Simultaneous determination of major and minor constituents in cement and steel by inductively coupled plasma atomic emission spectrometry.

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SIMULTANEOUS DETERMINATION OF MAJOR AND MINOR CONSTITUENTS IN CEMENT AND STEEL BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

by

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ABSTRACT

Methods for the simultaneous determination of major and minor constituents in cement and steel samples are developed in this thesis. The effect of matrix elements on analyte emission intensity has been evaluated. Dissolution procedures for these samples are based on the use of acids combined with a microwave-assisted digestion system and all measurements are then carried out by inductively coupled plasma atomic emission spectrometry.

The previous methods of analysis for these samples has been reviewed. This section includes methods which are recommended by many authorities as Standard Procedures. It was found that the use of a microwave-assisted digestion system, coupled with inductively coupled plasma atomic emission spectrometry, reduced the total analysis time and reduced operating costs.

The results obtained for the simultaneous elemental analysis of cement and steel using such methods are found to be in good agreement to the certified values. The methods developed offer the considerable advantages of rapid sample throughput, simplicity of use and are applicable for many routine analytical purposes.

STUDY PROGRAMME

As part of the research programme, I had attended selected lecture courses, within School of Science and Mathematics, research seminars and Departmental research meetings.

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CHAPTER 1 - INTRODUCTION

1.0 Introduction

Conventional elemental and molecular analytical techniques, which employ classical or wet chemical procedures, remain in use in many laboratories. Much analysis now, however, is performed by instrumental methods which use absorption and/or emission spectrometry at various wavelengths, electrochemical methods, mass spectrometry, chromatography and many other techniques. Many analytical chemists prefer to use efficient analytical instrumentation because this offers sensitivity, selectivity and efficiency for analyses which are tedious or time consuming if carried out by classical methods. Thus, in principle, instrumental techniques provide rapid analysis with cheaper operating costs, than the labour-intensive classical methods.

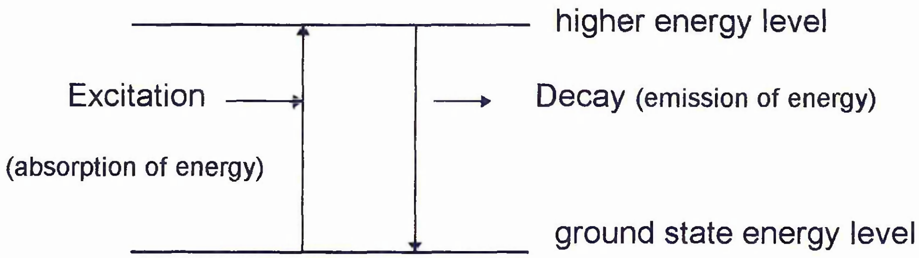
One of the techniques in use today is inductively coupled plasma atomic emission spectrometry which is an established technique used to perform elemental analysis at the trace, minor and major level in a wide range of sample matrices [1-10]. The introduction of inductively coupled plasma atomic emission spectrometry as an analytical technique has greatly facilitated the determination of many of the elements. Indeed, some determinations which were scarcely practicable by conventional methods and subject to inaccuracies may now be determined with relative ease. Nowadays, it is being increasingly adopted as the preferred procedure in many laboratories. It has been used to analyse metallic elements in biological samples [10-15], geological samples [16-24], metallurgical samples [1, 2, 4, 8, 25-32], environmental samples [33-35] and many other sample types. In this study, it will be used as an analytical device to analyse Standard Reference Materials based on cement and steel.

1.1 Theory Of Atomic Emission Spectrometry

In atomic spectrometry [36], a sample is decomposed as extensively as possible into its constituent atoms. The atoms, either neutral or charged, can then be analysed by a variety of methods. Atomic emission and atomic absorption are the most common techniques used by the analytical chemist. Both techniques can be used qualitatively and quantitatively.

In the hot flame or plasma environment, individual elements are raised to excited electronic energy levels. Excitation to a higher energy level is brought about by the heat of the flame or plasma.These excited levels have a short lifetime. Atomic emission occurs when an excited electron at a higher energy level falls back to the ground state, where, at the same time, it will be accompanied by an emission of photon of radiation (see Figure 1).

Figure 1. *Electronic excitation and decay process*



In atomic emission spectrometry, the process involves the following steps:

i. Atomisation

During the atomisation process, energy is absorbed which converts the elements in a compound to their free atoms. In the hot environment of a flame or plasma, which acts as an atomiser, numerous dissociation and association reactions lead to conversion of the constituents to the elemental state. The general equilibria formula would be such as:

$$MA \longrightarrow M + A \qquad \text{Eq. 1}$$

The efficiency of the atomisation process depends upon several factors one of which is the temperature. In atomic absorption spectrometry, the use of electrothermal furnace or fuel combinations of air-acetylene or nitrous oxide-acetylene typically have temperatures in the range 1700°C to 3150°C whereas plasmas have temperatures of 6000°C to 8000°C.

ii. Excitation

In the excitation stage, electrons at the ground state energy level in some of free atoms yielded during atomization will be excited to a higher energy level. The excited atoms are produced principally by collision of the ground state atoms with energetic species such as free electrons, other atoms or molecules that are present in the environment. This is known as an ionization process. Excitation of electrons to the higher energy level can be generated either by heat such as in a graphite furnace, flame or plasma; or by light produced by hollow cathode lamp or by an electrical discharge such as arc and spark. Theoretically, it would be possible to formulate the general excitation equilibrium as:

$$M + \text{energy} \longrightarrow M^{+} + e^{-} \qquad \text{Eq. 2}$$

The higher the temperature the more the equilibrium which exists between free atoms and ions is shifted towards the ionic state.

iii. Decay and Emission

Following the uptake of a quantum of energy an excited electron will decay back to the ground state spontaneously. When an electron falls back to a lower energy level then, at the same time, it will emit light at a specific wavelength. The following equation represents the equilibrium:

$$e^{-} + M^{+} \longrightarrow M + \text{energy} \qquad \text{Eq. 3}$$

At room temperature, virtually all the atoms of a sample of matter are in the ground state. During the excitation process, more than one electronic transition is possible. When the electrons fall back from the upper excited states to the ground state, they will emit light at a different wavelengths and this will yield atomic spectra. The emitted light intensity depends on the difference in the energies of the two states. This emitted energy can be transformed into a measurable signal. The energy, ΔE, is equivalent to Planck's constant multiplied by the frequency:

$$\Delta E = h\nu \qquad \text{Eq. 4}$$

Since frequency can be calculated as:

$$\nu = c/\lambda \qquad \text{Eq. 5}$$

Thus, combination of equation (4) and equation (5) will give the following equation:

$$\lambda = hc/E \qquad \text{Eq. 6}$$

Where, E is the energy, h is the Planck's constant, ν is the frequency, c is the speed of light and λ is the wavelength number. Equation (6) shows that the wavelength is dependent upon the energy level since h and c are both constant.

