



# Test method T1034

Chemical analysis of sodium in  
cementitious materials (By flame  
photometry)

NOVEMBER 2012



---

## Revision Summary

Ed/Rev Number	Clause Number	Description of Revision	Authorisation	Date
		New Method	K Porter	Nov 2007
	All	Revision by David Svolos. Method generally revised. Section 4 modified to allow for changes introduced by revised T1033	J Friedrich	Apr 2009
Ed 3/ Rev 0	All	Reformatted RMS template	J Friedrich	November 2012

Note that Roads and Maritime Services is hereafter referred to as 'RMS'.

The most recent revision to Test method T1034 (other than minor editorial changes) are indicated by a vertical line in the margin as shown here.

# Test method T1034

## Chemical analysis of sodium in cementitious materials (By flame photometry)

### 1. Scope

This test method sets out the procedure for the quantitative chemical analysis of sodium in cementitious materials using Flame Photometry.

### 2. General

- (a) The method is applicable to Portland cements and cement blends containing in excess of 0.2 ppm sodium. However, reporting is restricted to Na values  $\geq 0.01\%$
- (b) The test must be carried out in conjunction with T1033 and T1032 as samples are prepared and results provided by these tests
- (c) At least one of the sample analyses is to be performed in duplicate and the results compared to validate consistency of testing
- (d) OH&S requirements must be followed and must include handling of highly concentrated nitric and hydrochloric acids
- (e) The following materials are required for the test:
  - (i) Certified Reference Material (CRM) and/or a Reference Material with a known Na<sub>2</sub>O content
  - (ii) Nitric acid (70%, 1.42 g/ml)
  - (iii) Hydrochloric acid (32%, 1.16 g/ml)
- (f) The operation of the Jenway Flame Photometer must be in accordance with the "Jenway Model PFP7 Flame Photometer Operating and Service Manual". Ensure that the general, weekly, monthly and six monthly maintenance procedures follows the manual
- (g) Calibration of the Flame Photometer is required each day it is used
- (h) Readings are to be recorded in the Flame Photometer Worksheet
- (i) The following Documents provide background for the test:
  - (i) AS2134.1 Recommended practice for chemical analysis by atomic absorption spectrometry - Flame atomic absorption spectrometry
  - (ii) AS2850 Chemical analysis - Interlaboratory test programs – For determining precision of analytical method(s) – Guide to the planning and conduct
  - (iii) AS2929 Test methods – Guide to the format, style and content
  - (iv) Application Note Ref. 9 – The determination of sodium and potassium in cement. – Barlow Scientific

### 3. Apparatus

- (a) Jenway Model PFP7 Flame Photometer

*NOTE: The Jenway Flame Photometer operates using an oxygen/natural gas flame. Use only in a large space with adequate ventilation.*

- (b) A hotplate with the capacity to heat the sample digestion solution to boiling point, equipped with a magnetic stirrer
- (c) Fume cabinet
- (d) A balance accurate and readable to  $\pm 0.0001$  g
- (e) Air supply that is dry, clean and pulse free. The regulator set to supply air at a pressure between 100 kPa and 200 kPa

- (f) Natural gas fuel. However, if propane or butane gas is used refer to the “Jenway Operating and Service Manual” for appropriate fuel adjustment settings
- (g) Glassware that includes beakers, volumetric flasks, pipettes, watchglass and measuring cylinders. All glassware must be acid washed according to Step 4.1(c)

NOTE: *Acid washing removes traces of sodium that would affect the readings*

- (h) Water bottle
- (i) Calibrated stop watch

## 4. Preparation

### 4.1 General Requirements

- (a) Unless otherwise specified, all reagents shall be of analytical reagent grade
- (b) Water used shall be distilled water

**The acids used in this test are highly concentrated and appropriate OH&S requirements must be implemented.**

- (c) Acid wash with nitric acid solution all glassware used in the test procedures to prevent sodium contamination of solutions from the glassware:

- (i) In the fume cupboard, prepare the nitric acid solution by cautiously adding 1 part nitric acid (70%, 1.42 g/ml) to 2 parts distilled water

NOTE: *Addition of acid to water is an exothermic process that causes large amounts of heat to be evolved. A slow rate of addition will ensure that the final solution is not hot. Handling of hot acids is hazardous.*

