

# Robust Prediction of Gasoline Properties Using Spectroscopic Methods Dynamically Corrected with Lab Data

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## 1. Introduction

Spectroscopic methods for measuring in-line blended gasoline have many advantages over conventional on-line analyzers, such as very fast, very precise measurements, simultaneous multiple parameter measurements, and very high reliability, at a reasonable cost. Spectroscopic analysis methods in this paper refer only to FTIR, Raman, and Magnetic Resonance Analysis.

The major shortcomings of using spectroscopic methods or any inferential model-based parameter determination are:

- inaccurate inferential model predictions of parameters of interest, e.g. gasoline octane values,
- lack of a practical, how-to guide to build simple but reasonable inferential (chemometric) models.
- Lack of a simple methodology to dynamically correct the predicted parameter value of an imperfect inferential model by comparing it with a credible value, e.g. Lab

This paper addresses these problems with a robust solution and scheme for reliable gasoline (or any fuel) blend property parameter prediction (chemometric) model development method, and dynamic correction of the model parameter prediction with Lab data.

The scheme is based on well-known principles of inferential model-based prediction of process stream quality in place of a real parameter measuring device, e.g. octane knock engine. The model output is corrected periodically with Lab data to within the ASTM reproducibility of that parameter.

The described approach has been used since 1960's with the advent of practical process control computers to implement composition control without using on-line property analyzers [1], and later to validate octane knock engines and NIR-type spectroscopic analyzers since 1986 [2, 3], and is a derivative of tank quality integration used in in-line blend property control since its inception in 1965 [4].

The scheme is valid for:

- Any fuel blending (gasoline, diesel, bunker), or any mixture of liquids
- Any parameter for which an inferential model can be developed, e.g. AKI, RVP, etc.
- In-line fuel blending scheme, either rundown blending or component tank blending

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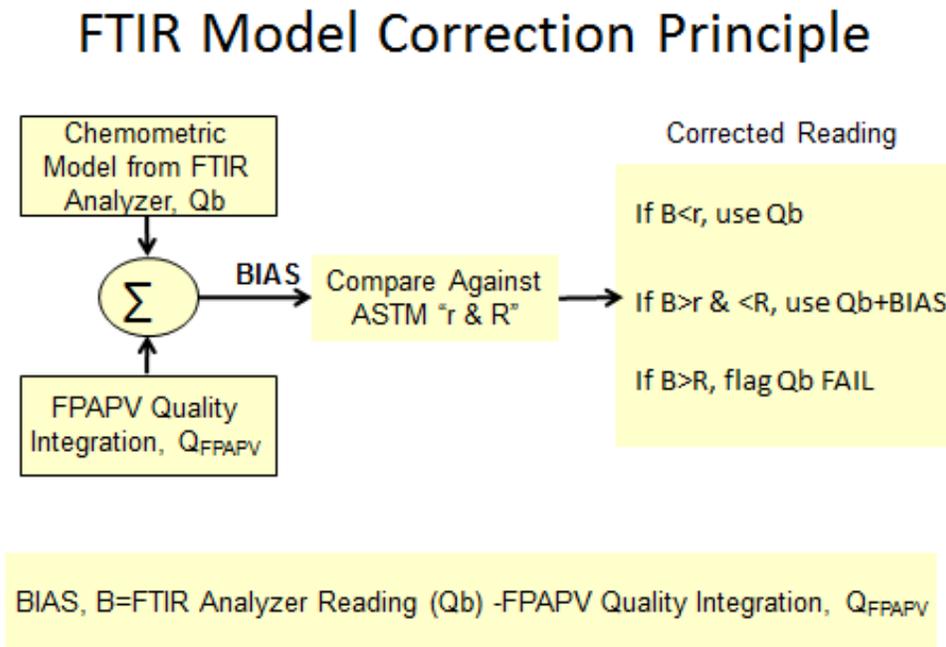
## 2. Summary of the “Robust” Scheme

The elements of the scheme are shown in Fig. 1, consisting of an inferential model used to predict process stream quality in place of a conventional on-line analyzer, e.g. octane knock engine, but corrected dynamically in real-time with Lab data .