1.2 Comparison Between Atomic Emission And Atomic Absorption

There are some differences between atomic emission and atomic absorption spectrometry. Firstly, in the atomic absorption process, an external light source such as that from hollow cathode lamp is required. Normally, the hollow cathode lamps contain a single element or a small group of elements capable of producing a particular light at the same energy or wavelength as that required by the absorbing analyte atoms for excitation to occur. However, the number of elements which can be configured in one lamp is limited. Thus, most of the elements have to be determined sequentially. The light, which is passing through the atom vapour, will then be absorbed by analyte atoms which are in the ground state and this process will reduce the light intensity. The different intensity between incident and emergent light will be recorded by the detector. The process of emission is the exact reverse of the absorption process. In atomic emission spectroscopy, the analyte atoms themselves become the light source and no external sources are required. All the light emitted by analyte atoms during the decay process will be read by the detectors.

In atomic emission, the signal arises from excited atoms and is strongly affected by the temperature because this variable has a significant effect on the ratio between excited and unexcited atoms. The ratio of excited and unexcited atom is represented by the Boltzmann distribution equation as follows:

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp -E_j / kT \qquad \text{Eq. 7}$$

Where;

N_j is the number of atoms in an excited state,

N_o is the number of atoms in ground state,

k is the Boltzmann constant (1.38×10^{-16} erg/deg),

T is the temperature in Kelvin, and

E_j is the energy difference in ergs between the excited state and ground state.

P_j and P_o are the statistical weights of the excited state and ground state, respectively.

In contrast, atomic absorption is less dependent upon temperature because measurements are based on absorption of light produced by a hollow cathode lamp by an unexcited atom rather than an excited one. The relatively low temperatures in atomic absorption spectrometry, however, contribute to the relatively low efficiency of the atomization process and this may lead to chemical interference. Chemical interferences, often referred to as stable compound or solute vaporisation interference, is by far the most frequently encountered type of interference in atomic absorption spectrometry. Basically, a chemical interference can be defined as anything that enhance or suppresses the formation of ground state atoms in the atomizer. A typical example is the interference produced by silicates and phosphates in the determination of magnesium, calcium and many other metals. This is due to the formation of low volatility silicates and phosphates, which are only poorly atomised to the ground state at the flame temperature being used.

Both atomic absorption spectrometry and atomic emission spectrometry, however, are influenced by many factors. Not only the slope of the calibration graph but also its curvature, the detection limit and the occurrence of interferences are dependent on the instrument and on its many variables.

1.3 Analytical Advantages Of The Inductively Coupled Plasma Atomic Emission Spectrometry

Since it became commercially available, inductively coupled plasma atomic emission spectrometry has moved quickly to replace many other techniques of analysis for metallic elements due to its many analytical advantages. Some of the advantages are as follows:

i. Rapid multi-element determination [8, 24, 37, 38]. It is capable of providing emission lines for a large number of elements. Unlike atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry can be operated for simultaneous or sequential multi-element determination of elements. This is because the analyte elements themselves become the light source and the inductively coupled plasma does not require an external primary source for the excitation of the atoms. Hence simultaneous determination is possible [39].

ii. High sample throughput [23]. A measurement can be taken in a few seconds.

iii. Low detection limit for most elements [8, 40]. Fassel and Kniseley [41] and Winefordner *et al.* [39] have had determined the detection limits of more than sixty elements using inductively coupled plasma atomic emission spectrometry and compared the results with flame atomic absorption spectrometer. Many elements showed better detection limits in the inductively coupled plasma atomic emission spectrometer than in the flame atomic absorption spectrometer.

iv. Comparative freedom from chemical interferences [32, 40]. The temperature in the plasma excitation source can reach 8,000K [42, 43], where, at this point, more free atoms will be formed from the dissociation of the precursor compound. As mentioned by some workers [44, 45] the much higher temperature and longer residence time of particles in the plasma should lead to a greater degree of conversion to free atoms. This very high temperature should also minimise the depressant effects of chemical interference that are common in flame spectrometers [44].

v. Large linear dynamic concentration range [2, 8, 32]. A large linear dynamic concentration range has particular advantages for simultaneous or sequential multi-element determination because high level concentrations and trace elements can be determined in the same solution. Thus, it will simplify sample preparation, calibration procedures and, in some cases, dilution may be avoided.

vi. Lower operating cost for analysis of number of elements per sample compared with atomic absorption spectrometry or conventional wet chemical techniques.

vii. Relative ease of operation [8].

viii. High sensitivity [32, 37].

In their paper, Greenfield *et al.* [46] listed the desirable properties in an excitation source.

They are;

i. capability of exciting a large number of elements
ii. high sensitivity
iii. good stability
iv. freedom from interferences
v. reproducibility in the introduction of samples
vi. convenience of operation

Winefordner *et al.* [39] had commented that: "...... *atomic emission using a rf inductively coupled plasma as an excitation source constitutes the most promising approach*". Later, Greenfield [47] then wrote: "...... *of all sources currently available, the inductively coupled plasma torch most nearly satisfies these* (the above) *criteria*". Although the inductively coupled plasma atomic emission spectrometer appears to have great potential application for the analysis of metal elements, its use has been limited by the high capital cost of the basic equipment.

1.4 The Main Components Of An Inductively Coupled Plasma Atomic Emission Spectrometer

An inductively coupled plasma - atomic emission spectrometer consists of three major components as follows:

i. the sample introduction system
ii. the excitation source
iii. the monochromator and the detection system

1.4.1 The Sample Introduction System

There are several types of sample introduction system for inductively coupled plasma spectrometers that cover slurries, solids, powders, gases and liquid samples. However, only a liquid sample introduction system has been used in this study. The liquid sample introduction system, which is the most common method employed in an inductively coupled plasma spectrometer [5], plays a vital role in bringing the sample solution into the excitation source. It normally consists of peristaltic pump, spray chamber, pneumatic or ultrasonic nebulizer and plasma torch. The main objective of the liquid sample introduction system is to generate an aerosol of the analyte solution in a carrier gas. Subsequently, the aerosol must be injected into the excitation source without causing the plasma to collapse [48].

1.4.1.1 The Nebulization System

The action of the excitation source in atomising and exciting an analyte is worthless if the analyte cannot be introduced in an appropriate form. Thus, most atomic spectroscopy instruments employ a nebulizer in their liquid sample introduction system as most samples can be converted into a solution [5, 49, 50]. The nebulizer may generate the aerosol pneumatically or ultrasonically. Both types of nebulizers are normally constructed from glass that is relatively chemically inert. In cases where hydrofluoric acid is used to digest the sample, polytetrafluoroethylene (PTFE) nebulizers may be employed. There are several types of pneumatic nebulizers that are used in inductively coupled plasma spectrometers. The two most common nebulizers in use are concentric and cross-flow. The cross-flow nebulizer, which was first designed by Kniseley and co-workers [51] has been reported as one of the most widely used for sample introduction [52]. As with the cross-flow nebulizer, all other pneumatic nebulizers employ a sample capillary tube and a gas orifice. A high velocity argon stream of nebulizer gas produces a low pressure at the capillary tip, drawing sample solution into the capillary, where the nebulizer gas collides with the sample stream and disrupts it into an aerosol. Note however that concentric and cross-flow nebulizers can also be used satisfactorily with samples containing a low amount of suspended solid. Since a narrow capillary tube is used for the sample introduction in the nebulizer, care has to be taken to ensure that the sample solution contains no suspended solid particles that can lead to nebulizer blockage [37]. A high salt containing solution is always likely to contribute blockage problems in the capillary by building up a precipitate at the capillary tip. This can be avoided by flushing the nebulizer with distilled water for several minutes. To overcome repeated blockage problems, some workers [53, 54] have constructed a nebulizer that is known as v-groove nebulizer. In this type of nebulizer, the solution is not confined to a narrow capillary tube and hence blockage should not be a problem. The v-groove nebulizer can be used satisfactorily to introduce a high solid content solution into the plasma. Besides the v-groove nebulizer, frit [55, 56], ultrasonic [57, 58] and Babington [59, 60] nebulizers can be used to nebulize a solution that contains suspended particles or high amounts of dissolved solid. Layman *et al.* [55] reported that the frit nebulizer has a great efficiency for aerosol production and this leads to generation of higher signal intensity compared to other pneumatic nebulizers.