*The nitric acid wash solution is extremely hazardous in contact with the skin or eyes. Appropriate safety wear must be worn at all times when working with this acid solution. This solution should not be removed from the fume cabinets.*

- (ii) Thoroughly wash all the glassware using the prepared nitric acid solution
- (iii) Thoroughly rinse glassware with distilled water

### 4.2 Standard Reference Solution

- (a) Prepare a fused specimen as described in T1033 where the “sample” is a Certified Reference Material (CRM) or a Reference Material. Record the mass of “sample” plus flux used ( $M_3$ ) to  $\pm 0.0001$  g
- (b) Determine the mass of the specimen on the analytical balance ( $M$ ) and record its mass to  $\pm 0.0001$  g
- (c) Prepare the diluted Hydrochloric Acid solution (1:1) by cautiously adding 1 part hydrochloric acid (32%, 1.16 g/ml) to 1 part distilled water

NOTE: *Hydrochloric acid is extremely hazardous both as a vapour and solution. Appropriate Safety wear must be worn at all times when using this acid.*

- (d) Place the weighed specimen in an acid washed beaker. Add 80 mL of 1:1 Hydrochloric Acid solution to the beaker. Add approximately 50mL of distilled water
- (e) Place the beaker on the hotplate in a fume cabinet, cover the beaker and set the speed of the stirrer to a rate that prevents loss of material
- (f) Heat the beaker and contents at a temperature suitable for dissolution until the sample is dissolved. *Care should be taken not to excessively heat the beaker causing vigorous boiling and splashing of contents.*

NOTE: *Dissolution will take approximately 20 minutes.*

- (g) After sample dissolution, remove beaker from the heat and add a further 50 mL of distilled water to the solution
- (h) Allow the solution to cool to room temperature
- (i) Quantitatively transfer the solution from the beaker to a 500 mL volumetric flask. (Filter the solution with fine grade filter paper if any insoluble residue is visible)

- (j) Rinse the stirrer bar, crucible and beaker thoroughly with distilled water and transfer the washings to the volumetric flask. Make up to the volume mark with distilled water (i.e. 500 mL)

NOTE: *Ensure that the quantity of washings does not exceed about 100 mL*

- (k) Store the Standard Reference Solution in a plastic container in a cool and dry location

NOTE: *The Standard Reference should be used within 6 months.*

- (l) Label the flask or plastic container “SR” (Standard Reference) together with the following information:

- (i) Name of Reference Material
- (ii) Total fusion mass (g)
- (iii) Date prepared

### 4.3 Blank and Quality Control Standard Solutions

- (a) Prepare a Blank Standard solution according to Steps 4.2(a) to 4.2(j) using the same quantity of flux but without any “sample”. The mass of flux must be  $M_f \pm 0.0001$  g

NOTE: *If the flux is difficult to dissolve, add a further 10 mL of 1:1 HCl*

- (b) Prepare a Quality Control Standard solution according to Steps 4.2(a) to 4.2(j) where the “sample” is a different Certified Reference Material (CRM) or Reference Material from that previously used in the calibration. Record the mass of reference material plus flux used ( $M_s$ ) to  $\pm 0.0001$  g

- (c) Label the flask “BS” (i.e. Blank Standard) and “QC” (i.e. Quality Control Standard) as appropriate together with the following information:

- (i) Name of material
- (ii) Total fusion mass (g)
- (iii) Date prepared

### 4.4 Working Standard Solutions

- (a) Prepare four (4) Working Standard solutions with 20x, 10x, 5x and 2x dilution factor ( $DF$ )

- (i) Pipette 5 mL, 10 mL, 20 mL, and 50 mL of the Standard Reference solution into separate 100 mL volumetric flasks

- (ii) Add 2 mL of 1:1 HCl solution to each working standard flask, to readjust the solution acidity after dilution

- (iii) Make up to the mark with distilled water. Label the Standard solutions as “WS” (Working Standard) with the dilution factor and date prepared

- (b) Calculate the sodium content for the four (4) Working Standard solutions using Calculation 6.2(a)

### 4.5 Sample Bead

- (a) Prepare a fused specimen as described in T1033

- (b) Analyse the specimen according to T1032

- (c) Determine the mass of the bead on the analytical balance ( $M$ ) and record its mass to  $\pm 0.0001$  g

