

## Examination of Rapid Quantitative Analysis of Metal in Fuel Oil

### 1. Overview

In addition to using fluorescent X-ray analysis as a method of quality control of prescribed metal content (Al, Si, S, V, Ni) in fuel oil, we examined the possibility of using it as a rapid, convenient, quantitative method of analyzing iron content causing clogged line filters.

### 2. Description of Examination

- 2.1 Applied FP Method
- 2.2 Detection limits of target elements and verification of quantitative limits
- 2.3 Repeatability precision
- 2.4 Effect of coexistent elements

### 3. Examination Method

#### 3.1 Analysis Conditions

**Table 1 Analysis Conditions**

Primary X-ray Beam Diameter	10 mm
Tube Voltage	15 kV
Tube Current	81 $\mu$ A
Target	Rh
Atmosphere	Air
Measurement Time	1000 seconds
Sample Conditions	Collect and place in mylar container

#### 3.2 Quantitative Method

The Fundamental Parameter (FP) Method is used for quantitative calculation. Results are based on two types of FP calculations: (1) pure material standard and (2) intensity correction by one standard sample. Al and Si were removed as target elements because they could not be detected at the time of quantitative analysis. Quantitative analysis was done for Si, V, Ni, and Fe. Also,  $C_1H_n$  is designated as the remaining element, depending on the C/H ratio (=n) of each sample.

#### 4. Analysis Results

Table 2-1 and 2-2 display the quantitative results.

**Table 2-1 Quantitative Results #1**

S %	Calibration Sample					Evaluation Sample			
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	SPL 1	SPL 2	SPL 3	SPL 4
Standard Value	3.73	2.3	1.3	0.95	0.69	3.42	2.3	0.64	0.64
P FP* <sup>1</sup>	2.91	1.75	1.07	0.75	0.53	2.47	1.49	0.52	0.52
1STD FP* <sup>2</sup>	3.6	2.14	1.3	0.904	0.63	3.05	2.1	0.62	0.63
V ppm									
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	SPL 1	SPL 2	SPL 3	SPL 4
Standard Value	500	250	100	50	10	52	34	46	46
P FP	296	146	57	22	0	25	12	15	19
1STD FP	549	260	100	38	0	45	23	25	33
Ni ppm									
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	SPL 1	SPL 2	SPL 3	SPL 4
Standard Value	300	150	60	30	6	22	14	27	27
P FP	186	93	38	16	3	12	7	9	14
1STD FP	316	152	60	25	4	20	15	14	22
Fe ppm									
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	SPL 1	SPL 2	SPL 3	SPL 4
Standard Value	6	10	25	50	100	6	5	14	14
P FP	5	7	17	33	67	4	7	7	11
1STD FP	8	10	25	48	97	7	14	10	16

Note: \*1: FP quantitative method based on pure material standard

\*2: FP quantitative method based on intensity correction by one standard sample (CAL 3)

**Table 2-2 Quantitative Results #2**

SPL 1	5 Repetitions			
	S(%)	V(ppm)	Ni(ppm)	Fe(ppm)
Average	3.39	62	27	11
Maximum	3.45	64	31	17
Minimum	3.18	55	24	8
SD	0.1	4	3	4
CV (%)	3.4	6.4	10	33.3

SPL 2	5 Repetitions			
	S(%)	V(ppm)	Ni(ppm)	Fe(ppm)
Average	2.21	30	17	11
Maximum	2.22	32	19	15
Minimum	2.2	28	15	6
SD	0.0082	1	2	3
CV (%)	0.37	4.56	10.7	32.3

**5. Summary**

**5.1 Applying the FP Method**

Using a single point on a standard sample greatly improves accuracy. The sulfur (S) content can be analyzed at an error of about 10%.