The inferential model, in our case a spectroscopic chemometric model, requires inputs of process data such as FTIR transmission or absorption spectrum, Raman spectrum, or magnetic resonance, etc.

The model predicted parameter is periodically updated by comparing the predicted value(s) with Lab value(s). It is important to set limits to the applicability of the model to avoid gross errors, in our case, the model output is bounded by the ASTM precision parameter ( $r$  and  $R$ )

Fig. 1 Principle of spectroscopic method property prediction correction scheme



The implementation of the scheme comprises the following four steps:

**Step 1:** Develop a multivariate property prediction model using conventional commercial chemometric software. The inputs for model building are the monthly gasoline recipes derived from a refinery-LP annual business plan; the recipes are hand-blended in the Lab to establish recipe vs. spectrum correlation.

This model does not need to be of very high fidelity, since its predictions will be corrected in real-time by Lab data, and bound by ASTM  $r$  &  $R$  to avoid gross errors.

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**Step 2:** Use in-line blending data reconciliation algorithm whereby we synthesize the in-line blended gasoline properties from blend component refinery Lab LIMS computer stored property data multiplied by flow volumes measured by blender flowmeters for each component (similar to quality integration with FPAPV described in ASTM D6624), and summing the result. The result is a calculated value of the properties of the blended liquid at the in-line blend header based on blend component Lab property data and flow volumes measured by flowmeters. This is done at the same frequency as the spectroscopic measurement ( every 1 to 2 minutes)

**Step 3:** We then compare the Lab-based “synthetically” calculated properties of the blend liquid, (e.g. gasoline) in the blend header from Step 2 against the spectroscopic method model prediction in Step 1. This comparison is done at the same frequency as the spectroscopic measurement (every 1 to 2 minutes)

**Step 4:** We take the results from Step 3 and we add a correction to the spectroscopic chemometric prediction while insuring that we set limits to the applicability of the model (i.e. within ASTM “r and R”) to avoid gross errors, as follows:

- Case 1 - If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is less than the ASTM repeatability, r, the Step 1 prediction is valid and can be used for property control or certifying a blend.
- Case 2 - If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is greater than than the ASTM repeatability, r, but less than the ASTM Reproducibility of the parameter, then we correct the Step 1 prediction by adding the difference between Step 1 and Step 2, as long as the difference is less than the ASTM Reproducibility of the parameter.
- Case 3 - If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is greater than the ASTM Reproducibility of the parameter, R, then we cannot use the Step 1 prediction, which is invalid and cannot be used for blend property control or certifying a blend. This requires a “root-cause” analysis to determine the cause, e.g. an outlier due to an unusual blend component or unusual recipe.

## 2. Spectroscopic Method Blend Property Prediction Model Development

The spectroscopic chemometric prediction model building “how-to Bible” it the ASTM E1655 practice. Contrary to claims in literature, the challenge with it is its practical implementation to cover the “representative recipe space” for the fuel grade of interest, which is beyond the “ordinary mortal” in a refinery, commercial “for-hire” blending facility, or spectroscopic analyzer/device supplier.

Why is that? Because blend recipes, with all the good will and effort, are not consistent and predictable even for the same grade and season, depending on process unit sometimes lousy operation causing significant property variability, components on hand, occasional opportunistic cargos with poorly know properties, inventory and storage constraints forcing unscheduled blends, and poorly configured planning tools (both at refinery LP level and blend planning tools, like Multi and Single Blend Optimizers, nonlinear blending, Ethanol boost, etc.).

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To circumvent these headaches, we pursue a different approach: build an approximate (lousy?) model which is periodically corrected with Lab data, with the model output bounded by the ASTM r&R for each predicted parameter.

Development of a multivariate property prediction model uses well-recognized, high quality commercial chemometric software, as follows:

## 2.1 The inputs for model building

The inputs for model building are the monthly gasoline recipes derived from a refinery-LP annual business plan; the recipes are hand-blended in the Lab to establish recipe vs. spectrum correlation.

The recipes are per grade, but cover all the seasons (Summer, Transition, Winter). The example in Fig. 2 indicates potential for further simplification, since examination of recipes for the Winter months shows four almost identical recipes which we can reduce them to one, and the same considerations applies to Summer gasolines.

