

Application News

No. X252

Total Organic Carbon Analysis, X-ray Analysis

TC Measurement and Elemental Composition Analysis of Fly Ash – Quantitation by TOC and XRF –

The fly ash and incineration ash generated by incineration plants and thermal power plants contain metal oxides such as silica, alumina, calcium oxide and iron as main components, as well as a few percent of incompletely combusted carbon. Elemental and composition analysis of principal components and trace heavy metals is typically conducted by ICP, atomic absorption and X-ray fluorescence, and carbon content is measured using a total organic carbon analyzer (TOC).

X-ray fluorescence permits qualitative and quantitative analysis of all elements (qualitative analysis of $^{4}\text{Be} - ^{92}\text{U}$, quantitative analysis by FP method¹⁾) with simple pretreatment and operation, but detection and quantitation of carbon (^{12}C) is difficult when concentrations are just a few percent or less. This limitation can be resolved by using the total carbon (TC) measured value obtained with a TOC solid sample measurement system.

Here, we introduce examples of fly ash analysis using the TC measurement values as standard values in conjunction with the calibration curve method associated with X-ray fluorescence.

(1) Overview of TOC + XRF

The TC value obtained in TOC is applied to the X-ray fluorescence FP method.

■ TC Measurement Using TOC

Fig. 1 shows the Fly Ash A TC measurement results. Total carbon content in Fly Ash A (average value from 3 measurements): 5.940 %

■ Quantitation by FP Method of XRF

The quantitative analysis results using the X-ray fluorescence FP method are shown in Fig. 2.

(a) Detected element oxide + carbon 5.940 % (TC measurement value)

(b) Detected element oxide only (assuming carbon is undetected)

In the case of (b) which does not take into account the approximately 6 % carbon, the values for silica and alumina increase, by 3.5 % and 1.4 % (underlined values), respectively, indicating that method (a) is clearly more effective.