Ultrasonic nebulizers generate an aerosol by the action of ultrasonic radiation on the liquid samples and has been recognized as a powerful method for aerosol generation [61, 62]. The ultrasonic radiation is generated by the vibrations of a piezo-electric membrane oscillating at very high frequency. As with pneumatic nebulizers, argon gas is used to carry the aerosol to the plasma with low sample loss. The detection limits with an ultrasonic nebulizer are reported to be better than with pneumatic devices providing the matrix is not too complicated [63].

1.4.1.2 The Peristaltic Pump

The peristaltic pump consists of a flexible tube or sample uptake tube that passes around a cylinder with a number of rollers on its surface. When the surface rotates, each roller rolls along the tube and this ensures a constant sample uptake rate [64, 65], especially for viscous samples. In some instruments, the speed of the peristaltic pump is adjustable, so that the sample uptake can be set at the desired rate. The peristaltic pump is used for both pneumatic and ultrasonic nebulizers as both require the sample to be force-fed [66].

1.4.1.3 The Spray Chamber

The aerosol generated by the nebulizer is injected into the plasma through a spray chamber, in which the larger droplets of the aerosol are segregated and drained out whilst the smaller droplets are transported into the plasma. Again, the spray chambers are constructed from chemically inert materials such as glass or polytetrafluoroethylene (PTFE) and are about 100 - 200 ml in volume. A large spray chamber takes a longer time for the signal to reach stability and this will increase the analysis time.

Browner and Boorn [49] have listed three requirements relating to the performance of a spray chamber.

The requirements are as follows:

i. the effective removal of larger droplets for interference-free measurement,
ii. rapid wash-out to reduce analysis time and to avoid cross-contamination, and
iii. smooth drainage of larger droplets to avoid pressure pulses in the atomizer

Concerning the third requirement, Belchamber and Horlick [67] have reported that an improper drain arrangement for the nebulizer spray chamber of an inductively coupled plasma system can lead to emission signal fluctuation proportional to spray chamber pressure fluctuation.

1.4.1.4 The Plasma Torch

The plasma torch used in this study consisted of concentric tubes that are prealigned. This type of torch permits an inner, intermediate and outer flow of argon gas. The inner flow, known as the sample gas flow, is used to transport the sample aerosol into the plasma while the intermediate flow is used for sustaining the plasma. The intermediate gas flow is known also as an auxiliary gas flow. The outer gas flow, also known as the coolant gas flow, is used to shape the plasma and to prevent it from contacting the outer tube of the torch [68]. Commercial inductively coupled plasma spectrometers require high coolant gas flows [66] and hence operations maybe impeded by a shortage of argon gas [69]. Thus water-cooled and air-cooled inductively coupled plasma torches have been proposed. In 1979, Kornblum *et. al.* [70] proposed the use of a water-cooled inductively coupled plasma torch that reduced the consumption of argon gas to 2 l min^{-1}. Later, Ripson *et. al.* [71] introduced an air-cooled inductively coupled plasma torch. Under optimum operating parameters, an air-cooled torch was found to give similar detection limits to those for a conventional plasma torch, but it is technically complicated and creates high noise in the laboratory environment [72]. By contrast, the water-cooled torch is easier to operate [73] but gives poorer analytical performance [74].

1.4.2 The Inductively Coupled Plasma As An Excitation Source

As an excitation source, an inductively coupled plasma offers great potential for the simultaneous [1] and sequential multi-element determination of metallic elements. An inductively coupled plasma can be generated by directing or coupling the energy of a radio frequency generator into an argon gas stream. When the generator supplies the radio frequency, which is normally at 27.12MHz or 40.68MHz, to the cooled induction coil with argon gas flowing upward in the torch, an intense oscillating magnetic field is formed. The plasma is initiated by seeding the non-conducting argon gas with electrons through such means as a spark. The electrons are accelerated in the magnetic field and rapidly reach ionisation energy. Collisions between electrons and argon atoms will then promote further ionisation until the argon gas becomes conductive and a self-sustaining plasma is formed almost instantly. The self-sustaining flame-like plasma will remain running as long as a high-frequency current is supplied to the load coil and gas is supplied to the tube. The aerosol gas stream of sample solution will penetrate the centre of the plasma creating a toroidal or doughnut-shape structure and sample constituents thus pass up through a long and narrow central axial channel. The plasma can achieve a temperature of 8,000K [42, 43, 75] in its hottest zone. This high temperature of an excitation source enables complete atomization and therefore results in a large linear dynamic range for most elemental analyses.

1.4.3 The Wavelength Selector And The Detection System

The spectrometer wavelength selector is used to collect and isolate the analyte wavelengths from other lines emitted by the excitation source. The common components of the wavelength selector are entrance slit, diffraction grating, exit slit and detector. The entrance slit is mounted on the spectrometer frame. The grating is used to diffract the radiation passed through the entrance slit and resolve it into its individual spectral lines for the detector to convert the radiation energy into a measurable electronic signal. The detection system will measure the intensity of the radiation and compare it with a series of known intensity analyte standards (calibration graph) for quantitative determination. The exit slits are accurately positioned on the focal curve immediately in front of the detector. There are two types of wavelength selector commonly in use with inductively coupled plasma atomic emission spectrometers. They are the sequential monochromator and the simultaneous polychromator. Most are evacuated or argon purged to enable the spectrometer to operate down to 160 nm in the ultra-violet region. In a sequential system, the characteristic radiation is focused onto a diffraction disperser or grating through entrance slit. The grating is then rotated to direct the wavelength of interest onto a detector through an exit slit. By choosing any wavelength from both ultra-violet and visible regions, this sequential system offers the flexibility of determining any element of interest. On the other hand, the simultaneous polychromator utilises a fixed grating and multiple exit slits. Each exit slit is equipped with its photomultiplier tube as a detector. The exit slits and detectors are precisely located at appropriate wavelength positions around the circumference of the 'Rowland Circle'. Simultaneous spectrometers obviously offer a rapid multi-element determination because they can be configured with up to sixty detectors. This criteria is very important when the sample is limited and large numbers of samples are to be analysed and times are limited.