- (d) Place the bead and a magnetic stirrer bar into a 150 mL beaker. Add 80 mL of 1:1 Hydrochloric Acid solution to the beaker. Add approximately 50 mL of distilled water

- (e) Place the beaker on the hotplate in a fume cabinet, cover the beaker and set the speed of the stirrer to a rate that prevents loss of material

- (f) Heat the beaker and contents at a temperature suitable for dissolution until the sample is dissolved. *Care should be taken not to excessively heat the beaker causing vigorous boiling and splashing of contents.*

NOTE: *The estimated time for total dissolution of the bead is 20 minutes.*

- (g) After sample dissolution, add approximately 50 mL of distilled water to the solution

- (h) Allow the sample solution to cool to room temperature

- (i) Quantitatively transfer the solution from the beaker to a 500 mL volumetric flask. (Filter the solution with fine grade filter paper if any insoluble residue is visible)
- (j) Rinse the stirrer bar and beaker thoroughly with distilled water and transfer the washings to the volumetric flask. Make up to the volume mark with distilled water (i.e. 500 mL)

*NOTE: Ensure that the quantity of washings does not exceed about 100 mL.*

- (k) Where storage of up to six months is required, transfer the sample solution to a sealable plastic container
- (l) Label the flask or plastic container with the following information:
  - (i) Sample number
  - (ii) Total bead weight (g)
  - (iii) Date prepared

## 5. Procedure

### 5.1 Transfer of solutions

- (a) Transfer the following solutions for calibration and analysis into 50-100 mL beakers ready to be aspirated into the flame:
  - (i) Blank Standard solution (BS)
  - (ii) Working Standard solutions (WS)
  - (iii) Standard Reference solution
  - (iv) Quality Control Standard solution (QC)
  - (v) Sample solutions

### 5.2 Ignition of the Flame Photometer

- (a) Before igniting the Flame Photometer, ensure the following:
  - (i) The sample uptake tubing is immersed in a distilled water solution
  - (ii) A waste receptacle is placed under the waste tubing
  - (iii) The inner tube of the waste trap and waste drainage tubing are filled with distilled water and free of air bubbles
  - (iv) All gas tubing is fastened tightly to avoid gas leaks
- (b) Turn on power to the Flame Photometer at the wall socket
- (c) When using natural gas as the fuel source, set the FUEL ADJUST knob to the fully open position (turn anti-clockwise). If propane or butane gas is to be used, refer to the "Jenway Operating and Service Manual" for the appropriate fuel adjustment settings

*NOTE: Avoid contact with the exhaust chimney as it becomes very hot when operating.*

- (d) Set Coarse and Fine Adjustment knobs to their lowest value (i.e. turned fully anticlockwise ↺)
- (e) Set the FILTER SELECT KNOB to 'Sodium'
- (f) Open the air tap on the gas cylinder
- (g) Open the fuel tap from the source
- (h) Turn on the power switch on the flame photometer
- (i) Depress the ignition switch and hold the ignition switch down for up to 20 seconds until the FLM indicator lights up. The FLM indicates a steady, stable flame.

*NOTE: The flame can be viewed from the window on the front of the chimney.*

### 5.3 Calibration of the Flame Photometer

- (a) Allow the Flame Photometer 15 minutes to warm-up and ensure that distilled water is being aspirated at all times
- (b) Check the sample uptake rate is between 2-6 mL/min. If not, consult the troubleshooting section of “Jenway Model PFP7 Flame Photometer Operating and Service Manual”
- (c) Aspirate the Blank Standard. After 20 seconds stabilisation time, adjust the ‘BLANK’ control knob to read zero. Set the position of the Decimal Point using the ‘DP’ Control knob
- (d) Aspirate the standard solution with the highest sodium concentration (i.e. either “SR” or “WS 2x”) and optimise flame conditions by adjusting the fuel flow using the COARSE and FINE control knob as follows:
  - (i) First, adjust the COARSE control knob, to set significant figures
  - (ii) Second, use the FINE control knob to adjust the reading as required
- (e) Aspirate distilled water into the flame until a stable reading is achieved to indicate that all traces of sodium have been removed
- (f) Aspirate the following solution in turn, allow 20 seconds for readings to stabilise and then record 3 Flame Photometer readings at 5 second intervals for each solution:
  - (i) The Blank Standard solution (BS)  
*NOTE: The Blank reading should be about  $0 \pm 0.01$ .*
  - (ii) Each Working Standards solution (WS) in order of increasing sodium concentration
  - (iii) The Standard Reference solution
- (g) Aspirate distilled water into the flame until a stable reading is achieved to indicate that all traces of sodium have been removed