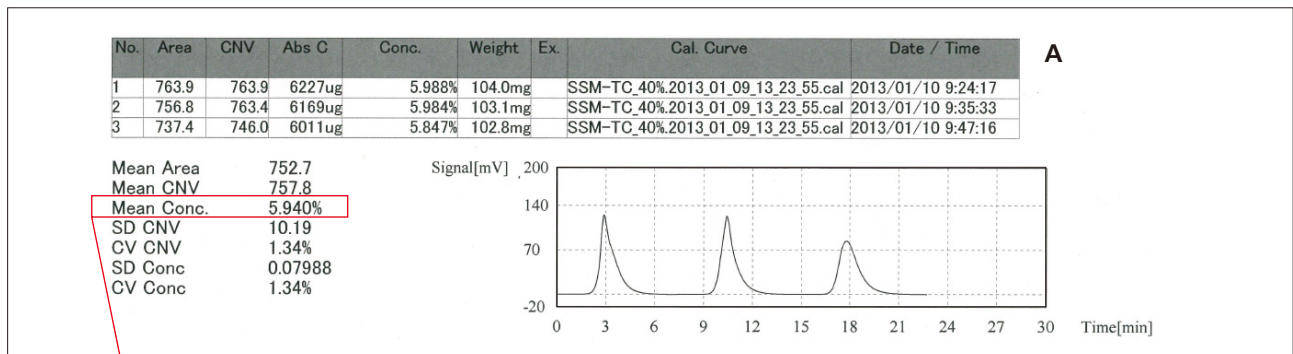


Fig. 1 TC Measurement Data for Fly Ash A

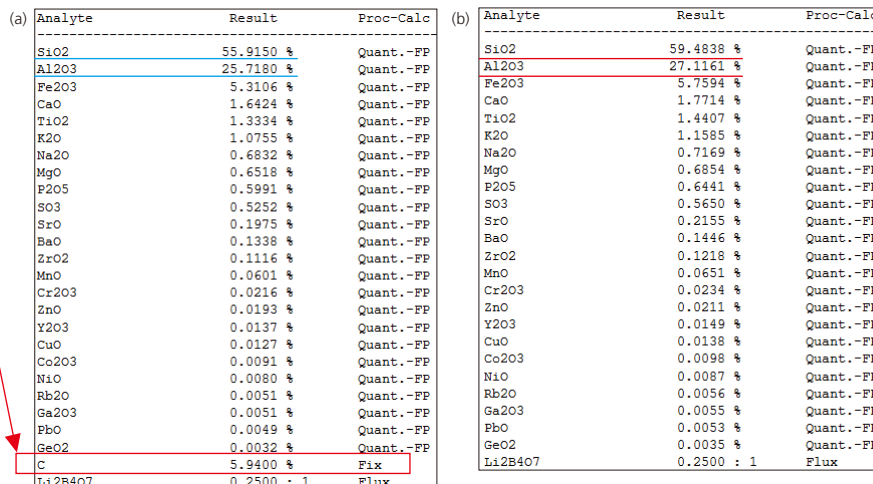


Fig. 2 Quantitation by FP Method of XRF (a) Oxides of Detected Elements + C (TC Value) (b) Oxides of Detected Elements

(2) Details of Measurement with TOC + XRF

For TC measurement, the solid sample measurement system²⁾ consisting of the TOC-L_{CSH} Total Organic Carbon Analyzer and the SSM-5000A Solid Sample Combustion Unit were used, and for elemental and composition analysis, the XRF-1800 Sequential X-ray Fluorescence Spectrometer was used.

■ Samples

Fly Ash A, B, C, D (4 samples in total)

■ TOC Measurement Data

Approximately 100 to 500 mg of fly ash powder was transferred as is to the SSM-5000A sample boat, then weighed using an electronic balance, and the sample boat together with the sample were set in the above system where TC measurement was then conducted. The measurement results are shown in Fig. 3 (Fly Ash A results are shown in Fig. 1), and summarized in Table 1. The TC values ranges from 0.3540 to 5.940 %, with about a 5 % width between samples. The coefficient of variation with 3 measurements was about 1 %, a small error due to uneven distribution and a level of error that can be ignored in the application of X-ray fluorescence analysis.

■ ⁵B – ⁹²U Qualitative Analysis by XRF

The fly ash qualitative analysis results for the 4 points of ⁵B – ⁹²U and their overlap are shown in Fig. 4 (next page). Although the detected elements among the 4 samples were about the same, there were differences in peak intensity, indicating different content quantities. Further, it is clear that there is a correlation between the carbon X-ray intensity and the TC measurement value (see (3) Calibration Curve by TOC+XRF, below).

■ Quantitation by FP Method of XRF

Assuming a fixed TC value obtained using TOC measurement, and other detected element substances as oxides, we conducted quantitative analysis (total 100 %) by the FP method. The quantitation results are shown in Table 2. By accurately obtaining the carbon concentration, qualitative and quantitative analysis of all elements, from those present at trace levels to principle components, can be conducted with good accuracy.

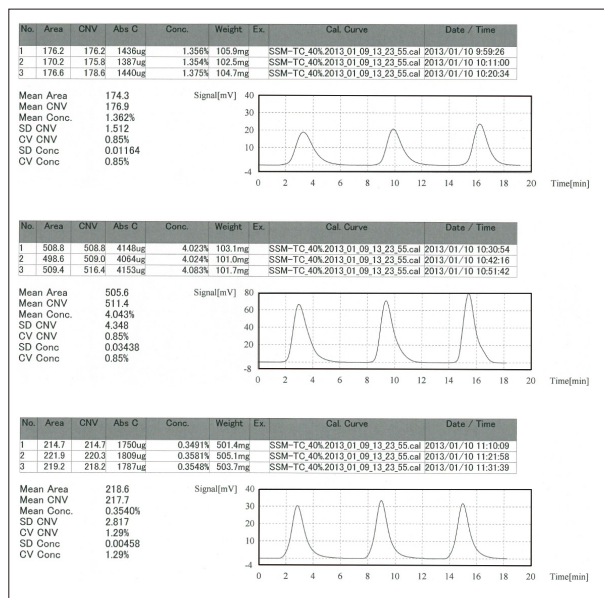


Fig. 3 TC Measurement Data of Fly Ash B, C, D

Table 1 TC Measurement Data for Fly Ash

Fly ash		A	B	C	D
Conc.	1 st measurement (%)	5.988	1.356	4.023	0.3491
	2 nd measurement	5.984	1.354	4.024	0.3581
	3 rd measurement	5.847	1.375	4.083	0.3548
	Average	5.940	1.362	4.043	0.3540
	Standard deviation (%)	0.07988	0.01164	0.03438	0.00458
	Coefficient of variation (%)	1.34	0.85	0.85	1.29
Weight	1 st measurement (mg)	104.0	105.9	103.1	501.4
	2 nd measurement	103.1	102.5	101.0	505.1
	3 rd measurement	102.8	104.7	101.7	503.7