1.5 Analysis Of Cement - Introduction

Ordinary Portland cement is manufactured from a feedstock comprising a material containing calcium carbonate (limestone) a clay or shale and a combustible element which is normally coke or coal. In cases where sulphate-resistant Portland cement is to be produced, the addition of a small amount of iron oxide becomes necessary. The mixed material is then passed through a rotating kiln to remove moisture. It is then heated at approximately 1450°C to produce a compound known as clinker. Next, gypsum is added into the clinker and the mixture is ground to ensure that all the components are intimately mixed giving a fine powder of cement. The common compounds in cement are calcium oxide, silicon dioxide, iron oxide, potassium oxide, phosphorus pentoxide, magnesia and alumina. In Malaysia, Ordinary Portland cement is classified as a 'safety product' and must pass a conformance test which consists of chemical and strength tests normally conducted by a government owned company called the Standards and Industrial Research Institute of Malaysia (SIRIM). The results of the test are fowarded to the Construction Industry Development Board (CIDB) for certification where the cement will be certified to be in compliance with CIDB requirements. These requirements not only ensure that the product is of acceptable quality and safe to be used, but also serves to protect the genuine cement traders from unscrupulous parties selling sub-standard material.

In Malaysia, there are several analytical methods or combinations of methods used for the quality control analysis of cement. Most of them employ wet chemical techniques, atomic absorption spectrometry and x-ray fluorescence spectrometry. At the Metals and Building Materials Laboratory of SIRIM, analysis of Ordinary Portland cement is carried out in accordance with the Malaysian Standard Testing Procedure [76, 77]. Testing procedures that employ wet chemical and spectrophotometric techniques are tedious, time consuming and difficult to use on a routine basis. This is because the standard operating procedure cited in the standard needs prior ashing of the cement sample in a muffle furnace with the use of some fusion agents. Subsequently, the ash is dissolved in an acid mixture. Generally, the wet digestion and fusion methods involve constant supervision and require a long time for complete dissolution. However, some laboratories are now using an instrumental approach such as atomic absorption spectrometry or x-ray fluorescence spectrometry to speed up the analysis. Although the atomic absorption spectrometer can be used to speed up the analysis, it is still considered slow because multi-element analysis has to be carried out sequentially. Alternatively, the x-ray fluorescence method needs standard reference materials for calibration purposes which are expensive and sometimes difficult to obtain.

Capacho-Delgano *et al.* [78] have determined aluminium, titanium, silicon, magnesium, iron, manganese, sodium, potassium, lithium and strontium in cement by atomic absorption spectrometry. Titanium, manganese and lithium were determined in the undiluted acid-soluble solution. Subsequently, the same solution was ten times diluted to allow determination of aluminium, iron, strontium, sodium and potassium. For the determination of silica, an aliquot of the fusion solution was diluted 40 times with water. Magnesium was reported to give high sensitivity to atomic absorption spectrometry. The time taken to determined silicon, magnesium, aluminium, iron, titanium, sodium and potassium in four cement samples were reported to be five hours, approximately. Clearly this level of sample throughput is unacceptable nowadays.

Determination of silica in cement by mean of atomic absorption spectrometry was carried out by Price *et al*. [79]. Due to its lack of sensitivity to atomic absorption, an instrument optimization procedure was carried out to obtain the optimum operating parameters for silicon. In their work, the cement sample was treated with a mixture of nitric acid and hydrochloric acid and a matrix effect, which was reported to occur with the presence of aluminium, calcium, iron and sodium, was reported.

A comprehensive scheme for the analysis of cement by using atomic absorption spectrometry was published by Roos and Price [80] in 1969. Ten elements were analysed. They were aluminium, calcium, iron, magnesium, manganese, potassium, silicon, sodium, strontium and zinc. The sample was digested in a mixture of hydrochloric and hydrofluoric acid and good precision was reported for all elements except calcium. They reported that about eight hours or one normal working day was required to complete the analysis of all ten elements in five samples. Again the throughput would nowadays be considered low.

Analysis of major oxides such as silicon dioxide, iron oxide, alumina and calcium oxide in cement has been reported by Choi and co-workers [81] in 1994. A mixture of lithium tetraborate and sodium carbonate was used as a fusion agent and then the fusion cake dissolved by hydrochloric acid. Total time required to analyse all four major oxides was one hour. They reported that the accuracy and precision of results obtained were better than results found from x-ray fluorescence.

In 1970, Nestoridis [82] described a combination method to be used for the analysis of Portland cement. According to his work, only a single sample solution containing 1-gram of cement was required for the determination of all the chemical components of cement. This avoided numerous weighing procedures and the lengthy separation of insolubles was eliminated. Silica was determined by a combined gravimetric-colorimetric method, while the remaining elements were determined either spectrophotometrically, complexiometrically or flame photometrically. However, only two or three cement samples can be analysed for determination of eleven components by one operator in a single working day.

In their research, Casetta *et al.* [83] have applied inductively coupled plasma atomic emission spectrometry to the determination of calcium, silicon, aluminium, iron, magnesium, sodium, potassium and titanium in cement. The sample was attacked with hydrofluoric acid and aqua regia in a teflon pressure vessel at 160°C. It was found that lines at 309.284 nm and 396.152 nm were unsuitable for analysis of aluminium due to a partial overlapping of the calcium line. Hence they chose a line at 308.215 nm to be used for the analysis of aluminium in Portland cement. The cement sample was analysed by atomic absorption spectrometry and wet chemical techniques to compare the results obtained with those from inductively coupled plasma atomic emission spectrometry.

X-ray emission has been used for the analysis of cement raw mix by Andermann [84] in 1961. In his work, he found that inhomogeneity within the particles lead to an error in the values found by this technique. He reported that the analysis of silicon dioxide in cement raw mix samples was inaccurate for unfused samples due to the inhomogeneity. However, he suggested that the cement may be fused or dissolved to improve homogeneity before being analysed by x-ray emission spectrometry.

Frechette and co-workers [85] conducted a study on the analysis of cement using x-ray fluorescence spectrometry. They observed that a fusion method of 40% cement and 60% pure lithium tetraborate as flux agent during sample preparation gave a complete elimination of particle size effects which is a common problem in pellet-formed sample.

In 1987, Caurtault and co-workers [86] analysed calcium, silicon, aluminium, iron, magnesium, titanium, manganese and strontium on a simultaneous inductively coupled plasma spectrometer. Sodium, potassium, barium, phosphorus and sulphur were determined on a sequential spectrometer. Samples were fused with $LiBO_2$ in a platinum crucible and yttrium was chosen as an internal standard. Calibration was at five points using Standard Cement material.

Degre [87] determined calcium, silicon, aluminium, iron, magnesium, sodium, potassium, titanium, manganese, phosphorus, strontium and chromium in cement samples using inductively coupled plasma atomic emission spectrometry. The cement sample was decomposed in a platinum crucible with lithium carbonate and B_2O_3. He used Standard Reference cement which was solubilized in the same way as the sample for calibration. In all measurements, nickel was chosen as the internal standard.