### 5.4 Sample Analysis by Flame Photometer

- (a) Aspirate the Blank Standard solution (BS), allow 20 seconds for readings to stabilise and then record 3 Flame Photometer readings at 5 second intervals  
*NOTE: Ensure that the BS has not been contaminated.*
- (b) Aspirate distilled water into the flame until a stable reading is achieved to indicate that all traces of sodium have been removed
- (c) Aspirate the sample solution, allow 20 seconds for readings to stabilise and then record 3 Flame Photometer readings taken at 5 second intervals
- (d) Where the average reading for the sample indicates a higher sodium concentration than the calibration range, bring the reading into the calibrated range by diluting the sample appropriately
- (e) For each remaining sample solution, repeat Steps (b) to (d)
- (f) Perform one of the sample analyses in duplicate and repeat Steps (b) to (d)
- (g) On completion of sample analyses perform a Quality Control check. Aspirate the Quality Control Standard solution (QC), allow 20 seconds for readings to stabilise and then record 3 Flame Photometer readings at 5 second intervals

### 5.5 Instrument shut down

- (a) Before shutting down the instrument, check the validation requirements are met in Step 6.5
- (b) When all readings are complete, aspirate distilled water through the instrument for at least 10 minutes before shutdown, in order to maintain cleanliness of the nebuliser, mixing chamber and burner
- (c) Turn off the instrument using its power switch and close the fuel and air supply taps at the source
- (d) Switch off the power at the power source

## 6. Calculations

### 6.1 Concentration of Sodium in a Standard solution

- (a) Calculate the mass of Reference Material in the fusion ( $M_f$ ):

$$M_f = \frac{M_3}{5}$$

Where:

$$\begin{aligned} M_f &= \text{Mass of Reference Material in preparation (g)} \\ M_3 &= \text{Mass of Reference Material + flux used in calibration in preparation (g – obtained from T1033)} \end{aligned}$$

- (b) Calculate the concentration ( $C$ ) of the Standard solution:

$$C = \left( \frac{M_1}{V_1} \right) \times 10^6$$

Where:

$$\begin{aligned} C &= \text{Concentration of Standard Solution (mg/L)} \\ M_1 &= \text{Mass of Reference Material in preparation (g)} \\ V_1 &= \text{Volume of Standard Solution (mL)} \end{aligned}$$

- (c) Calculate the LOI Factor ( $L$ ) for the Reference Material:

$$L = 1 + \left( \frac{LOI}{100} \right)$$

Where:

$$\begin{aligned} L &= \text{Factor for the Standard solution} \\ LOI &= \text{Loss on Ignition of Reference material (% from T1033)} \end{aligned}$$

- (d) Calculate the Corrected  $\text{Na}_2\text{O}\%$  ( $S_{corr}$ ) for the Reference Material:

$$S_{corr} = S \times L$$

Where:

$$\begin{aligned} S_{corr} &= \text{Corrected Na}_2\text{O} (\%) \\ S &= \text{Known Na}_2\text{O} \text{ content of the Standard solution} (\%) \\ L &= \text{LOI Factor for the Reference material} \end{aligned}$$

## 6.2 Sodium content of Working Standard solutions

- (a) For each Working Standard solution, calculate the content of sodium in ppm ( $S_{ppm}$ ) by converting  $\text{Na}_2\text{O}$  % to Na:

$$S_{ppm} = \frac{0.7419 \times C \times \left( \frac{S_{corr}}{100} \right)}{DF}$$

Where:

- $S_{ppm}$  = Na content for the Working Standard (ppm)  
 $C$  = Concentration of Reference Standard solution (mg/L)  
 $S_{corr}$  = Corrected  $\text{Na}_2\text{O}$  (%)  
 $DF$  = Dilution Factor of the Working Standard

