



NEW YORK STATE DEPARTMENT OF TRANSPORTATION
MATERIALS BUREAU ALBANY, NY 12232-0861

TEST METHOD

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SUBJECT: Analysis of Oxides in Fly Ash by Atomic Absorption Spectroscopy

APPROVED:

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Supersedes: n/a
Dated:

1. SCOPE

1.1 This method covers the chemical analysis of Fly Ash by Atomic Absorption for the oxides as listed in Table 1.

Concentration Range, % Oxide	Fly Ash
0 to 7	Al ₂ O ₃
0 to 6	Fe ₂ O ₃
18 to 26	SiO ₂

Table 1

1.2 This method is based on the "Rapid Methods of Chemical Analysis of Hydraulic Cement" ASTM STP 985 and "Standard Test Methods of Chemical Analysis of Hydraulic Cement" ASTM C114-07 and was modified and developed by New York State Department of Transportation, Instrumental Inorganic Unit of the Chemistry Laboratory.

2. METHODS

2.1 The sample is prepared for fusion by layering into a pre-ignited purified graphite crucible: 0.5000 g of anhydrous LiBO₂, 0.5000 g sample and 0.5000 g of anhydrous LiBO₂. The crucible is placed in a 1000° C furnace for 20 minutes. The molten mass is poured into a nitric acid solution and dissolved. The solution is filtered to remove carbon particles and diluted to a fixed volume. A portion of the solution or suitable aliquot is aspirated into the flame of an atomic absorption spectrophotometer and the absorbance measured at the analytical line of the desired element.

3. INTERFERENCE AND LIMITATIONS

3.1 These procedures were developed primarily for the analysis of Fly Ash. Limitations are noted in the procedure for specific constituents.

4. REAGENTS

- 4.1 HNO₃ sp gr 1.42
- 4.2 Distilled Deionized water, H₂O (as per ASTM D1193-06)
- 4.3 Anhydrous Lithium Metaborate, LiBO₂, (Analytical Grade)
- 4.4 Calcium Chloride, CaCl₂ (Reagent Grade)

Analysis of Oxides in Fly Ash

5. APPARATUS AND MATERIALS

- 5.1 Atomic Absorption Spectrophotometer, with a self-contained digital readout, automatic zero, curve correction and a nitrous oxide burner head.
- 5.2 100 ml, 250 ml and 500 ml volumetric flasks with stoppers
- 5.3 250 ml Nalgene beakers
- 5.4 Suitable Pipettes
- 5.5 Graphite Crucibles, 8.4 ml capacity, high purity
- 5.6 Medium Textured Filter Paper
- 5.7 Muffle furnace-should be capable of continuous operations up to 1000° C
- 5.8 A source of clean moisture-free compressed air controlled by low-pressure regulators. An air filter with a removable cartridge should be installed in the line
- 5.9 Cylinders of AA grade acetylene and nitrous oxide with two-gage, two stage pressure reducing regulators
- 5.10 Hollow cathode lamps, of high spectral purity and high intensity
- 5.11 A vent to remove noxious fumes

6. PREPARATION OF STANDARDS

6.1 **Stock Standards** Dilutions are made from Stock solutions. The concentration of the Standard depends on the concentration of the oxide present in the sample, and should fall within the linear range for the element. All standards should be dated and replaced when necessary. (The addition of 0.2% CaCl_2 to the Fe standard may increase sensitivity; however it must also be added to the sample dilution for the Fe analyses.)

7. PREPARATION OF SAMPLES and BLANK

7.1 **Fly Ash 2000 ppm** The sample is prepared for fusion by weighing and layering into a high purity, pre-ignited graphite crucible: 0.5000 g of anhydrous LiBO_2 , 0.5000 g sample of blended cement and 0.5000 g of anhydrous LiBO_2 . The crucible is then placed in a 1000° C furnace for 20 minutes. Remove from the furnace with tongs and gently swirl the crucible to incorporate any particles remaining on the crucible walls and immediately pour the molten melt into a 250 ml polypropylene beaker containing 125 ml distilled water, 15 ml HNO_3 conc, and a magnetic stirring bar. The fusion melt bead shatters and will go into solution after about 1 hour of stirring. The solution is filtered to remove carbon particles and diluted to 250 ml.

7.2 **Fly Ash 500 ppm** For Al analysis pipet a 25 ml aliquot of the 2000 ppm fly ash sample into a 100 ml volumetric and bring to volume.

7.3 **Fly Ash 100 ppm** For Si analysis pipet a 5 ml aliquot of the 2000 ppm fly ash sample into a 100 ml volumetric and bring to volume

7.4 **Fly Ash 40 ppm** For Fe analysis pipet a 2 ml aliquot of the 2000 ppm fly ash sample solution into a 100 ml volumetric and bring to volume. (The addition of 0.2% CaCl_2 to both the standard and sample may increase sensitivity.)

7.5 **Blank** A blank should be made of deionized H_2O and contain all the reagents used in the sample preparation.

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8. PROCEDURE

8.1 Refer to the manufacturer's optimum standard conditions and parameters for your instrument. Aspirate the blank solution and set to zero. Calibrate the standard(s), being sure that the analyte absorbance falls within the linear range for that element. Aspirate the sample solution and adjust the concentration as needed to be sure that the analyte absorbance also falls within the linear range for that element. Instruments with a direct readout can be calibrated to read directly in any desired concentration (ppm, % etc).

8.2 To analyze for the oxides Al_2O_3 , Fe_2O_3 , and SiO_2 using the Atomic Absorption Spectrophotometer, the concentration of Standards and Samples listed in Table 2 works well for most Fly Ash.

Oxide	Standard Concentration	Sample Concentration
Al_2O_3	75 ppm Standard Stock	500 ppm
Fe_2O_3	5 ppm Standard Stock	40 ppm
SiO_2	20 ppm Standard Stock	100 ppm

Table 2**9. CALCULATIONS:**

$$\% \text{Al}_2\text{O}_3 = \frac{\text{Al ppm} \times 1.8895 \times 100}{500 \text{ ppm}}$$

$$\% \text{Fe}_2\text{O}_3 = \frac{\text{Fe ppm} \times 1.4297 \times 100}{40 \text{ ppm}}$$

$$\% \text{SiO}_2 = \frac{\text{Si ppm} \times 2.1393 \times 100}{100 \text{ ppm}}$$

10. PRECISION AND BIAS

10.1 Samples are tested with precision and accuracy in accordance with ASTM C114-07. Multi laboratory results are routinely conducted with the CCRL Proficiency Sample Program.

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11. Problems Encountered

11.1 SiO_2 has a tendency to cause a buildup of carbon on the burner slit due to the rich $\text{C}_2\text{H}_2/\text{N}_2\text{O}$ flame required for SiO_2 determination. It is necessary to thoroughly clean the burner slit before SiO_2 analysis and to complete the analysis within approximately 20 to 30 minutes operating time to avoid erratic results. SiO_2 analysis requires care in setting up optimum instrument parameters to obtain good precision and accuracy.

11.2 Silicon depresses the Fe_2O_3 signal, and may be reduced by an addition of 0.2% CaCl_2 .

11.3 Many interferences can be reduced or eliminated in a nitrous-acetylene flame, but sensitivity will be reduced and is not recommended for this iron determination.

11.4 Selecting the number and the concentrations of standards is very important. If the analyte concentration falls within the linear range, one calibration standard should be used and the curve will be a straight line. Generally, two calibration standards are optimum in cases of moderate (10% to 15%) curvature as with Al_2O_3 , and occasionally SiO_2 determinations. A third standard may be used for severe curvature, but it is not an advantage to use more standards than necessary.