1.5.1 Standard Procedures For The Analysis Of Cement

In many Standard Test Methods for the analysis of cement, different methods of sample decomposition have been recommended for use for the determination of different compounds and a wide variety of analytical techniques have been used. For the American Society of Testings and Materials [88], only sodium oxide and potassium oxide were determined by flame photometry or atomic absorption spectrometry, while the rest of the constituents were determined by conventional procedures such as titrimetric, colorimetric or gravimetric analysis. The British Standard [89] still uses conventional techniques to determine all the constituents except manganese which is determined photometrically. All the procedures used in these Standard Methods [76, 77, 88, 89], however, are not suitable for the analysis of cement samples on a routine basis. Thus, practical techniques which offer rapid and accurate procedures have to be designed as an alternative, which will cut the cost, shorten the analysis time and satisfy all parties concerned. Clearly a single digestion, single analysis procedure is required.

1.5.2 Previous Methods Of Digestion Of Cement Sample

Generally, in instrumental methods such as atomic absorption spectrometry or ultra violet-visible spectrophotometry, the sample has to be completely dissolved. A fusion technique is commonly used for converting the insoluble matrix, which is mainly silicates, to the acid soluble form. Fusion agents such as sodium hydroxide, lithium tetraborate, lithium metaborate and sodium carbonate have been used for siliceous materials such as coke, coal, cement and carbonate rocks. However, each of the fusion agents has its own disadvantage. For example, lithium metaborate is expensive which will cause the operating costs to increase. Lithium tetraborate takes a long time to digest with a combination of hydrochloric and nitric acid. The use of sodium hydroxide requires the use of a platinum or a gold crucible. Furthermore, the use of fusion agents may cause incomplete attack with some refractory minerals and failure to produce a stable solution of the silica when the fused mixture is dissolved in nitric acid [17]. Thus, a new method is required which is less time consuming, more reliable and capable of dissolving the silica completely.

1.6 Analysis Of Steel - Introduction

The analysis of metallurgical sample such as steel for process and production control as well as quality assurance is an important part of the steel-making operation. Major and minor elements in steel are important for an evaluation of the physical and chemical properties of the material. Impurities or incorrect elemental ratios within the sample can greatly affect strength and in some cases cause structural failure [90]. However, residual copper levels enhance the hardness properties of low alloy engineering steels and addition of copper provides a significant improvement in the atmospheric corrosion resistance of strip and structural steels [91]. In another example [92], both yield strength and tensile strength of low alloy steel have been found to increase with chromium content, while the elongation decreases. It has also been reported that the minor elements in steel, such as phosphorus and carbon, change the galvanic reaction not only qualitatively but also quantitatively [93]. Thus, it is important to determine the chemical composition of the steel because different industries require different types of steel. Therefore, these demands require a rapid technique without sacrificing the precision and the accuracy of the results.

In many laboratories, especially in developing countries [94], classical wet chemical procedures such as gravimetry, titrimetry and spectrophotometry are still widely employed. These procedures are normally too laborious and time consuming [24, 32, 95] when compared with the use of high speed instrumentation. Sometimes they present a safety hazard, require constant operator attention and often require large amounts of strong acids to carry out the analysis [15]. Nowadays, in developed countries, most of the analyses of metallurgical samples are performed spectrochemically and wet chemical analyses are seldom used as they are slow, expensive and sometimes inaccurate due to human error. Solid sample dissolution allows the use of established instrumental techniques such as flame and graphite furnace atomic absorption spectrometry and inductively coupled plasma atomic emission or mass spectrometry.

In many metallurgical laboratories, an atomic emission spectrometry source such as an arc and spark emission spectrometer was used because of rapid sample turnaround and the ease of operation [24] coupled with adequate sensitivity for most applications [96]. Although non-destructive multi-element analysis is possible with these instruments, a certified or precise matrix matched Standard Reference Materials is required. These are often not available [24, 32] or very expensive [97]. Furthermore, if the metal sample is in the form of chips or ground to a fine powder, it is then difficult to analyse them by means of this instrumentation. An alternative technique, for example inductively coupled plasma atomic emission spectrometry (ICP-AES), is preferable since calibration can be by use of a synthetic standard solution. The determination of metals in complex samples by ICP-AES requires the destruction of the sample matrix to give a solution of the analyte ready for analysis. It may seem that some of the advantages of inductively coupled plasma atomic emission spectrometry are lost by the requirement for sample dissolution which can be time consuming [96, 97].

Ion chromatography coupled with sequential inductively coupled plasma atomic emission spectrometry detection was employed by Giglio and co-workers [4] to determine chromium, molybdenum, manganese and nickel in a Standard Reference Material steel sample, after digestion with nitric acid. They reported that the use of ion chromatography eliminated spectral interference problems from iron which is normally encountered in plasma emission systems for the analysis of such samples. The determined concentrations of all elements were reported to be close to the certified values, except for chromium, which was not quantitative.

Nakahara [8] reported a simple method to determine phosphorus in steels and copper metals by inductively coupled plasma atomic emission spectrometry in the vacuum ultraviolet region of the spectrum. For this purpose, the monochromator and optical path between the plasma torch and the entrance slit have to be purged with inert gas to reduce light absorption by oxygen in ambient air. In his work, a phosphorus atomic emission line at 178.29 nm was used as an analytical line because it was considered to be free from spectral interferences from iron and copper lines. For accurate determination of phosphorus, a closely matched standard was used for the construction of calibration curves. The results obtained were in good agreement with the certified values. However, it was concluded that some spectral interferences from minor elements in the sample still remained.

An experimental study of the determination of boron in steels by inductively coupled plasma atomic emission spectrometry has been carried out by Coedo and co-workers [98] in 1993. Samples were dissolved by employing a microwave digestion system and a comparison was made of spark ablation and pneumatic nebulization.

1.6.1 Standard Procedures For The Analysis Of Steel

There are many standard procedures dealing with analysis of steels [99-112]. Generally, determination of analytes has been carried out individually and involved different techniques of analysis for the determination of different elements. The most commonly recommended techniques are titrimetry, gravimetry and spectrophotometry. In many cases, the standard procedures recommend a unique method of sample digestion prior to the determination of a particular element. All these factors make the standard procedures too tedious to be practised as routine analytical tool since they give low reproducibility due to operator error.

1.7 The Use Of Microwave-Assisted Digestion In The Analytical Laboratory

Microwave heating of various types of sample in the presence of acids under pressure is now a well-known method for rapid and reproducible digestion prior to elemental analysis [113]. Microwaves are electromagnetic waves whose frequencies range from 300MHz to 1000GHz and most applications of microwave technology make use of frequencies in the 1 to 40 GHz range [114]. The heating property of microwave power is very useful in a wide variety of functions in modern life. A good example of this is a microwave oven used in the kitchen. In a microwave oven, the penetration depth of microwaves is larger compared with the infrared waves in an ordinary oven. The entire volume of food is heated directly and uniformly by the microwave radiation. Thus, microwave cooking can be accomplished in about one-tenth the time required by conventional methods. In the chemical laboratory, microwave ovens or microwave-assisted digesters have been used by some workers to digest many types of sample in an acid medium [115-121]. Nadkarni [122] has reported the digestion of some geological samples and has proposed a possible mechanism of microwave action. He reported that the microwave power is simply acting as a source of intense energy to rapidly heat the sample. However, a chemical reaction is still necessary to complete the dissolution of the sample into an acid solution. As microwave heating is internal as well as external, the heat conduction stage is avoided because energy is instantly transferred to the sample by absorptive polarisation rather than by molecular collisions. He considered that local internal heating, taking place on individual particles, can result in the rupture of the particle, thus exposing a fresh surface to the reagent contact. He added that heated dielectric liquids or the medium in contact with the dielectric particles would generate heat orders of magnitude above that of the surface of a particle. This can create a large thermal convection current which can agitate and sweep away the stagnant surface layers of dissolved solution and thus expose fresh surface to fresh solution. Additionally, the use of a closed pressurised vessel helps digestion by increasing the temperature of the sample solution, hence the required boiling point is achieved more rapidly. In this study, the beneficial properties of the microwave are used to digest steel and cement samples.

