



*Technologies*

# A guide to **Flame Photometer** Analysis

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## 1. Introduction

The estimation of the alkali metals by flame photometry is by far its most important application in routine chemical analysis.

For this widespread requirement, low temperature flame photometry provides the most reliable and convenient procedure available.

This technique has considerable appeal; in the clinical chemistry field it provides a rapid and reliable means of estimating Sodium, Potassium and Lithium in body fluids. The methodologies of such analyses are well known and indeed well established and shall therefore not be discussed in this guide.

However, the estimation of the alkali and alkaline earth metals is commonly required in a simple matrix, which does not lend itself to simple and direct analysis involving only a dilution step, e.g. Sodium in fuel oil.

This guide therefore aims to guide the user towards making successful determinations in a wide variety of sample media by providing in detail a large selection of procedures using flame photometry from which other methodologies may be appended with relative ease.

## 2. Brief History

As a direct result of the work done by Kirchoff and Bunsen in the early 1860's, the possibility of using the characteristic radiation emitted by atoms excited in flames for quantitative analysis was realised.

Soon after, an instrument was developed for the quantitative analysis of Sodium in plant ash using a Bunsen flame

The major problems experienced over the next 60 years were that of finding a reproducible method of introducing a sample into a flame and to then find a convenient technique to measure the emission of intensity.

Lundegardh largely overcame these difficulties in the 1920's whose apparatus included a nebuliser that enabled the sample to be presented to the air/acetylene flame in aerosol form. The emission was dispersed by a quartz prism spectrograph and recorded photographically. Precision was typically 5 – 10%

Greater convenience resulted from the introduction of simple coloured filters for wavelength selection, together with photocell/galvanometer combinations for measuring intensities directly. As a result simple and inexpensive instruments of this type using air/coal gas or air/acetylene flames became widely available from the late 1940's for the determination of Sodium, Potassium, Lithium and Calcium.

Work on many other elements then became possible with the use of grating spectrometers equipped with photo multiplier detectors through to the development of atomic absorption in the late 1960's, which restricted the use of flame emission.

However, there is a widespread requirement for the estimation of the alkali metals and for this purpose low temperature flame photometry provides the most reliable and convenient procedure available.

### 3. Principles of Flame Photometry

The basis of low temperature flame photometry is the same as that of the simple quantitative analytical flame test. This exploits the fact that compounds of the alkali and alkaline earth metals are thermally dissociated into atoms at the temperature of a Bunsen burner flame and that some of the atoms produced are further excited to a higher energy level. When these 'excited' atoms return to the ground state, they emit radiation, which for the elements of these two groups lies mainly in the visible region of the electromagnetic spectrum.

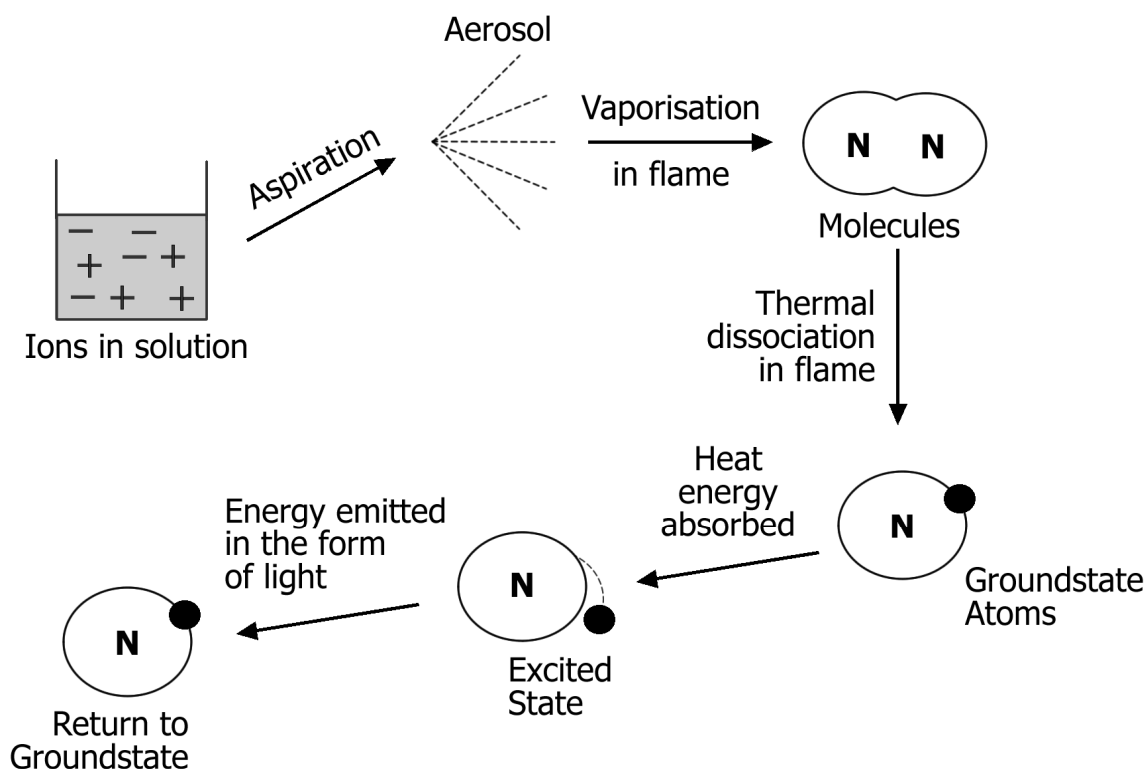


Fig. 1. The process involved in flame photometry.

The wavelength of the light emitted from the flame is characteristic of the particular element.

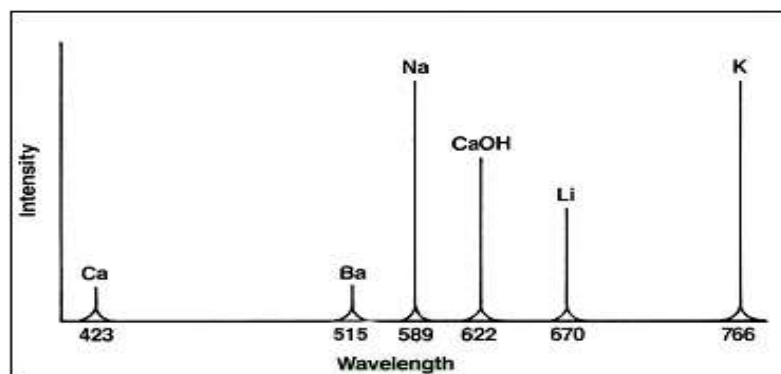


Fig. 2. Intensities of emissions of the elements at equal concentrations and their wavelengths.

The intensity of this light is, in most cases, proportional to the absolute quantity of the species present in the flame at any moment. The number of atoms returning to the ground state is proportional to the number of atoms excited, i.e. the concentration of the sample.

Note: This relationship applies only at low concentrations

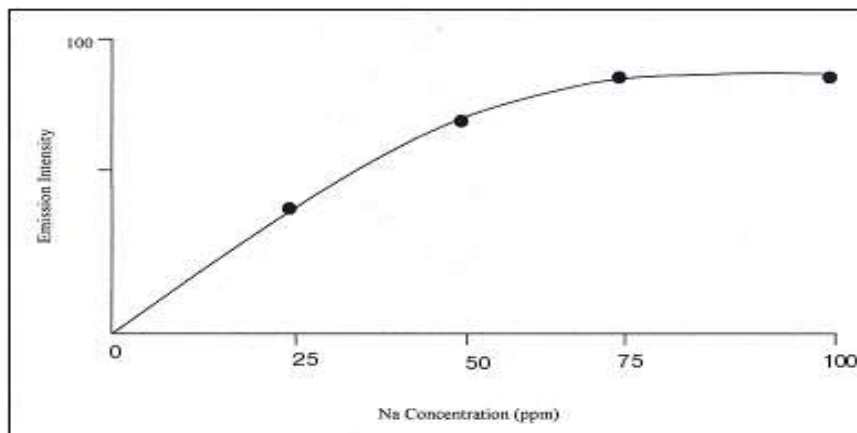


Fig. 3. An example of a calibration curve for an industrial measurement of Sodium concentration.