Fig. 2 Refinery LP Annual Business Plan Gasoline Monthly Average Recipes for CG87 for 2004

Example: Refinery LP Annual Business Plan: Gasoline Production (KBPD) for CG87 octane												
Component	Jan	Feb	March	April	May	June	July	August	Sept	Oct	Nov	Dec
Butane	9	8	7	0	0	0	0	0	0	7	8	9
Alkylate	7	7	3	7	4	3	5	5	5	8	6	6
Poly Gasoline	2	2	1	2	2	2	1	2	2	2	2	2
LCN	9	17	17	18	15	14	19	15	18	20	17	20
HCN	22	26	24	25	24	24	26	29	24	29	26	25
Reformate	12	12	15	20	21	25	26	34	29	16	26	19
Raffinate	11	5	11	7	7	10	13	10	10	8	15	7
C9Aromatics	18	16	21	20	18	22	27	11	20	18	20	17
MTBE	10	10	12	14	16	16	16	16	16	12	11	10
Total	100	103	111	113	107	115	133	121	123	119	131	115

If you contemplate blending RBOB's and CBOB's, you have two additional choices:

- 1) may wish to add 10 v% Ethanol to the "neat" hand blends to build also a model for direct Ethanol Gasoline "match" blends
- 2) regress the 10 v% Ethanol hand-blends to come up with "Ethanol Boost" prediction equations that can be pre-programmed in the spectroscopic analyzer measuring the neat blend, and then using them to calculate the resulting "boost" in octane, RVP, etc.

## 2.2 The Lab Hand Blends for Model Building

This step requires a Lab to hand blend the recipes derived from step 2.1

The most challenging part is blending Butane (LPG!) in the hand blend flask, which is a lost art...

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Once you have the hand blend, you do two things with the hand blend sample:

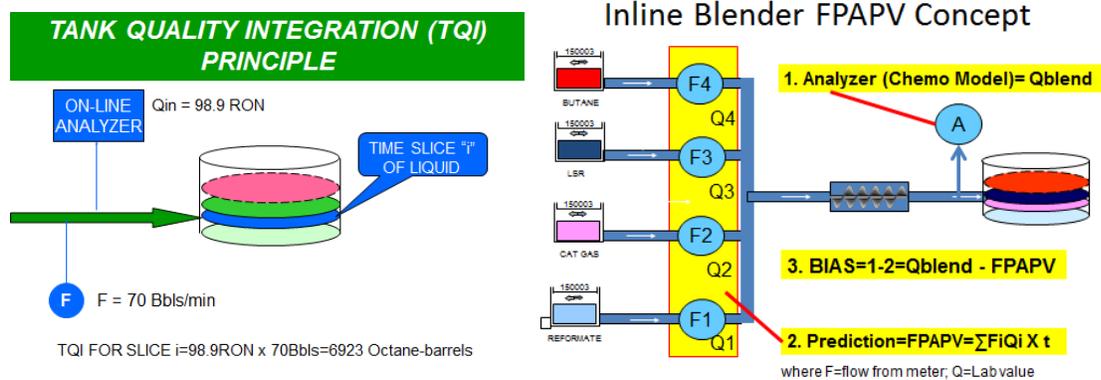
1. Conventional Lab analysis of the hand blend properties
2. Obtaining the spectra of the hand blend sample by using a Lab-installed spectroscopic analyzer

These are part of the input to the spectroscopic chemometric model-building software

### 3. Development of FPAPV Property (Quality-Barrels) Integration Algorithm

In this step, we use in-line blending data to calculate a prediction of the in-line blended gasoline properties from blend component refinery Lab LIMS-stored property data, Q, multiplied by flow volumes measured by flowmeters, F, for each component to get the property-barrels (similar to classical Tank Quality Integration (TQI), or alternatively ASTM D6624 quality integration method called FPAPV, Flow-Proportioned Average Property Value for a Collected Batch of Process Stream Material Using Stream Analyzer Data ), and summing the result.

Fig. 3 Scheme for doing the TQI integration calculations for FPAPV



The prediction could be improved somewhat by taking into account analyzer dead time and transport lag into account, using run of the mill dead-time compensators.