**5.2 Evaluation Method of Quantitative Limits**

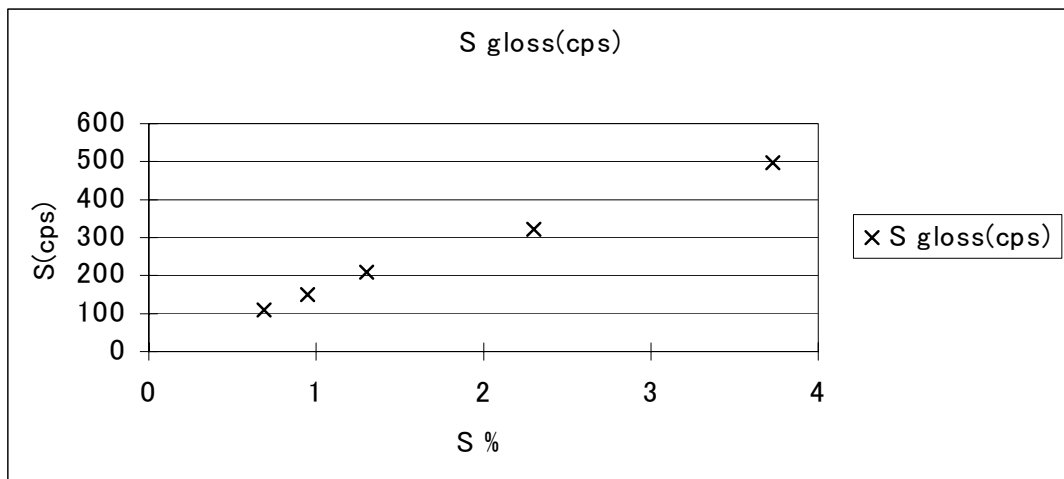
The calibration sample was used to evaluate quantitative limits. Graphs 1 to 4 show that the density of the matrix is high for calibration sample 1, therefore, the effect of absorption to V, Ni, and Fe is great. And since elements near the quantitative lower limit for calibration sample 5 are included, they were excluded from this evaluation.

We created calibration curves for each element with calibration samples 2, 3, and 4 and defined the background statistical variation of 10 sigma as the quantitative limit. Table 3 shows the quantitative limit of each element.