The emitted radiation is isolated by an optical filter and then converted to an electrical signal by the photo detector.

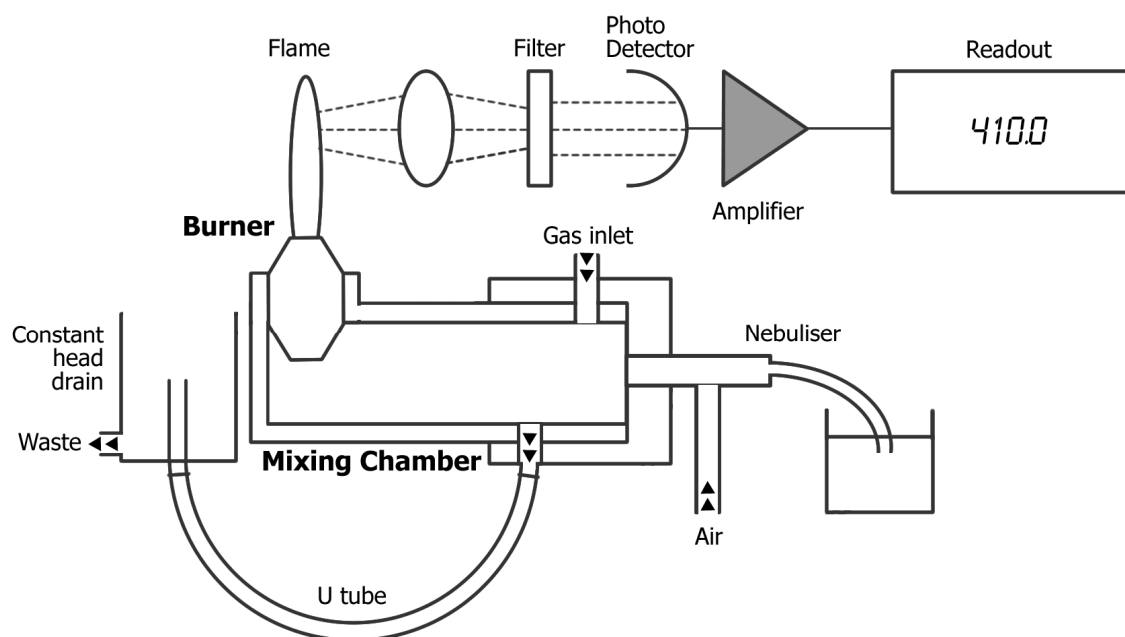


Fig. 4. Basic components

A simple flame photometer consists of the following basic components:

1. A flame that can be maintained in a constant form and at a constant temperature: "The Burner" (see Fig. 4).
2. A means of transporting a homogeneous solution into the flame at a steady rate: "Nebuliser and mixing chamber" (see Fig. 4).
3. A means of isolating light of the wavelength to be measured from that of extraneous emissions: "Simple colour filters" (interference type) (see Fig. 4).

4. A means of measuring the intensity of radiation emitted by the flame: "Photo detector"  
(see Fig. 4).

## 4. Flame Photometer Operating Data

The analysis of alkali and alkaline earth metals by flame photometry has two major advantages.

1. Their atoms reach the excited state at a temperature lower than that at which most other elements are excited
2. Their characteristic wavelengths are easily isolated from those of most other elements due to wide spectral separation.

Mixture	Temperature (0C)
Acetylene/Oxygen	3,100 - 3,200
Acetylene/Nitrous Oxide	2,900 - 3,000
Natural gas/Oxygen	2,700 - 2,800
Hydrogen/Oxygen	2,500 - 2,700
Acetylene/Air	2,100 - 2,400
Hydrogen/Air	2,000 - 2,100
Propane/Air	1,900 - 2,000
Butane/Air	1,300 - 1,900
Natural Gas/Air	1,700 - 1,800

Table 1. Temperatures achieved by a variety of gas mixtures

The analysis of Na, K, Li, Ba and Ca are typically determined at low temperatures, i.e., 1500-2000°C. The BWB FLAME PHOTOMETER is designed for mixtures of propane/air, butane/air and combinations of the two.

### Characteristic Wavelengths of the Elements

It is common knowledge that when Sodium is introduced into a flame it emits a radiation in the yellow region of the visible spectrum. Table 2 gives details of the measurable atomic flame emissions of the alkali and alkaline earth metals in terms of the emission wavelength and the colours produced.

Element	Emission Wavelength (nm)	Flame Colour
Barium (Ba)	515 *	Lime Green
Calcium (Ca)	622 **	Orange
Lithium (Li)	670	Red (Carmine)
Potassium (K)	766	Violet
Sodium (Na)	589	Yellow

Table 2

Table 2 Notes:

\* Barium is measured at 515nm to avoid interference with the Ca band at 554nm.

\*\* Calcium is measured by using the Calcium hydroxide band emission at 622nm. However, the main atomic emission occurs at 423 nm.



## 5. What You Will Need

The list given in this section outlines the basic equipment and reagents required to perform analysis with the BWB FLAME PHOTOMETER low temperature flame photometer.

1. BWB Flame Photometer
2. Regulated gas supply (propane, butane, or a combination of the two, LPG)
3. Power supply (90-250V ac)
4. Stock standard solutions, e.g. 10,000ppm Na, K, Li, etc.
5. Volumetric flasks for standard and sample dilution
6. Glass beakers or suitable sample vessels.
7. Good quality distilled or deionised water.
8. Diluent Concentrate.

NOTE: For medical systems a diluter is commonly used while in many industrial applications sample preparation involves the use of common laboratory equipment, e.g. centrifuge, muffle furnace, filtration equipment, etc.

Medical sample concentrations are commonly expressed in mmol/l (millimoles per litre) in contrast to ppm (parts per million), which is the typical unit used for industrial analysis. The relationship between the two is as follows.

$$\text{ppm} = A \times \text{mmol/l}$$

$$\text{mmol/l} = \text{ppm} \div A$$

where A = atomic mass of the atom being analysed



BWB Technologies Flame Photometers

## 6. Preparing For Analysis

### 6.1. Initial Precautions

It is of the utmost importance to become familiar with the flame photometer and ancillary equipment prior to analysis. If familiarity is not achieved, inaccuracy of results or even a hazard to safety could result. Therefore, always read the instrument's instruction manual.

There are several practical points, which should be adhered to, to achieve the required accuracy in your analysis.