1.8 Aims And Objectives

The aim of this study is to develop an analytical protocol for the simultaneous determination of major and minor constituents in cement and steel samples. Test will be performed to find the simplest procedure for stable and total dissolution of all samples for their quantitative determination. The scope of the project will cover the development of digestion procedures of related samples by a microwave-assisted digestion system prior to elemental determination. The developed methods will then be proved to be scientifically valid by use of appropriate Standard Reference Materials. The technique of choice is inductively coupled plasma atomic emission spectrometry (ICP-AES) which is now established as an analytical technique. All measurements of intensities and/or concentration of the analyte will be carried out simultaneously, and therefore, a single sample solution is required for determination of all elements without further dilution.

CHAPTER 2 - EXPERIMENTAL

2.0 Experimental

2.1 Apparatus And Instrumentation

To perform the project, the following instruments are required:

2.1.1 The Spectrometers

Two models of inductively coupled plasma atomic emission spectrometer were used to perform this study, namely a Thermo-Jarrel Ash and a Spectroflame. A Thermo Jarrel Ash model ICAP 9000 (hereinafter known as a Jarrel-Ash-ICP), is a simultaneous multi-element inductively coupled plasma atomic emission spectrometer and was used for the analysis of steel samples. The instrument was manually operated but all the data was processed through a computer which was interfaced to the instrument. The instrument was configured with 30 fixed analytical channels and allowed single and simultaneous multi-element analysis. With the use of the nearby lines technique, however, more elements could be analysed both qualitatively and quantitatively. Radio frequency forward power of the instrument ranged from 0.5 kW to 2.5 kW and operated at 27.12 MHz. The spectrometer was under vacuum while the optical path was argon purged to allow determination of elements in the ultraviolet region. The argon gas flow rates for coolant, carrier and auxiliary were adjustable from 0 to maximum of

20 l min^{-1}, 5 l min^{-1} and 2 l min^{-1}, respectively. The nebuliser pressure was fixed at 30 psi and adjustment was limited. Thus all experiments related to the analysis of steel samples were conducted at the same nebuliser pressure. Throughout the study, a pneumatic cross-flow nebuliser has been employed to produce the aerosol. The nebuliser consisted of a sample capillary tube at right angles to a capillary tube carrying the high velocity argon nebuliser gas stream, set in a Teflon body. Since there was no built-in peristaltic pump, an external multi speed peristaltic pump was used to introduce the sample solution into the nebulizer. The peristaltic pump (Gilson Minipulse) had a variable speed control to set the sample solution flow at the desired rate. The software, which was installed in the Apple II microcomputer, allowed the user to perform wavelength and time scans which were important during method development. All the data acquisition was also controlled from the same software.

The Spectroflame-ICP was used for measurement of the intensity of all solutions related to the analysis of cement. This spectrometer contained a combination of polychromator and monochromator and any desired analytical lines which were not in the polychromator system were selected by the monochromator. Hence this instrument could be used for simultaneous or sequential multielement determination. There was in-built operating and data acquisition software which enabled the user to operate the instrument through the keyboard. The instrument was equipped with single speed build-in peristaltic pump, therefore, an external peristaltic pump, as used in the Jarrel-Ash-ICP, was added, for method development work.

2.1.2 The Microwave-Assisted Digestion System

The microwave-assisted digestion system was a Milestone Model MLS-1200 MEGA. It had an unlimited variable time setting and the heating cycle was based on power settings. The power emission was microprocessor controlled from 0 to 1000 W operating at a frequency of 2450 MHz, which was equivalent to a wavelength of 12.25 cm. This microwave-assisted digestion system was capable of holding ten 100 ml volume Teflon vessels at one time and was equipped with an exhaust tube to allow venting of vapour generated during digestion, evaporation or drying of samples inside the microwave cavity and to ensure cooling of the carousel during operation. The exhaust flow rate was 5 $m^3 min^{-1}$.

Ordinary laboratory glassware used included Class A 50 ml and 100 ml capacity borosilicate volumetric flasks, 100 ml capacity beakers and micropipettes.

2.2 Chemicals And Reagents

The following reagents were used to perform this study:

i. Hydrochloric acid, 35%, 'Aristar' grade, Specific gravity of 1.18

ii. Nitric Acid, 69%, 'Aristar' grade, Specific gravity of 1.42

iii. Hydrofluoric Acid, 40%, 'Aristar' grade

iv. Orthoboric acid, 'Aristar' grade

v. 10,000 $\mu g\ ml^{-1}$ Standard Solution, 'Spectrosol' grade each for iron and calcium

vi. 1,000 $\mu g\ ml^{-1}$ Standard Solution, 'Spectrosol' grade each for phosphorus, silicon, potassium, nickel, sodium, aluminium, molybdenum, manganese, magnesium, chromium and cobalt.

All the chemicals and standard solutions, except that for silicon, were obtained from BDH Laboratory Supplies, Poole, England. The silicon standard solution was obtained from Hopkin and Williams, Chadwell Heath, Essex, England.

2.3 Standard Reference Materials

All the validation of the methods developed in this study was performed using Standard Reference Materials. Listed below are the Standard Reference Materials for low alloy steel, high alloy steel and cement.

A. Low Alloy Steel

1. BCS/SS-CRM No. 402/2 (Low Alloy Steel)
2. EURONORM-CRM No. 186-1 (Silico-Manganese Steel)

B. High Alloy Steel

1. EURONORM-CRM No. 292-1 (Niobium Stabilised Stainless Steel)
2. EURO-CRM No. 281/1 (Highly Alloyed Steel)

C. Cement

1. BCS-CRM No. 372/1 (Ordinary Portland Cement)

All the Standard Reference Materials listed above were purchased from Bureau of Analysed Samples Limited, Newham Hall, Middlesbrough, England.

2.4 Choice Of Analytical Lines

Analytical lines for all elements were selected directly from the computer. However, in the Spectroflame-ICP, if there was no analytical line or lines provided within the simultaneous system or they were badly interfered with by other elements, an alternative line was chosen from the sequential system. Since the Jarrel-Ash-ICP was equipped with a fixed simultaneous system, an alternative analytical line could only be identified by performing 'nearby-line' wavelength scanning.

2.5 Instrument Profiling

It is essential to evaluate the spectrometer before performing any analysis to ensure that the instrument is in calibration. As recommended by the manufacturer, evaluation was carried out by aspirating a copper solution into the plasma and monitoring the copper line at 324.754 nm.