### 4. Putting It All Together

After doing steps 2) and 3) above, we have all the pieces we need to do the confidently the actual blend property prediction.

The display (Fig. 4) summarizes the actual spectroscopic analyzer performance, using the synthetic prediction of what is in the in-line blender header, the spectroscopic chemometric model prediction (based on the recipes), the comparison calculation, and corrections, if need be.

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The overall scheme relies on comparing the “synthetically” predicted properties of the gasoline in the blend header from Step 3 against the spectroscopic method model prediction in Step 2.

Fig. 4 Spectroscopic (NIR) Analyzer Performance Monitoring Display

NIR ANALYZER PERFORMANCE MONITORING							
		BLEND NUMBER	200402011	PRODUCT CODE	22094	DATE/TIME	2/15/04 9:04
QUALITY	ENG	ANALYZER	PREDICTION	BIAS	CORRECTED	ASTM "r"	PASS/FAIL
RON	ON	91.60	91.70	0.10	91.60	0.20	PASS
MON	ON	82.50	82.40	-0.10	82.50	0.20	PASS
RVP	psi	6.63	6.64	0.01	6.63	0.17	PASS
T10	degF	141.00	142.00	1.00	141.00	6.30	PASS
T50	degF	222.00	221.00	-1.00	222.00	6.30	PASS
T90	degF	327.00	330.00	3.00	327.00	6.30	PASS
FBP	degF	412.00	413.00	1.00	412.00	6.30	PASS
E200	VOL%	40.00	41.00	1.00	40.00	2.50	PASS
E300	VOL%	81.00	82.00	1.00	81.00	3.50	PASS
API GRAVITY	DEG API	57.20	57.30	0.10	0.02	0.20	PASS
AROMATICS	VOL %	27.40	27.70	0.30	27.40	1.30	PASS
BENZENE	VOL %	1.17	1.41	0.240	FAIL	0.030	FAIL
OLEFINS	VOL %	11.00	11.90	0.90	11.00	1.80	PASS
OXYGEN CONTENT	WT%	2.70	2.76	0.06	2.76	0.02	PASS?
		NO OF READINGS	153	NO OF VALID READ:	149	SERVICE FACTOR	0.97
		LAST PROTO CK	1/31/2004 11:29	PROTO OFFSET	PASS	LAST PROTO FILL	1/29/2004 10:07
F1-HELP		F2-PROTO		F3-SQC		F6-PREV	
						F9-PRINT	
						F10-MENU	

The real-time analyzer monitoring display labels are:

ANALYZER= raw readings from the actual NIR analyzer chemometric model; these might be analyzer lag and transport lag corrected

PREDICTION=predicted blend header properties synthesized using FPAPV “octane-barrels” volumetric calculations using flowmeter and blend component properties measured in the Lab

BIAS=difference between NIR analyzer readings and prediction calculations

CORRECTED=NIR analyzer readings corrected by biasing results depending on difference between ANALYZER and PREDICTION magnitude using ASTM “r or R” as described above

To summarize, there are 3 comparison cases:

1. If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is less than the ASTM repeatability, r, the Step 1 prediction is valid and can be used for property control or certifying a blend.

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2. If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is greater than the ASTM repeatability,  $r$ , but less than the ASTM Reproducibility of the parameter, then we correct the Step 1 prediction by adding the difference between Step 1 and Step 2, as long as the difference is less than the ASTM Reproducibility of the parameter.
3. If the difference between the value of the spectroscopic model prediction and “synthetic” volume average calculation is greater than the ASTM Reproducibility of the parameter,  $R$ , then we need to do a “root cause analysis” to determine the source of error. We cannot use the Step 1 prediction, which is invalid and cannot be used for blend property control or certifying a blend.

## 5. Conclusion

The method described above is robust because it depends primarily on the Lab-measured properties of the blend components and reliable flowmeters, and only secondarily on the spectroscopic chemometric model. It was successfully used in an in-line gasoline blending project since 1998. The system used a NIR analyzer measuring 10 properties once a minute. The results were compared against FPAPV using turbine meters and blend component Lab data; the refinery Lab verified the long term precision and stability of the spectroscopically determined parameter prediction.

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