1. Avoid handling samples with fingers. This leads to serious contamination. If a finger is immersed in 20 ml of deionised water the resulting  $\text{Na}^+$  concentration will exceed that of a 10 ppm standard.
2. Standards should be stored in sealed non-glass vessels and in high concentrations. Store the standards as a stock 10,000ppm solution and prepare dilutions when required. The long-term storage of low concentration standards is not recommended due to degradation of the ionic species.
3. All analyses involve the use of a diluent. Whenever possible use Diluent Concentrate diluted 1:999 with deionised water. This should be of the highest quality water for accurate flame analysis. Sodium, Potassium and Calcium are present in high concentrations in tap water and thus efficient deionisation is essential if any of the common flame analytes are to be determined.
4. Species that cause interference should be removed from samples or the equivalent concentration of the interferent should be present in the standards so as to avoid erroneous results. For example, if a sample of approximately 10 ppm Na contains approximately 1000 ppm  $\text{Ca}^{2+}$  then  $\text{Na}^+$  analysis can only be achieved by removing  $\text{Ca}^{2+}$  using oxalate/oxalic acid or by ensuring all standards contain 1000 ppm  $\text{Ca}^{2+}$ .

Always follow a well-documented analytical procedure (see section 7), which should contain information pertaining to interference removal when applicable.

5. Standards and samples should not be exposed to the atmosphere for long periods due to contamination from air-borne particles and evaporation of the solvent leading to elevated concentrations.

When in doubt about equipment or application the operator should contact the manufacturer for advice.

### 6.2. Sample Preparation

The sample, if not already a solution, must be converted to a media that is suitable for direct introduction into the flame photometer, i.e. the sample should be aqueous with no solid matter present.

This is achieved by:

- a) Extracting the salts from solid samples using deionised water or suitable extractants, e.g. Saturated  $\text{CaSO}_4$  for Sodium in soil. Extraction is made more successfully using a blender, macerator or shaking machine.
- b) If the sample is organic then the organic material should be removed by ashing. The remaining oxides are then dissolved using strong acids.

- c) Filtration or the use of a centrifuge to remove solid debris.

When aqueous, the sample can then be diluted to a known, accurately measured volume using deionised water. If it is a concentrated sample then the dilution ratio should be increased. If the sample concentration is low then a small volume of diluent and initial extractant should be used.

### 6.3. Standard Preparation

When preparing standards always observe the following:

1. Standards must always contain the constituents that are present in the samples in the same concentration ratios (element being sensed not included), i.e. if samples are prepared in 0.05M HCl then the standards should also contain 0.05M HCl.
2. Always ensure that the standards encompass the expected range of sample concentrations.
3. Use a good quality distilled or deionised water.
4. Use the same batch of diluent (1 part Diluent Concentrate to 999 parts water) to dilute both standards and samples.

NOTE: The Blank Standard should contain all the constituents of the standard solutions except the element that gives rise to the emission.

## 7. Making a Measurement

### Aspiration

All Blank, Standard and sample solutions are introduced into the flame by aspiration. One end of small diameter tubing is placed into the sample cup. The other end of the tubing is attached to an Aspiration Needle. Compressed air is forced through a small orifice and past the tip of the needle. The high velocity of the air stream causes the solution to form an aerosol. This enters the Mixing Chamber where it is mixed with the fuel gas and larger droplets are excluded. The small droplets make their way to the flame undergoing the excitation/emission process.

It is important that all solutions be clear of particulates that would block the tubing or needle.

### Calibration

Until recently all flame photometry instruments required the operator to do analyses by either of two methods.

1. Stay in the lower concentration ranges (under 50ppm). Calibrate with a Blank and one Standard and read the results directly from the meter or display.
2. To manually graph a calibration curve of a Blank and many Standards. Results are then interpolated from the graph.

The BWB Flame Photometer has simplified and computerised the process. When calibrating, the BWB will prompt the operator to aspirate the Blank and Standards (with the option of one or several Standards) and enter their numerical values. The BWB FLAME PHOTOMETER electronically monitors for stable readings, stores all data points, develops the calibration curve, and interprets the sample readings.

### Sample Determination

Once calibrated, sample determination is simply done by aspirating the samples and reading the results from the display.

## 8. Applications Methods

The following applications methods will enable the user to determine alkali and alkaline earth metal concentrations in a wide variety of sample media.

It is envisaged that, from the information given in this section, further applications methods will be appended with relative ease. The procedures detailed in this section are as follows:

Code	Title
BWB/1	The Determination of Sodium in Raw Pine Oil
BWB/2	The Determination of Exchangeable Sodium in Soils
BWB/3	The Determination of Sodium in Fuel Oil
BWB/4	The Determination of Sodium in Glass
BWB/5	The Determination of Sodium in Straw
BWB/6	The Determination of Sodium and Potassium in Silicates, Minerals and Ore
BWB/7	The Determination of Sodium and Potassium in Fruit Juice
BWB/8	The Determination of Potassium in Fertilisers
BWB/9	The Determination of Potassium in Plant Material
BWB/10	The Determination of Available Potassium in Soils
BWB/11	The Determination of Potassium in Mixtures Containing Plant Derived Resins
BWB/12	The Determination of Potassium in Glass
BWB/13	The Determination of Lithium in Grease
BWB/14	The Determination of Calcium in Beer
BWB/15	The Determination of Calcium in Biological Fluids
BWB/16	The Estimation of Calcium in Milk
BWB/17	The Simple Flame Photometric Determination of Calcium
BWB/18	The Determination of Calcium in Fruit Juice
BWB/19	The Determination of Calcium in Biscuits
BWB/20	The Simple Flame Photometric Determination of Barium
BWB/21	The Determination of Alkalis in Cement
BWB/22	The Determination of Sulphate

## Method BWB/1: The Determination of Sodium in Raw Pine Oil

This method is used to determine Sodium in raw pine oil from a minimum concentration of 1 ppm.

### Equipment Required:

1. BWB Flame Photometer
2. Small crucible (nickel or porcelain)
3. Bunsen burner, tripod, etc.
4. Accurate balance weighing to  $\pm 0.0005\text{g}$

### Reagents:

Anhydrous Sodium sulphate (Reagent)  
Concentrated sulphuric acid  
Distilled water

### Standard Preparation:

1. Stock Standard (1000 ppm Na): Dissolve 1.5435g of anhydrous Sodium sulphate in distilled water and dilute to 500ml. Store in an airtight non-glass bottle.
2. Working Standard (5 ppm Na): Dilute 5ml of the stock standard to about 900mls with distilled water. Add 10ml of concentrated sulphuric acid and dilute to the mark with distilled water.
3. Prepare 3, 2 and 1ppm Na standards by dilution of the working standard ensuring that each contains the equivalent of 1ml concentrated  $\text{H}_2\text{SO}_4$  per 100mls.
4. The Blank should be the same concentration of  $\text{H}_2\text{SO}_4$ .

### Sample Preparation:

1. Weigh accurately 1g of raw pine oil into a small clean crucible.
2. Heat the sample under a Bunsen burner in a fume cupboard. Ignite the vapours and ensure the sample burns freely. Re-ignition may be necessary to ensure only a char remains.
3. Transfer the crucible to a muffle furnace pre-heated to  $500-525^\circ\text{C}$  and maintain this temperature until all carbon is burned off.
4. Allow the crucible to cool and wash the ash off the sides with a little distilled water.
5. Add 1ml of concentrated sulphuric acid to fully dissolve the ash
6. Carefully add distilled water to the crucible and transfer the solution and washing to a 100ml volumetric flask.
7. Dilute to the mark using distilled water.

NOTE: If carbon is present the solution should be filtered. However, all carbon should be removed by correct heating (stages 2 and 3).

### Method:

1. Aspirate the Blank and Standards into the BWB Flame Photometer entering each value when prompted.
2. Aspirate the sample solution into the flame and record the display reading.

NOTE: Calcium may be determined using the same sample solution.