2.6 Optimization Of The Operating Parameters

In order to obtain optimum operating parameters, optimization was performed with respect to the inductively coupled plasma instrument and to the sample introduction system. Since a simultaneous analysis technique was used, the inductively coupled plasma was optimized by introducing a solution which contained all the analyte elements, allowing a compromise set of operating parameters to be chosen. The optimization process for the inductively coupled plasma instrument covered observation height, radio frequency forward power, plasma argon flow rate and coolant argon flow rate. For the sample introduction system, wherever applicable, the optimization process included the carrier argon flow rate, the nebulizer gas pressure and the sample up-take rate. For optimization purposes, the signal to background ratio (SBR) of the ICP-AES was calculated according to the following equation :

$$\text{Signal To Background Ratio, SBR} = I_n / I_b \qquad \text{Eq. 8}$$

where;

I_n is the net analyte emission intensity, and

I_b is the background emission intensity

Then, a graph of SBR against parameter under study was plotted and from the graph, a compromise set of operating parameters was selected.

2.7 Matrix Effect

During the analysis, the presence of a matrix effect may cause enhancement or depression of analyte emission intensity, thus introducing errors into the analytical procedure. To study the matrix effect, a solution containing analyte elements without and with the presence of matrix was introduced into the plasma at the same operating parameters. The analyte concentration was kept constant in all solutions while the matrix concentration was varied in a series of known concentrations. The percentage of matrix effect, M %, was then calculated according to the following equation :

$$\text{Matrix Effect, M \%} = [(I_m - I_n) / I_n] \times 100 \qquad \text{Eq. 9}$$

where;

I_n is the net analyte emission intensity in distilled water

I_m is the net analyte emission intensity in the presence of matrix

The matrix effects studied were:

i. volume of acid used, and

ii. the effect of major elements on the determination of minor elements.

2.8 Inter-Element Correction

Inter-element spectral interferences occur when elements in the sample contribute a significant emission intensity at a wavelength which is close to the analyte analytical line. The intensity contributed by the matrix elements will normally enhance the concentration of the analyte element. Inter-element correction, then, must be applied to all the analytes to minimize the effects of interfering element emissions. In this study, the inter-element correction factor was determined as follows. Aspiration of 100 $\mu g\ ml^{-1}$ of the single analyte solutions, by using the method developed for the analysis of the sample, gave the apparent concentration values produced at each channel. The other elements should have read zero or less than the detection limit for the element. If the apparent concentration of other elements was higher than the detection limit, then the inter-element correction factor was calculated as follows:

$$\text{Inter Element Correction Factor, IEC} = Ce / Ca \qquad \text{Eq. 10}$$

where;

Ce is the concentration of analyte found from interfering element

Ca is the concentration of interfering element

2.9 Preflush Time

Preflush time was the time required before any measurement was made. To assess this, a sample solution was aspirated into the system after a blank solution of distilled water was introduced, taking note of the time when the sample uptake tube was switched into the sample solution. The intensity of each analyte was recorded at intervals until no significant changes in the intensity was observed. A graph from the resulting data was plotted and inspected in order to obtained the time required for each element to reach the steady state condition for stable emission.

2.10 Memory Effect

Memory effects are effects which depend upon the relative concentration differences between samples or standards when analysed sequentially. Sample deposition on the uptake tube, nebulizer, spray chamber or torch, may affect the extent of the memory interferences which may be present. To verify that memory effects did not have an adverse impact on data obtained from the instrument, the memory test was performed on the instrument before any analysis was conducted. A sample solution was aspirated into the system for a normal sample exposure time. Secondly, a blank solution of distilled water was introduced, taking note of the time when the sample uptake tube was switched into the blank solution. The resulting data was inspected to identify the time required for each element to reach a constant emission. If a memory problem existed for a given analyte, then the rinsing time or the speed of peristaltic pump or both were increased until the memory effect was minimised.

2.11 Sample Digestion Procedure

All samples were digested by using a combination of acids in the microwave-assisted digestion system. As the main aim of this project was to develop the method of digestion of cement and steel samples all the digestion procedures used will be discussed in detail in Chapter 4.

2.12 Expression Of Results.

The percentage by mass of each element is given by the expression:

$$\text{Percentage by mass, \% (m/m)} = \frac{(b-c) \times D \times F \times 100 \times 100}{10^6 \times m} \qquad \text{Eq. 11}$$

$$= \frac{(b-c) \times D \times F}{100 \times m} \qquad \text{Eq. 12}$$

Where:

b is the concentration of element in the test solution expressed in $\mu g\ ml^{-1}$

c is the concentration of element in the reagent blank solution expressed in $\mu g\ ml^{-1}$

m is the mass, in grams, of the test portion

D is the dilution factor applied in 'standard addition' procedure

F is the conversion factor of each element to their oxide compound. However, this conversion factor is applicable only for analysis of cement and the values were 2.139, 3.779, 2.859, 1.399, 1.658, 1.873, 2.409, 2.696 and 4.583 for silicon, aluminium, iron, calcium, magnesium, manganese, potassium, sodium and phosphorus, respectively.

CHAPTER 3 - INSTRUMENTATION

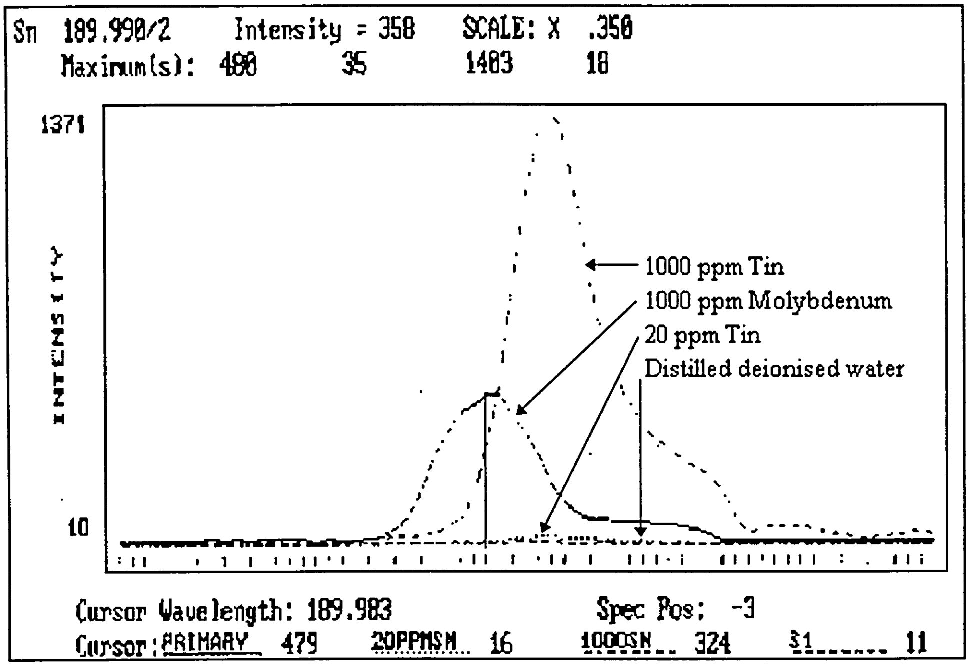
3.0 Introduction

This chapter is concerned with instrumentation which involves selection of analytical lines, optimisation of analytical lines, and a study of spectral and matrix interferences.