Table 2 Quantitative Results by TOC and FP Method of XRF

[wt%]

Fly ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	K ₂ O	Na ₂ O	MgO	P ₂ O ₅
A	55.92	25.72	5.31	1.64	1.33	1.08	0.68	0.65	0.60
B	60.74	23.24	5.23	2.66	1.48	1.39	0.61	1.04	0.88
C	63.61	16.81	4.43	5.90	0.80	1.81	0.37	0.63	0.25
D	60.78	26.71	2.99	2.81	1.56	0.30	1.44	1.51	0.21

Fly ash	SO ₃	SrO	BaO	ZrO ₂	MnO	Cr ₂ O ₃	ZnO	Y ₂ O ₃	CuO
A	0.53	0.20	0.13	0.11	0.060	0.022	0.019	0.014	0.013
B	0.82	0.20	0.11	0.076	0.037	0.028	0.028	0.013	0.019
C	0.91	0.10	0.06	0.070	0.13	0.013	0.011	0.010	0.012
D	0.61	0.11	0.28	0.091	0.027	0.022	0.11	0.015	0.018

Fly ash	Co ₂ O ₃	NiO	Rb ₂ O	Ga ₂ O ₃	PbO	GeO ₂	C	Li ₂ B ₄ O ₇
A	0.009	0.008	0.005	0.005	0.005	0.003	5.940*	0.25**
B	0.014	0.017	0.009	0.009	0.008	0.004	1.362*	0.25**
C	0.009	0.010	0.008	0.005	0.007	0.003	4.043*	0.25**
D	0.020	0.019	0.005	0.012	0.011	0.005	0.354*	0.25**

* Fixed value from TC measurements

** Flux ratio: Ratio of sample forming additive substances (binders), etc. in a sample, assuming the sample as 1 (refer to sample preparation).