## Method BWB/2: The Determination of Exchangeable Sodium in Soils

### Equipment Required:

1. BWB Flame Photometer
2. Balance weighing to  $\pm 0.0005\text{g}$
3. Centrifuge
4. Sodium chloride (Reagent)
5. 1 M Ammonium Acetate solution

### Standards:

Prepare a 5ppm Sodium standard in 1 M neutral Ammonium Acetate solution.

Prepare from the above 2ppm and 1.25ppm Na standards in 1 M Ammonium Acetate solution.

Use 1M neutral Ammonium Acetate as the Blank.

### Method:

1. To 10g (accurately weighed) soil, add 200ml of 1 M neutral Ammonium Acetate solution. Allow to stand for 18 hours, stirring occasionally.
2. Withdraw and centrifuge the suspension.
3. Transfer 5ml of the supernatant liquid to a 50ml volumetric flask and dilute to the mark using the 1 M Ammonium Acetate solution.
4. Aspirate the Blank and Standards into the BWB Flame Photometer and enter each value when prompted.
5. Aspirate the sample and record its display reading.
6. Multiply the ppm Sodium value by 2 to give mg Sodium per 10g soil.

## Method BWB/3: The Determination of Sodium in Fuel Oil

The sample is burned in air in a silica crucible on a hot plate and the residue ashed in a muffle furnace at 525°C. The ash is dissolved in sulphuric and nitric acids and the Sodium content is determined using a BWB Flame Photometer.

### Equipment Required:

1. BWB Flame Photometer
2. Silica crucible
3. Hot Plate
4. Muffle furnace
5. Accurate balance

### Reagents:

1. 1000 ppm Sodium stock standard solution. Dissolve 1.5435g anhydrous Sodium Sulphate (Reagent) in distilled water and dilute to 500ml. Store in an airtight non-glass bottle.
2. Concentrated sulphuric acid
3. Concentrated nitric acid

### Working Standards Preparation:

Prepare 5ppm Sodium by diluting 5ml of the stock standard to 500ml with deionised water in a 1 litre volumetric flask. Add 20ml of concentrated  $\text{H}_2\text{SO}_4$  and 20ml of concentrated  $\text{HNO}_3$  and mix well. Dilute to the mark with deionised water.

From the acidified 5 ppm Sodium standard prepare a series of diluted standards ensuring that each contains the equivalent of 20ml concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  per litre.

Use deionised water, containing the equivalent of 20mls of concentrated  $\text{H}_2\text{SO}_4$  and 20mls concentrated  $\text{HNO}_3$  per litre as the blank solution.

### Method:

1. Heat the sample for 30 minutes at 60°C. Shake well.
2. Transfer about 10g into a clean, dry vessel and leave to cool to room temperature.
3. Weigh 10g accurately into a clean, dry silica crucible.
4. Heat the crucible and contents on a hot plate and ignite the oil. Re-ignite if necessary to produce a solid residue. Perform this step in a fume hood.
5. Transfer the crucible to a muffle furnace heated to 500°C and maintain the temperature until all of the carbon is burned off.
6. Allow to cool. Rinse down any ash from the side of the crucible with a few ml of deionised water.
7. Add 1ml of sulphuric acid (conc.) and 1ml of nitric acid (conc.).
8. Replace on the hot plate and heat until fumes of  $\text{SO}_3$  evolve.
9. Allow to cool. Add 10ml of deionised water.
10. Wash the contents of the crucible into a 50ml volumetric flask and dilute to the mark with deionised water. Carry out the test as soon as possible.
11. Aspirate the Blank and Standards and enter their values when prompted.
12. Aspirate the sample solution and read the result on the display.

Note: Dilute the sample if necessary using the blank solution to bring the Sodium concentration within the standard range.

### Calculation:

To obtain the weight of Sodium in mg present in the original 10g of sample multiply the sample concentration reading obtained by 0.05.



## Method BWB/4: The Determination of Sodium in Glass

### Equipment Required:

1. BWB Flame Photometer
2. Platinum crucible with lid
3. Accurate balance weighing to +/- 0.0005g

### Reagents:

1. Potassium carbonate (Reagent)
2. BWB 10,000 ppm Na Standard
3. Potassium hydroxide
4. Potassium chloride
5. Glacial acetic acid
6. Hydrochloric acid

### Reagent and Standards Preparation:

- Buffer Solution:** Dissolve 28g KOH in 300 ml deionised water in a 600 ml beaker. When completely dissolved add 30 ml glacial acid. Add 37 g KCl and dissolve. Cool to ambient temperature and dilute to 1 litre in a volumetric flask with deionised water.
- Blank Preparation:** To a 1 litre volumetric flask add 150 ml buffer solution and dilute to 1 litre using deionised water.
- Standard Preparation:** To a 1ml of BWB 10,000 ppm Na standard in a 1 litre volumetric flask add 150 ml buffer solution. Adjust to pH 7.5 with HCl. Dilute to the mark with deionised water. This is 10ppm Potassium. From the 10 ppm K standard prepare 7.5, 5 and 2.5ppm standards using the blank solution as diluent. Ensure all standards have a pH value of 7.5

### Sample Preparation:

Fuse an accurately weighed powdered sample with 2g Potassium Carbonate in a platinum crucible. When a clear fused melt is obtained continue heating for approximately 1 minute. Remove the crucible from the burner and pour the contents onto a cooling plate.

Place the crucible, crucible lid and cooled melt into a 400 ml beaker, add 75 ml buffer solution and dilute to 200ml using boiling deionised water.

Place the beaker on a water bath for 30 minutes to loosen the melt from the crucible. Remove crucible and crucible lid from beaker. Filter the solution into a 1 litre volumetric flask ensuring that deionised water washings from the beaker are also filtered.

Dilute to 300ml and adjust the pH to 7.5 with 1:3 HCl. Dilute to the mark with deionised water.

### Method:

1. Set the flame photometer up as in its instruction manual.
2. Set the zero using the blank solution.
3. Aspirate the standards into the instrument entering each value when prompted.
4. Aspirate the sample solution and record the display reading. (If the value is higher than that of the top standard, dilute sample with blank until the value falls in the range of the calibration curve.)
5. Multiply the Sodium concentration of the sample by the dilution factor.

## Method BWB/5: The Determination of Sodium in Straw

Sodium hydroxide is added to cellulose animal feeds to improve digestibility. The Sodium concentration is determined using a flame photometer.

### Equipment Required:

1. BWB industrial flame photometer
2. Balance weighing to  $\pm 0.0005\text{g}$
3. Filtration apparatus (or centrifuge)
4. Volumetric glassware

### Reagents:

1. BWB 10,000ppm Sodium flame photometer standard
2. 1 Molar ammonium chloride/1 Molar  $\text{NH}_4\text{OH}$  solution
3. Deionised water

### Reagent Preparation – Extractant solution

Dissolve 53.49g  $\text{NH}_4\text{Cl}$  with deionised water in a 1 litre volumetric flask. In a fume cupboard add to this solution 55mls of ammonia (SG – 0.88). Dilute to the mark with deionised water.

### Standard Preparation:

Dilute the 10,000 ppm Na standard 1:1000 with deionised water giving a 10 ppm top standard. From this prepare a 6, 4 and 2 ppm standard by dilution with deionised water.

