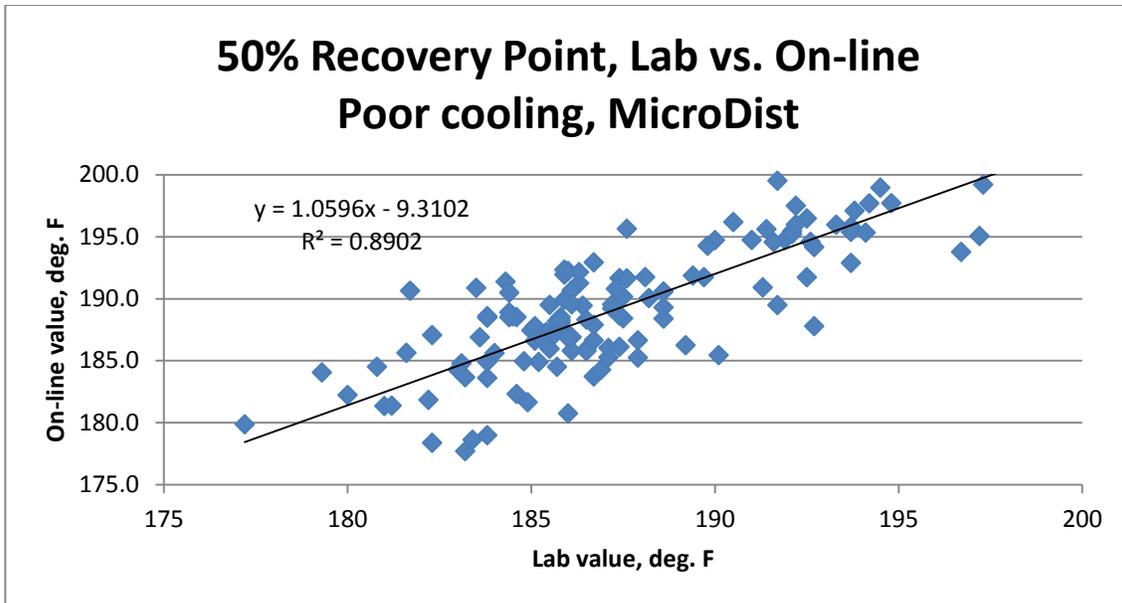


FIGURE 10 50% POINT, LAB VS. ON-LINE REPRODUCIBILITY, POOR COOLING

The benefits delivered by on-line analyzers far outweigh the costs. The increased availability of on-line versus laboratory results is the key to capturing the value. Critical installation factors are to shorten distances of the analyzers to the sample point and return lines to prevent lag time, keep the analyzers in temperature controlled shelters, and use the recommended sample conditioning and cooling techniques.

CONCLUSION

Refiners have to deal with a lot of factors in controlling the specifications of the final product. The on-line versus laboratory correlation is important in validating the on-line results. This can involve cross correlation of different ASTM methods. On-line analysis can provide crucial information to prevent giveaway and reprocessing and can go a long way to optimize the gasoline blending process. On-line analysis also makes sure the specifications are met to satisfy environmental concerns and target blending requirements. Well maintained on-line systems will have a short pay-off period and result in optimal product.

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