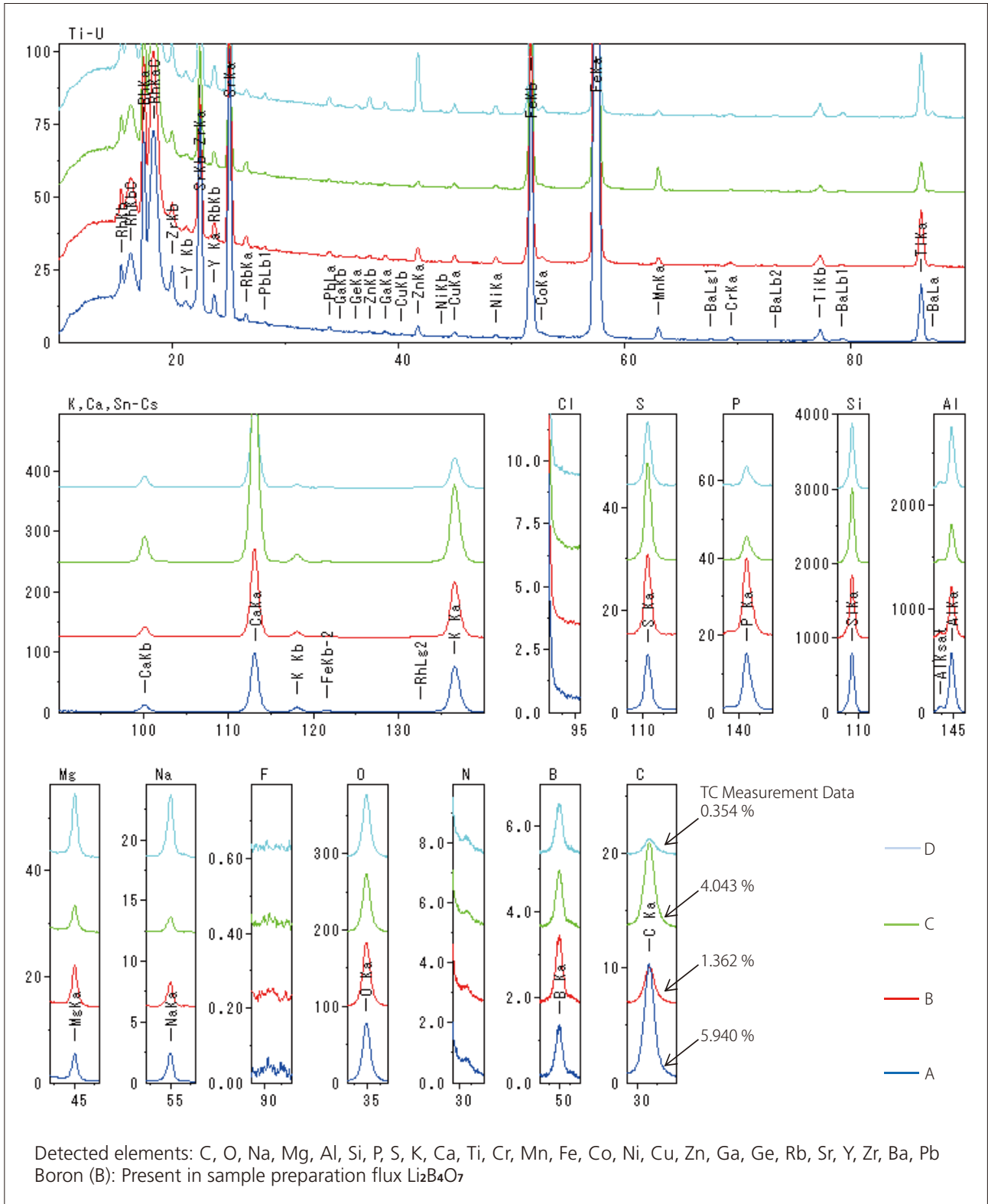


Fig. 4 ⁵⁵B – ⁹²U Qualitative Results for Fly Ash A, B, C, D by XRF, Overlapped Profiles

(3) Calibration Curve by TOC + XRF

Using the TC value obtained from TOC measurement as a standard value (horizontal axis), we evaluated the calibration curve with respect to the X-ray fluorescence $CK\alpha$ intensity (vertical axis). Also, for comparison, the difference is shown when loss on ignition is used as the standard value.

A total of 5 samples were used, consisting of the above-mentioned 4 fly ash samples, A, B, C, D, as well as the heat-treated A with zero concentration.

■ TC Value as Standard

Fig. 5 shows the carbon calibration curve generated when the TC measurement value (excerpted from Table 1) is used as the standard value. The good correlation at 0.15 % accuracy demonstrates that quantitative analysis of carbon at a few percent or less is possible using X-ray fluorescence.

Excerpt from Table 1

Fly ash	A	B	C	D
TC value	5.940	1.362	4.043	0.3540

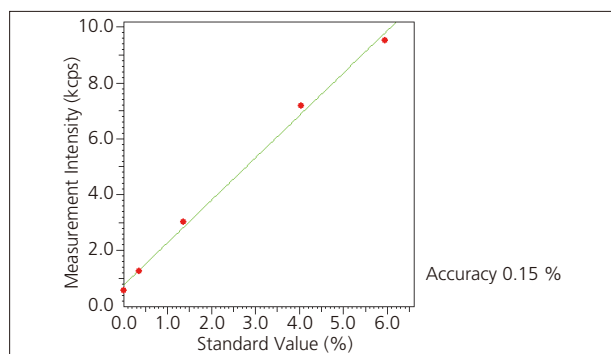


Fig. 5 Calibration Curve for C using TC as Standard

■ Loss on Ignition (LOI) as Standard

Up to now X-ray fluorescence could not be used for analysis of moisture, carbon and organic matter, or calculation has been conducted using Loss on Ignition (LOI).

Table 3 shows the LOI for fly ash at 4 points, and Fig. 6 shows the calibration curve for carbon using LOI as the standard. With 0.39 % accuracy, the value is more than twice that of the TC measurement value.