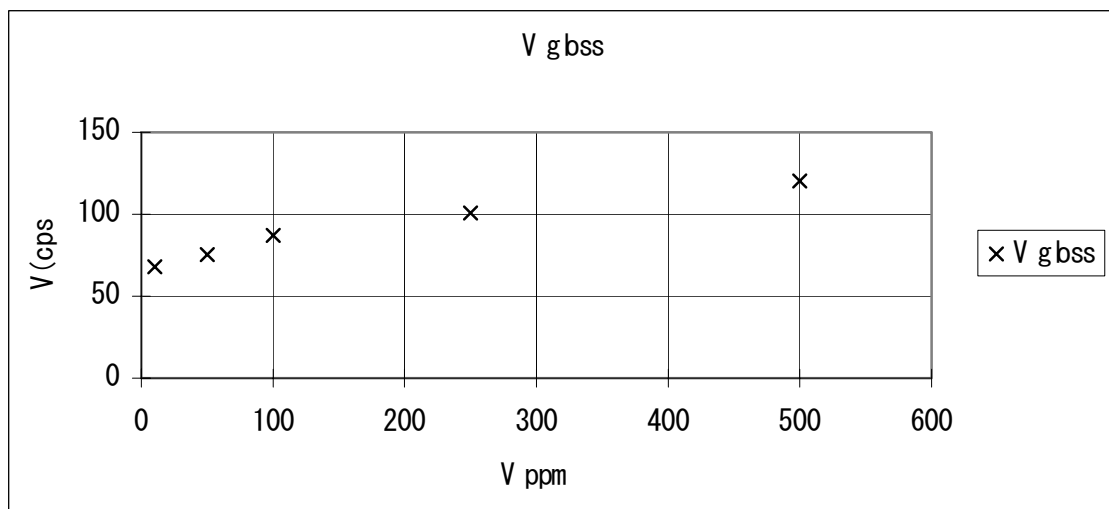
**Table 3 Quantitative Limits**

	S	V	Ni	Fe
Quantitative Limits	750ppm	15ppm	12ppm	10ppm

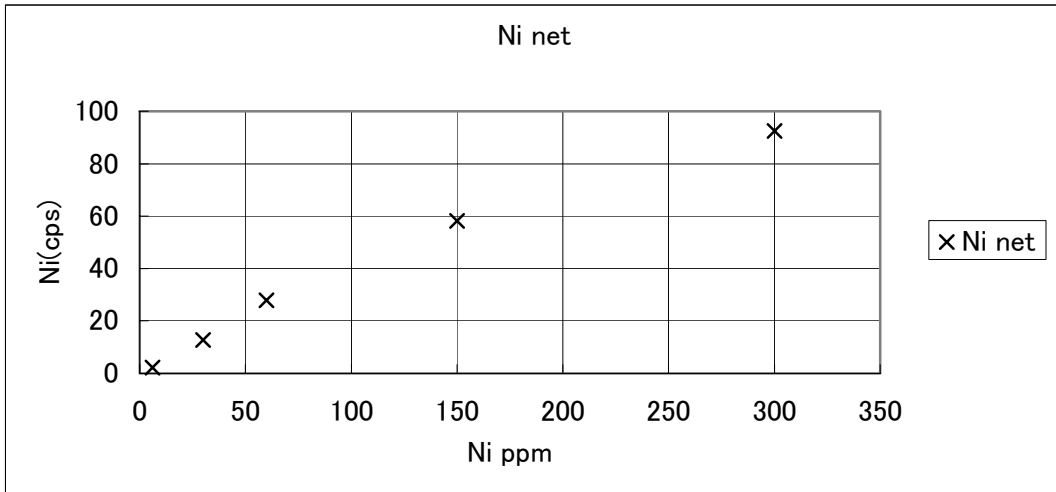
Graph 1 S content



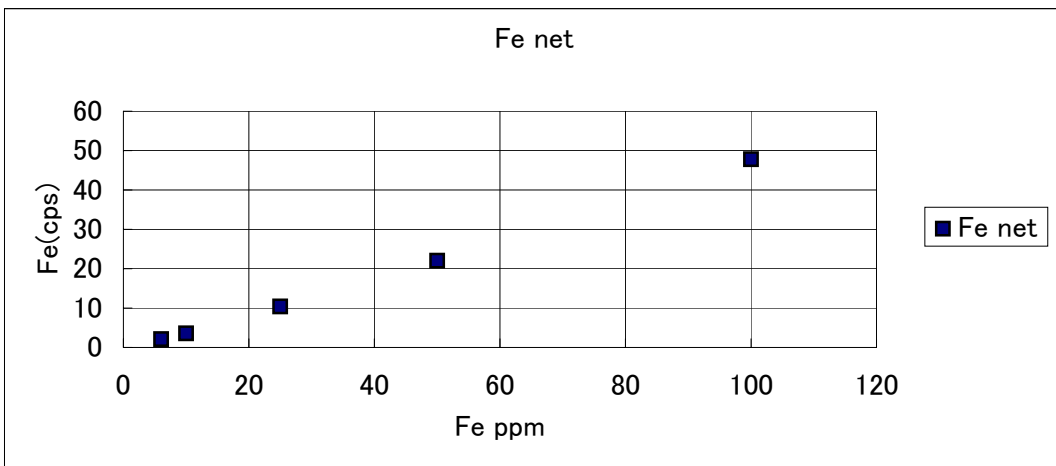
Graph 2 V content



Graph 3 Ni Content



Graph 4 Fe Content



### 5.3 Repeatability Precision

The results of five measurement repetitions of evaluation samples 1 and 2 are shown in Table 2.2. Measurements were done in separate mylar containers for each sample and each measurement. Results clearly show that the CV value is 10 to 30% near the quantitative limits of Ni and Fe.

### 5.4 Effect of Coexistent Elements

As predicted, the net intensity decreases for samples that have a high C/H. As for quantitative results, the sulfur content had no error because of changes in the C/H ratio. Results show that differences in the C/H ratio are reflected in trace components such as V, Ni, and Fe; however, it is hard to say the error predominates when considering the error from statistical variation.