### Sample Preparation:

1. Weigh accurately 3g straw and place in a 100 ml volumetric flask
2. Add 80 ml of extractant solution and shake vigorously
3. Stand for at least 30 minutes intermittently shaking the solution
4. Filter or centrifuge to remove solid matter. (Note: The solid must be washed with extractant solution and washings collected with supernatant) In a 100 ml volumetric flask dilute the washings and supernatant to the mark with deionised water
5. Dilute this solution 1 in 100 with deionised water. The sample is ready for analysis

### Method:

1. Set the flame photometer up as in its instruction manual.
2. Set the zero using the blank solution
3. Aspirate the standards into the instrument entering each value when prompted.
4. Aspirate the sample solution and record the display reading.
5. Multiply the Sodium concentration of the sample by the dilution factor

### Calculation:

To obtain the result in % Na in the original straw sample divide the sample concentration in ppm by 3.

## Method BWB/6: The Determination of Sodium and Potassium in Silicates, Minerals and Ore

### Equipment Required:

1. BWB Flame Photometer
2. Accurate balance
3. Platinum crucible
4. Volumetric glassware

### Reagents:

48% Hydrofluoric acid

Concentrated Sulphuric acid (analytical quality)

10% (V/V) Hydrochloric acid

### Standard Preparation:

Prepare a series of Sodium and Potassium standards from the chlorides (10, 6, 4 and 2 ppm), ensuring that each standard contains the same concentration of HCl as the samples. The Blank should also have the same concentration of HCl.

### Sample Preparation:

1. Transfer 1gm, accurately weighed, of sample to 30ml platinum crucible.
2. Moisten the sample with about 5 drops of water and an equal volume of concentrated sulphuric acid.
3. Add 5 ml hydrofluoric acid.
4. Place the platinum dish in a porcelain dish. Heat the porcelain dish on a hot plate at a rate that will slowly evolve white fumes of sulphuric acid without boiling or splattering.
5. When the sample is almost dry add a second portion of  $H_2SO_4$  and HF and repeat the slow evaporation.
6. Repeat a third time to make sure that the rock is completely decomposed.
7. On the third evaporation take care to evaporate the sample to complete dryness driving off as much Fluoride as possible. There is a tendency to splatter at this point and the heat must be carefully controlled.
8. Use hot 1:9 HCl to transfer the metallic sulphates to a 250ml beaker. About 175mls of hot acid are sufficient with heating and stirring using a glass rod.
9. Transfer the solution to a 200ml volumetric flask, cool and fill to the mark with 10% (V/V) hydrochloric acid. This provides a 0.5% solution of the rock sample in 10% (V/V) HCl.

Having prepared the sample in this way a further dilution may be necessary prior to presentation of sample to nebuliser.

### Method:

1. Aspirate and enter values for the Blank and Standards into the BWB Flame Photometer.
2. Aspirate the unknown solution and read the concentration on the display.

## **Method BWB/7:**

### **The Determination of Sodium and Potassium in Fruit Juice**

This method involves the dilution of the fruit juice sample with water followed by filtration and finally aspiration directly into the BWB Flame Photometer.

#### Equipment Required:

1. BWB flame photometer
2. Filtration apparatus
3. Volumetric glassware

#### Reagents:

1. BWB 10,000 ppm Sodium and Potassium standards
2. Deionised water/Diluent Concentrate solution (999:1).

#### Method:

1. Prepare by dilution of the stock standards 20, 15, 10 and 5ppm Na and K standards. Deionised water/Diluent solution is the blank.
2. To 10 ml of the fruit juice add 50 ml deionised water.
3. Filter this solution through an ashless filter paper (e.g. Whatman 540) into a 1 litre volumetric flask. Ensure that the solid particles retained by the paper are washed thoroughly and washings directed into the same 1 litre flask. Dilute to the mark with deionised water, stopper the flask and mix by inversion.
4. Set up the flame photometer as outlined in its instruction manual.
5. Aspirate the Blank and Standards entering their values when prompted.
6. Aspirate the sample solution and note the results on the display.

Note: If the Na and K concentrations in the fruit juice are outside the range of standards the sample should be diluted accordingly.

#### Calculation:

Multiply the concentration of Na and K obtained from the display by the dilution factor, i.e. x 100, to express the result in ppm or mg/l of Na or K in the original fruit juice.

## Method BWB/8: The Determination of Potassium in Fertilisers

### Equipment Required:

1. BWB Flame Photometer
2. Balance accurate to  $\pm 0.0005\text{g}$ .
3. Filter paper,
4. Potassium chloride (Reagent)

### Method:

1. Prepare a series of Potassium standards covering the range 0-10 ppm using Potassium chloride diluted with distilled water.
2. Weigh out accurately 10g fertilizer and add 300ml distilled water. Shake for 30 minutes.
3. Transfer the solution to a 500ml volumetric flask and dilute to the mark using distilled water.
4. Filter the solution,
5. If necessary dilute the filtrate to produce an expected concentration within the range 0-10 ppm Potassium
6. Aspirate a Blank and the Potassium Standards into the BWB Flame Photometer and enter each value as prompted.
7. Aspirate the sample into the flame photometer and record the result from the display.
8. The percentage Potassium contained in the fertilizer can be determined taking into account the dilution factor.

## Method BWB/9: The Determination of Potassium in Plant Material

### Equipment Required:

1. BWB Flame Photometer
2. Balance weighing to  $\pm 0.0005\text{g}$
3. Water bath and oven
4. 10 Molar Hydrochloric acid
5. Potassium chloride (Reagent)

### Standards:

1. Prepare a 5ppm Potassium standard by dissolving KCl (Reagent) in an HCl/water mixture containing 2ml conc. HCl per 100ml.
2. Prepare progressive dilutions of the 5ppm standard using the HCl/water mixture as diluent.
3. Use the HCl/water mixture as the Blank.

### Method:

1. Accurately weigh 2-3g of the ground, oven-dried sample. Completely oxidise at  $500-525^{\circ}\text{C}$ .
2. Dissolve the ash in 10 molar Hydrochloric acid and allow it to digest on a steam bath for 20 minutes.
3. Evaporate the solution to dryness and heat the residue in an oven for 30 minutes at  $105^{\circ}\text{C}$ .
4. Allow to cool, return to the water bath and add 10ml 10 molar Hydrochloric acid. Warm to dissolve.
5. Transfer 2mls to a 100ml volumetric flask and dilute to the mark with distilled water
6. Aspirate the Blank and each standard into the BWB Flame Photometer, in turn, and enter each value when prompted.
7. Aspirate the samples and read from the display.
8. The amount of Potassium in the plant material sample can be calculated taking into account the dilution factor

## Method BWB/10: The Determination of Available Potassium in Soils

### Equipment Required:

1. BWB Flame Photometer
2. Whatman No. 30 filter paper
3. Potassium chloride (Reagent)
4. Balance weighing to  $\pm 0.0005\text{g}$
5. Ammonium acetate
6. Acetic acid

### Solutions and Standards:

Prepare 0.5M aqueous solution of ammonium acetate/acetic acid by taking 38.55g ammonium acetate and dissolving it in 29mls of glacial acetic acid and diluting to 1 litre with distilled water. Use this solution as Blank and to dilute Standards and samples.

Prepare standard Potassium solutions to cover the range 0-100 ppm as follows:

1. Accurately weigh 1.907g Potassium chloride in about 50mls ammonium acetate/ acetic acid solution.
2. Transfer to a 500ml volumetric flask and dilute to the mark with ammonium acetate/acetic acid solution. This solution contains 2000ppm Potassium.
3. Transfer 25mls of this stock solution into a 500ml volumetric flask and dilute to the mark with ammonium acetate/acetic acid solution. This is the 100ppm Potassium solution.
4. From this prepare 80, 60, 40 and 30ppm standards using the  $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$  solution as diluent.