## 6.3 Calibration of sodium content using the Flame Photometer

- (a) Evaluate the correlation between the average Flame Photometer Reading ( $FPR$ ) and sodium content ( $S_{ppm}$ ) for the Blank, each Working Standard solution and Standard Reference if used. Derive the correlation coefficient  $R^2$

*NOTE: Generally six standards shall be used for the calibration graph, but no fewer than four standard calibration solutions are required.*

$$FPR = m \times S_{ppm} + b$$

Where:

- $FPR$  = The Flame Photometer reading  
 $S_{ppm}$  = Na content (ppm)  
 $m$  = Gradient of the linear equation  
 $b$  = The intercept on the 'x-axis'

- (b) The calibration range of the calibration equation is limited to  $FPR$  that lie between the lowest and highest  $FPR$  used to derive the equation

## 6.4 Sodium Content of the Sample

- (a) Calculate the mass of sample in bead ( $M_S$ ):

$$M_S = \left( \frac{M_4}{5} \right)$$

Where:

- $M_S$  = Mass of Sample in Bead (g)  
 $M_4$  = Mass of bead (g)

- (b) Calculate the Concentration of Sample Solution ( $C_S$ ):

$$C_S = \left( \frac{M_S}{V_S} \right) \times 10^6$$

Where:

- $C_S$  = Concentration of Standard Solution (mg/L)  
 $M_S$  = Mass of Sample in Bead (g)  
 $V_S$  = Volume of Sample Solution (mL)

- (c) Calculate the Sample LOI Factor:

$$L_S = 1 + \left( \frac{LOI_S}{100} \right)$$

Where:

$$\begin{aligned} L_S &= \text{LOI Factor for the sample} \\ LOI_S &= \text{Loss on Ignition of the sample (\%from T1033)} \end{aligned}$$

- (d) Calculate Na (ppm) of the sample (
- $S_{ppm}$
- ) using the calibration equation (refer to Calculation 6.3):

$$S_{ppm} = \frac{(FPR - b)}{m}$$

Where:

$$\begin{aligned} S_{ppm} &= \text{Na of the sample (ppm)} \\ m &= \text{Gradient of the equation} \\ FPR &= \text{Flame Photometer Reading} \\ b &= \text{The intercept on the 'x-axis'} \end{aligned}$$

- (e) Calculate the quantity of Na
- <sub>2</sub>
- O (%) in each Sample (
- $S_S$
- ):

$$S_S = \frac{\left( \frac{S_{ppm} \times DF_S}{0.7419 \times C_S} \right) \times 100}{L_S}$$

Where:

$$\begin{aligned} S_S &= \text{The content of Na}_2\text{O in the sample (\%)} \\ S_{ppm} &= \text{Na content of the sample (ppm)} \\ DF_S &= \text{Dilution Factor of the sample} \\ C_S &= \text{Concentration of the sample (mg/L)} \\ L_S &= \text{Factor for the sample} \end{aligned}$$

## 6.5 Precision Validation

- (a) If any of the following criteria is not met, repeat the whole Calibration Step 5.3:
- The Quality Control Standard solution (QC) reading is within 0.05% of the known sodium content
  - The regression coefficient for the calibration equation  $R^2 \geq 0.98$  (refer to 6.3(a))
- (b) If any of the following criteria is not met, discard the result and obtain a new set of 3 FPR readings:
- The average Relative Standard Deviation (RSD) of each set of three Flame Photometer readings is  $\leq 5\%$

NOTE: The RSD is also known as the Coefficient of Variation.

$$RSD = \left( \frac{s}{\bar{x}} \right) \times 100$$

Where:

$RSD$  = Relative Standard Deviation (%).

$s$  = Standard Deviation of 3 sample readings.

$\bar{x}$  = Average of the 3 sample readings.

(ii) For corresponding duplicate testing, the average results of each set of analyses ( $\bar{x}$  and  $\bar{y}$ )

are such that  $\frac{|\bar{x} - \bar{y}|}{\left( \frac{\bar{x} + \bar{y}}{2} \right)} \times 100 \leq 10\%$ .

## 7. Reporting

Include the following results in the report:

(a) Report the sample and percent by mass Sodium Oxide (SS) to the nearest 0.01%

*NOTE: The results of the analysed samples will be in association with T1032.*

(b) Reference to this test method