Table 3 Loss on Ignition for Fly Ash

Fly ash	A	B	C	D
Loss on ignition	6.40	2.20	4.20	1.20

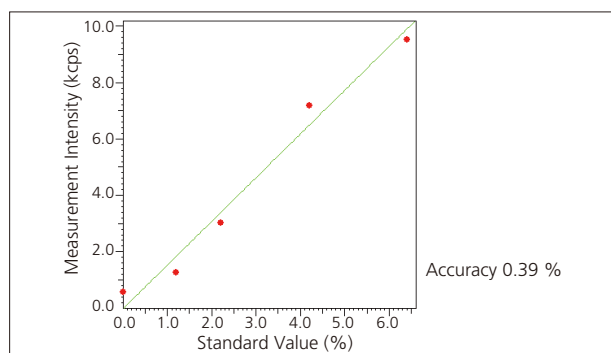


Fig. 6 Calibration Curve for C Using LOI as Standard

■ Consideration

Loss on ignition includes fly-off constituents as well as carbon and water content. However, in the case of fly ash, sulfur is the main constituent aside from carbon, because almost no water is present (Fig. 7). Therefore, the calibration curve generated from TC measurement for carbon alone will provide better accuracy than that using loss on ignition.

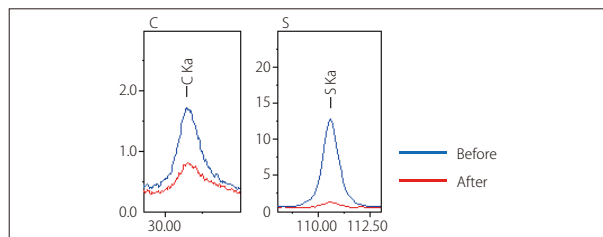


Fig. 7 Difference of XRF Intensity for C and S by LOI (Fly Ash D)

(4) Conclusion

The TOC Solid Sample Measurement System permits very easy and accurate measurement of total carbon content in fly ash. By applying those results to X-ray fluorescence quantitative analysis, accurate compositional analysis, including carbon, becomes possible.

In addition to fly ash and incineration ash, this method can similarly be used for soil, compost, and metal smelting slag, etc., and can be especially effective when there is no available standard sample. Applications of this TOC + X-ray fluorescence analysis method can be expected to include a wide range of products and raw materials.

Measurement Conditions < TOC >

Analyzer	: Shimadzu TOC-LC _{SH} Total Organic Carbon Analyzer + SSM-5000A Solid Sample Combustion Unit
Cell length	: Short cell
SSM carrier gas	: 500 mL/min, oxygen gas
SSM furnace temperature	: 900 °C
Measurement item	: TC
Calibration curve	: 40 % C glucose powder sample, 1-point calibration curve
Sample	: Fly ash; ≈100 – 500 mg

Measurement Conditions <X-Ray Fluorescence>

Instrument	: Shimadzu XRF-1800 Sequential X-ray Fluorescence Spectrometer
X-ray tube	: 4 kW, Rh target, Be thin window
Tube voltage	: 40 kV
Tube current	: 95 mA
Dispersive crystal	: LiF, Ge, PET, TAP, SX
Detector	: SC, FPC
Scan speed	: C: 8 deg/min B, N-U: 20 deg/min (qualitative analysis)
Integration time	: 40 sec (calibration curve)

Sample Preparation <X-Ray Fluorescence>

Briquet press	: MP-35
Pressure conditions	: 30 ton / 30 sec
Molding ring	: Vinyl chloride ring
Flux (forming additive)	: Lithium tetraborate Li ₂ B ₄ O ₇ reagent powder
Flux ratio	: 0.25 (sample 4 g, flux 1 g)
Mixing	: Mix manually for 30 min using an agate mortar/Mix mechanically for 10 min using an auto mixer

Loss On Incineration Conditions

Temperature	: 975 °C
Time	: 6 hours

- 1) Ochi Hiroto, Okashita Hideo: Shimadzu Review Vol. 45 (1-2), 51 (1988)
- 2) Shimadzu Application News No. 0035, 0040
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