### Method:

1. Accurately weigh 10g of soil and transfer to a plastic bottle together with 50ml of acetate/acetic acid solution.
2. Stopper the bottle and shake using an automatic shaker for 30 minutes.
3. Remove from the shaker, allow to stand for several minutes. Filter the solution through a Whatman No. 30 filter paper.
4. Aspirate the Blank and Standards into the BWB Flame Photometer and enter the values when prompted.
5. Determine the Potassium content of the soil extract by spraying the solution, without further dilution, into the flame photometer and reading result on the display.

## Method BWB/11: The Determination of Potassium in Mixtures Containing Plant Derived Resins

This method is used to determine Potassium in the presence of plant-derived resins. The sample mixture is expected to contain about 10%  $K_2CO_3$ .

The sample is firstly converted into an inorganic residue by ashing, the residue dissolved in hydrochloric acid is diluted with distilled water and Potassium is determined using a BWB Flame Photometer

### Equipment Required:

1. BWB Flame Photometer
2. Small crucible (nickel or porcelain)
3. Bunsen burner, tripod etc.
4. Accurate balance weighing to 0.0005g.

### Reagents:

1. Potassium Dihydrogen Ortho Phosphate (Reagent)
2. 10 molar Hydrochloric acid

### Sample Preparation:

1. Weigh accurately 1g of the resin sample into a small clean crucible.
2. Heat the sample using a Bunsen burner in a fume cupboard. Ignite the vapours and ensure the sample burns freely. Re-ignition may be necessary to ensure only a char remains.
3. Transfer the crucible to a muffle furnace pre-heated to 500-525°C and maintain this temperature until all the carbon is burned off.
4. Dissolve the ash in hydrochloric acid and allow it to digest on a steam bath for about 20 minutes.
5. Evaporate the solution to dryness and heat the residue in an oven for 30 minutes at 105°C.
6. Return to the water bath and add 20ml of 10 molar HCl, warm to dissolve.
7. Transfer 2ml of the solution to a 1 litre volumetric flask containing approximately 200ml distilled water. Dilute to the mark with distilled water. The sample is now ready for analysis.

### Standard Preparation:

1. Dissolve 3.481g of Potassium Dihydrogen Ortho Phosphate (previously dried for one hour at 105°C) in a 1 litre volumetric flask and dilute to the mark with distilled water. This is the 1000ppm Potassium standard.
2. Prepare from the stock standard 10, 6, 4 and 2ppm Potassium standards ensuring that each standard contains the equivalent of 2mls 10 molar HCl per litre.
3. The Blank is deionised water with 2ml of 10 M HCl added.

### Method:

1. Aspirate the Blank and Standards entering their values when prompted.
2. Aspirate the sample solution into the flame and record the display reading.
3. This gives concentration of Potassium sample.

Calculation:

To calculate Potassium concentration in mg/g of the resin mixture, multiply the concentration of the sample from the display by 10.



## Method BWB/12: The Determination of Potassium in Glass

### Equipment Required:

1. BWB Flame Photometer
2. Platinum crucible with lid
3. Accurate balance weighing to +/- 0.0005g

### Reagents:

1. Sodium carbonate (Reagent)
2. BWB 10,000 ppm K Standard
3. Sodium hydroxide
4. Sodium chloride
5. Glacial acetic acid
6. Hydrochloric acid

### Reagent and Standards Preparation:

- Buffer Solution:** Dissolve 20g NaOH in 300 ml deionised water in a 600 ml beaker. When completely dissolved add 30 ml glacial acetic acid. Add 29g NaCl and dissolve. Cool to ambient temperature and dilute to 1 litre in a volumetric flask with deionised water
- Blank Preparation:** To a 1 litre volumetric flask add 150 ml buffer solution and dilute to 1 litre using deionised water
- Standard Preparation:** To 1mls of BWB 10,000 ppm K standard in 1 litre volumetric flask add 150 ml buffer solution. Adjust to pH 7.5 with HCl. Dilute to the mark with deionised water. This is 10ppm Potassium. From the 10 ppm K standard prepare 7.5, 5 and 2.5ppm standards using the blank solution as diluent. Ensure all standards have a pH value of 7.5

### Sample Preparation:

Fuse an accurately weighed powdered sample with 2g Potassium Carbonate in a platinum crucible. When a clear fused melt is obtained continue heating for approximately 1 minute. Remove the crucible from the burner and pour the contents onto a cooling plate.

Place the crucible, crucible lid and cooled melt into a 400 ml beaker, add 75 ml buffer solution and dilute to 200 ml using boiling deionised water.

Place the beaker on a water bath for 30 minutes to loosen the melt from the crucible. Remove crucible and crucible lid from beaker. Filter the solution into a 1 litre volumetric flask ensuring that deionised water washings from the beaker are also filtered.

Dilute to 300 ml and adjust the pH to 7.5 with 1:3 HCl. Dilute to the mark with deionised water.

### Method:

1. Set the flame photometer up as in its instruction manual
2. Set the zero using the blank solution
3. Aspirate the standards into the instrument entering each value when prompted.
4. Aspirate the sample solution and record the display reading. (If the value is higher than that of the top standard, dilute sample with blank until the value falls in the range of the calibration curve.)
5. Multiply the Potassium concentration of the sample by the dilution factor.

## Method BWB/13: The Determination of Lithium in Grease

This method is suitable for the determination of Lithium in conventional soap thickened greases. It may be used for both new and used samples but with less accuracy in the latter case.

### Equipment Required:

1. BWB Flame Photometer
2. Accurate balance weighing to  $\pm 0.0005\text{g}$ .
3. Muffle furnace
4. Platinum crucible
5. Bunsen burner

### Reagents Required:

1. BWB Lithium standard (10,000 ppm)
2. Hydrochloric acid (conc.)
3. BWB blank diluent

### Standards

From the stock Lithium standard prepare 10, 7.5, 5 and 2.5ppm standards using BWB blank as diluent.

BWB blank solution is made with 1ml Diluent Concentrate and 999ml deionised water.

### Method

1. Weight accurately about 1 gm of grease in a platinum crucible.
2. Ignite by gentle heating over a Bunsen burner. When all volatile matter has burned off, transfer to a muffle furnace at  $500^{\circ}\text{C}$  and heat until all carbon is removed.
3. Allow to cool, cover the crucible with a watch glass. Add carefully 2 ml concentrated HCl, using the watch glass to retain splashes.
4. When the reaction has ceased, wash splashes from watch glass into the crucible with a small volume of deionised water and heat to dryness on a water bath.
5. Dilute (quantitatively) the sample with BWB blank until the expected concentration falls within the 0-10 ppm range.
6. Aspirate the Blank and Standards entering their values when prompted.
7. Aspirate the sample record the value from the display.
8. Adjust the sample concentration by taking account of the dilution ratio.

NOTE: If the sample contains significant concentrations of other cations, prepare standard solutions containing similar concentrations of these elements.

## Method BWB/14: The Determination of Calcium in Beer

The determination of Calcium in beer may be carried out by preliminary separation of Calcium as oxalate followed by the addition of perchloric acid, which releases the Calcium from the inhibiting effect of the oxalate

### Equipment required:

1. BWB Flame Photometer.
2. Graduated stoppered centrifuge tube.

### Reagents:

1. Standard Calcium solution 100 ppm (in 0,2 molar perchloric acid)
2. 1% ammonium oxalate solution.
3. 0.5% ammonium oxalate solution
4. 25% ammonia solution
5. 4M perchloric acid

### Method:

1. Pipette 5ml beer into a 10ml graduated stoppered centrifuge tube.
2. Add 5mls 1% ammonium oxalate and 3 drops ammonia solution
3. Shake, and allow to stand for 30 minutes
4. Centrifuge at 2000 rpm for 2 minutes
5. Decant the supernatant and allow the tube to drain inverted for 30 seconds
6. Add 0.5ml 4M perchloric acid and shake
7. Heat for 1 minute in a boiling water bath
8. Cool and dilute to the mark with distilled water
9. Calibrate the flame photometer using 40ppm, 60ppm and 100ppm  $\text{Ca}^{2+}$  standards containing 50mls 4M  $\text{HClO}_4$  per litre.
10. Aspirate the sample directly into the flame photometer
11. The Calcium concentration is then shown on the meter.

## Method BWB/15: The Determination of Calcium in Biological Fluids

Calcium is precipitated out of the sample with an ammonium oxalate/oxalic acid mixture, which also acts as a pH buffer. The mixture is then centrifuged and the supernatant fluid decanted off to be used for Sodium and Potassium determination if required. The precipitate is dissolved in perchloric acid and then aspirated into the calibrated BWB Flame Photometer.

### Equipment Required:

1. BWB Flame Photometer
2. Balance weighing to +/- 0.0005g.

### Reagents Preparation:

Ammonium Oxalate/Oxalic acid

1. Dissolve 12.6g  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  to 1 litre distilled water in a volumetric flask. This is 0.1M oxalic acid.
2. Dissolve 12.2g  $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$  to 1 litre of distilled water in a volumetric flask. This is 0.1M ammonium oxalate.
3. To 5ml of 0.1M oxalic acid in a 100ml volumetric flask add 0.1M ammonium oxalate up to the mark.

0.05 Perchloric acid.

Half fill a 1 litre volumetric flask with distilled water, add 5mls of 60% perchloric acid and dilute to the mark.

Standard Preparation:

1. Dissolve 1.834g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Reagent) in 0.05M perchloric acid and dilute to 500mls. This is the Calcium 1000mg/l stock standard.
2. Dilute the stock standard 1:10 with 0.05M perchloric acid. This is the Calcium 100mg/l standard.
3. A range of standards is now prepared by successive dilution of the 100mg/l standard with 0.05M perchloric acid.

### Method:

1. Pipette 2mls of serum into a rounded centrifuge tube and add 3mls of Ammonium oxalate/oxalic acid mixture.
2. Mix and let stand for 30 minutes.
3. Centrifuge well and decant the supernatant fluid and drain the sample.
4. Add 4ml of 0.05M perchloric acid to the pellet, vortex or shake vigorously to dissolve the precipitate fully. The sample is now ready for analysis.
5. Treat 2ml of the Calcium 100mg/l standard in the same way as the sample, i.e. Stages 1 – 4, to obtain a Blank Solution.
6. Aspirate the Blank Solution and Calcium standards into the BWB flame photometer and enter the values of standards.
7. Aspirate the sample solution into the flame photometer and read the Calcium concentration.

## Method BWB/16: The Estimation of Calcium in Milk

### Equipment required:

1. BWB Flame Photometer
2. Accurate balance

### Reagent Preparation:

Dilute concentrated hydrochloric acid 1:4 with distilled water

CAUTION: Always add acid to water with great care. Never add water to concentrated acid.

#### Blank Preparation:

2.5ml of diluted hydrochloric acid

2.0ml 10% lanthanum chloride

Make up to 100ml with distilled water. This gives reagent blank.

#### Standard Preparation:

Place 1.249gm A.R. Calcium carbonate in approximately 50ml H<sub>2</sub>O, adding drop wise, concentrated hydrochloric acid until Calcium carbonate is dissolved (should take about 10ml). Cool and bring to one litre. This will give 500ppm stock Calcium standard.

The stock solution should be diluted to give standards of 2.5, 5.0, 7.5 and 10 ppm Ca<sup>2+</sup>.

#### Sample Preparation:

1. Place 4gm (accurately weighed) of milk in a dry silica crucible.
2. Ash sample at 500-525°C in an oven.
3. When cool, dissolve ash in 5ml of 1:4 diluted concentrated hydrochloric acid.
4. Transfer to 100ml volumetric flask; make up to mark.
5. Filter through filter paper, pipette 50ml of filtrate into 100ml volumetric flask.
6. Add 2ml of 10% lanthanum chloride. Make up to mark with distilled water.

### Method:

1. Spray reagent blank and enter.
2. Spray 10ppm standard and enter value.
3. Spray intermediate standards entering each value.
4. Spray test samples and read values from display.
5. This gives you Calcium in parts/million of Calcium for milk.

If percent Calcium required:

Multiply Ca<sup>2+</sup> ppm sample reading by 0.025-percent Ca<sup>2+</sup> in milk. Normal level for milk, approximately 0.11%

## **Method BWB/17:**

### **The Simple Flame Photometric Determination of Calcium**

If aqueous samples of Calcium are to be analysed which contain no interferent ions the following method should be employed.

#### Method:

1. From the BWB 10,000 ppm Calcium stock standard prepare diluted standards of 100, 75, 50 and 25 ppm using deionised water/Diluent Concentrate (999:1) as diluent.
2. If the samples to be analysed are of lower concentration then prepare 50, 40, 20 and 10ppm standards.
3. Aspirate the Blank and Standards entering their values when prompted.
4. Aspirate the aqueous sample
5. Record the result from the display.

If there are interferent ions present, Calcium should be precipitated as Calcium Oxalate, dissolved in  $\text{HClO}_4$  and then analysed.

## Method BWB/18: The Determination of Calcium in Fruit Juice

The determination of Calcium in fruit juice may be carried out by preliminary separation of Calcium as oxalate formed by the addition of perchloric acid, which releases the Calcium from the inhibiting effect of the oxalate.

### Equipment Required:

1. BWB Flame Photometer.
2. Graduated stoppered centrifuge tube

### Reagents:

1. Standard Calcium solution 100 mg/l (containing perchloric acid)
2. 1% ammonium oxalate solution
3. 0.5% ammonium oxalate solution
4. 25% ammonia solution
5. 4M perchloric acid

### Method:

1. Pipette 5 ml fruit juice into a 10 ml graduated stoppered centrifuge tube
2. Add 5mls 1% ammonium oxalate and 3 drops ammonia solution
3. Shake, and allow to stand for 30 minutes.
4. Centrifuge at 2000 rpm for 2 minutes
5. Decant the supernatant and allow the tube to drain inverted for 30 seconds
6. Add 0.5ml 4M perchloric acid and shake
7. Heat for 1 minute in a boiling water bath
8. Cool and dilute to the mark with distilled water
9. Calibrate the flame photometer using a 100 ppm  $\text{Ca}^{2+}$  standard containing 50mls 4M  $\text{HC10}_4$  per litre from which 75, 50 and 25 ppm  $\text{Ca}^{2+}$  solutions have been prepared
10. Aspirate the sample directly into the flame photometer
11. The Calcium concentration is then shown.

## Method BWB/19: The Determination of Calcium in Biscuits

Calcium is extracted with Lithium Acetate solution and analysed directly by flame photometry.

### Equipment Required:

1. BWB flame Photometer
2. Accurate balance
3. Volumetric glassware
4. Filtration apparatus

### Reagents:

1. BWB 10,000 ppm  $\text{Ca}^{2+}$  solution
2. Extractant solution
3. Deionised water

### Extractant Solution:

Prepare 0.8 Molar Lithium Chloride – 0.2 Molar Lithium Acetate solution in deionised water. This solution, when diluted 1 in 2 with deionised water, is the Blank solution.

### Sample Preparation:

To 5g of dried accurately weighed sample, in a sealable glass container, add 250 of extractant solution. Seal and shake vigorously for 15 minutes (intermittently), stand the solution for 2 hours (or overnight if convenient).

Filter the solution through filter paper (e.g., Whatman No. 6) into a 500 ml volumetric flask and dilute to the mark with deionised water.

### Standard Preparation:

From the BWB 10,000 ppm  $\text{Ca}^{2+}$  standard prepare a 100ppm  $\text{Ca}^{2+}$  by adding 1ml of the stock standard to 50ml of extractant solution in a 100ml volumetric flask and diluting to the mark with deionised water.

Prepare also a 75, 50 and 25 ppm  $\text{Ca}^{2+}$  solution ensuring each standard contains a 1 in 2 solution of the extractant solution.

### Method:

1. Set up the flame photometer as outlined in its instruction manual.
2. Aspirate the Blank and Standards entering their values when prompted.
3. Aspirate the sample and note its' reading. The Calcium concentration can now be obtained. Calculate by multiplying by the dilution factor.

N.B. If the Calcium concentration of the sample is outside the standard range then dilute with the blank solution.

The method of extraction is suitable for most samples, however if a more vigorous technique is required operate the extraction using an  $\text{HCl}/\text{CH}_3\text{COOH}$  solution followed by autoclaving for 20 minutes at 20 psi and adjusting the pH to 4.5 with  $\text{NH}_3$  solution.



## Method BWB/20: The Simple Flame Photometric Determination of Barium

This method is suitable for aqueous samples only which contain no interferent ions, e.g.  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ , etc.

### Method:

1. From the BWB 10,000 ppm Barium standard prepare standards of 1000, 750, 500 and 250 using deionised water/Diluent Concentrate (999:1) as diluent.
2. For lower concentration samples a set of Ba standards of 300, 200, 100 and 50 should be prepared. Do not set a lower top standard than 300 due to insensitivity of the technique to low Ba concentrations.
3. Aspirate the Blank and Standards entering their values when prompted.
4. Aspirate the aqueous sample
5. Record the result from the display.

If there are interferent ions present, Barium should be precipitated as Barium Sulphate, dissolved in ammonia EDTA and then analysed.

## Method BWB/21: The Determination of Alkalis in Cement

This method describes how soda and potash may be estimated in cement using a BWB Flame Photometer.

The addition of aluminium nitrate solution suppresses the interference caused by concentrations of lime up to 350ppm, which is the equivalent concentration for cement, allowing for the effect of silica and alumina already present in solution.

For materials other than cement, the addition of aluminium nitrate can be adjusted according to the lime concentration expected. 30ml of the solution is sufficient for a CaO concentration of 1g/litre. Excess of aluminium nitrate is not harmful,

### Equipment Required:

1. BWB Flame Photometer
2. Balance weighing  $\pm 0.0005\text{g}$
3. Whatman No. 40 filter paper
4. Sodium chloride (Reagent)
5. Potassium chloride (Reagent)
6. Concentrated HCl
7. Aluminium (high grade)
8. Concentrated  $\text{HNO}_3$

### Reagent Preparation:

#### Standard Solution

Dissolve 0.7915g KCl and 0.4715g NaCl with distilled water in the same 1 litre volumetric flask. Dilute to the mark with distilled water and mix well by inversion. This solution contains 500ppm  $\text{K}_2\text{O}$ . Dilute exactly 20mls of this solution in a 1 litre volumetric flask with 500ml distilled water and add 10ml concentrated HCl very slowly. Dilute to the mark with distilled water.

This is the universal standard containing 10ppm  $\text{K}_2\text{O}$  and 5ppm  $\text{Na}_2\text{O}$  and can be used for all purposes.

#### Aluminium Nitrate Solution:

Dissolve 30g of aluminium known to have a low alkali content (high grade) in 400ml of 50%  $\text{HNO}_3$ . When the aluminium has dissolved and the solution cooled dilute to 1 litre with distilled water.

### Method:

1. Mix 0.500g cement with 20-30ml of distilled water, add 5ml of concentrated HCl and dilute to about 50ml.
2. Heat the solution to boiling.
3. Filter the solution through a 9cm No. 40 Whatman filter paper into a 500ml volumetric flask.
4. Wash the filter paper 6 times with 20ml each of hot distilled water.
5. Add 10ml of the aluminium nitrate solution.
6. Cool the solution and dilute to the mark with distilled water.

7. Prepare a series of standards by dilution of the universal standard ensuring that each prepared standard contains the equivalent of 1ml of concentrated HCl per 100mls.
8. Aspirate the set of standards directly into the Flame Photometer and enter each value of standards.
9. Aspirate the cement sample solution and read off the  $\text{Na}_2\text{O}$  concentration.
10. Calculate the alkali content of the cement by multiplying the ppm  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  present in the sample solution by the dilution factor.

## Method BWB/22: The Determination of Sulphate

The sulphate present in the sample is dissolved in water and precipitated out of solution using an excess of Barium chloride. The precipitate is removed by centrifugation and is then dissolved in Ammonium Ethylenediaminetetraacetate. The  $\text{Ba}^{2+}$  complex formed is then aspirated directly into the flame and the sulphate content of the sample calculated from the Barium concentration recorded. Samples must be free of anions that produce insoluble Barium salts other than sulphate.

### Equipment Required:

1. A BWB Flame Photometer.
2. An accurate balance weighing to  $\pm 0.0005\text{g}$ .
3. Centrifuge

### Reagents:

1. Sodium sulphate (Reagent)
2. Concentrated hydrochloric acid
3. Barium chloride solution (0.1% W/V)
4. Ammonium Ethylenediaminetetraacetate solution: Dissolve 5g of Ethylenediaminetetraacetic acid in 100ml deionised water, add 50ml of ammonia solution (S.G. 0.88) and dilute to 500ml with deionised water.

### Preparation of Stock Standard:

Dissolve 0.6713g Sodium sulphate (Reagent) in deionised water and dilute to 100mls. This is 2000 ppm  $\text{SO}_4^{2-}$  stock standard.

### Method:

1. Accurately weigh a sample containing not more than 0.2g of sulphate. Dissolve in deionised water and transfer the solution to a 100ml volumetric flask.
2. Add 10ml of concentrated HCl. Mix thoroughly and dilute to the mark with deionised water.
3. Pipette 5ml of the sample solution into a 10ml calibrated centrifuge tube and add 5ml 0.1%  $\text{BaCl}_2$ . Mix the solution well and spin in a centrifuge for three minutes at 4000 rpm.
4. Discard the supernatant liquid.
5. Re-suspend the pellet in 10ml of deionised water and spin again for 3 minutes at 4000rpm.
6. Discard the supernatant liquid.
7. Add Ammonium Ethylenediaminetetraacetate solution and stir until the pellet completely dissolves. Use gentle heat if necessary.
8. Dilute exactly up to the 10ml calibration mark with the Ammonium Ethylenediaminetetraacetate solution.
9. Subject a 5ml portion of the stock sulphate standard to identical treatment (i.e. Stages 1-9). This yields a final solution containing 1000 ppm  $\text{SO}_4^{2-}$ .
10. Using the Ammonium Ethylenediaminetetraacetate solution as diluent prepare additional standards of 600, 300 and 100 ppm  $\text{SO}_4^{2-}$  from the stock standard.
11. Using the Barium channel, aspirate the Standards and Blank, entering their values when prompted.
12. Aspirate the sample into the flame and take reading from the Barium channel.

Calculation: To obtain the mass of sulphate in the original sample in mg divide the sample sulphate concentration from the graph by 5.

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