3.1 Selection Of Analytical Lines

There are two main criteria to be considered when choosing an analytical line: sensitivity and freedom from spectral interference [18, 123]. Sensitivity becomes very important especially when a low concentration of an element is to be analysed. In this study, sensitivity is defined as signal per unit concentration ratio, where the higher the ratio the higher the sensitivity. Besides the sensitivity, spectral interferences must also be minimised to maximise the value of the analytical results. Although the Jarrel-Ash-ICP used for the analyses of high and low alloyed steels in this study was fitted with 30 fixed channels for different elements which included almost all the desired elements in steel and cement (except phosphorus), each analytical line still had to be checked for spectral interferences. This was because the channel configuration of the spectrometer used was set up primarily for water and waste water analyses and was not specifically designed for either the analysis of steels or cements. However, the versatility of the spectrum shifter offset technique allowed the user to make use of wavelengths that were not programmed in the original configuration. For example a wavelength scan, showed that the analytical line for molybdenum at 202.030 nm is severely interfered with by chromium. Since both elements are present in steel, an alternative analytical line for molybdenum must be chosen by using the nearby line or the spectrum shifter offset technique which was available within the operating software. The same technique has also been used to investigate the analytical line for phosphorus. From the wavelength scans (Figure 2), it was found that the analytical line for tin at 189.990 nm can be used for the determination of molybdenum. However, this only can be done by assuming that the concentration of tin in steel is at a very low level and thus it will not affect the intensity of 'molybdenum' response. The same procedure was used to investigate the analytical line for phosphorus and it was found that there is a phosphorus line at either the calcium channel (Figure 3) or the potassium channel (Figure 4). By assuming that the presence of calcium and potassium in steel is negligible (a reasonable assumption), the use of an analytical line which is very close to a calcium or a potassium line to determine the concentration of phosphorus should not be a problem. However, the potassium line was chosen to be used for the quantitative determination of phosphorus as the sensitivity of phosphorus at this line is much higher compared to the sensitivity obtained from the calcium line. This investigation also found that the nickel channel at 231.604 nm cannot be used for quantitative measurement because the peak is broadened. However, a new analytical line for nickel was obtained from near the cadmium line (Figure 5).

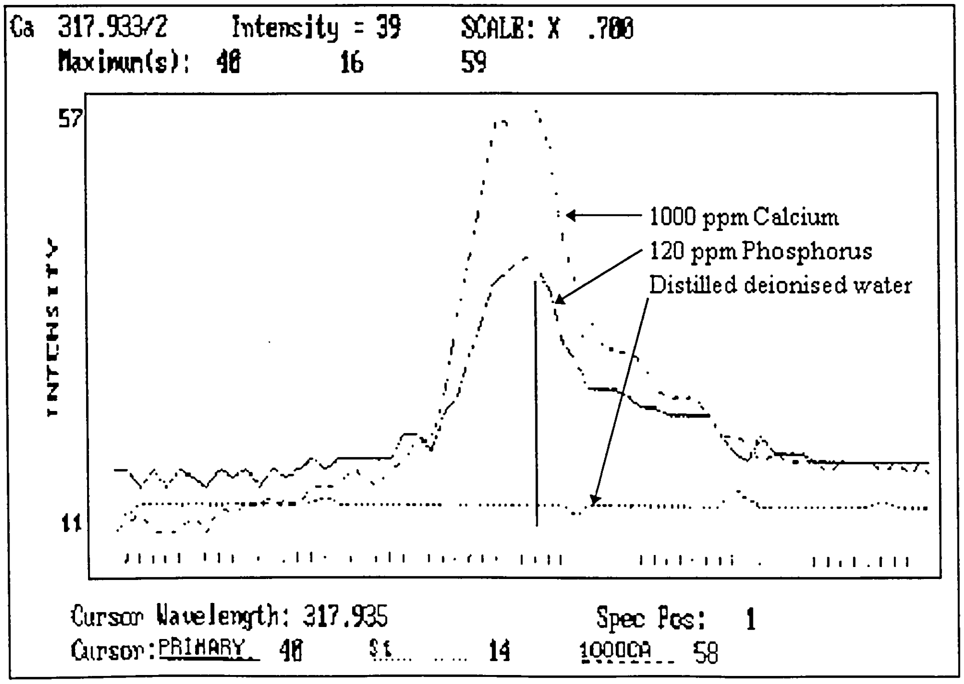
Figure 2. *Wavelength scan of molybdenum, tin and distilled water at tin analytical channel.*



Sn 189.990/2 Intensity = 358 SCALE: X .350
Maximum(s): 480 35 1403 10

Cursor Wavelength: 189.983 Spec Pos: -3
Cursor:PRIMARY 479 20PPMSN 16 1000SN 324 $1 11

Figure 3. *Wavelength scan of phosphorus, calcium and distilled water at calcium analytical channel*



Ca 317.933/2 Intensity = 39 SCALE: X .700
Maximum(s): 40 16 59

Cursor Wavelength: 317.935 Spec Pos: 1
Cursor:PRIMARY 40 $1 14 1000CA 58

Figure 4. *Wavelength scan of phosphorus, potassium and distilled water at potassium analytical channel.*

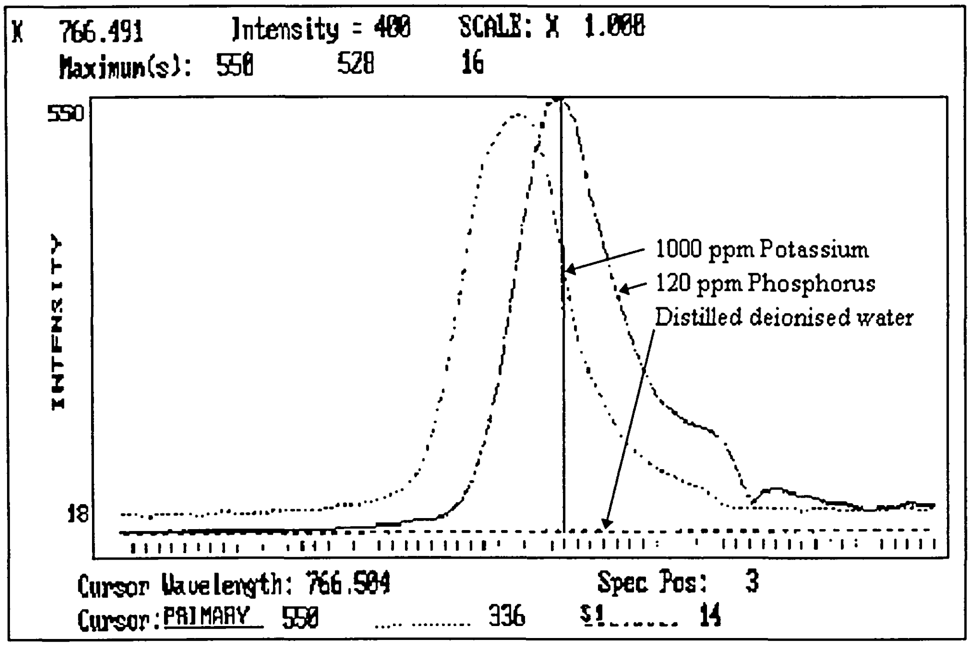
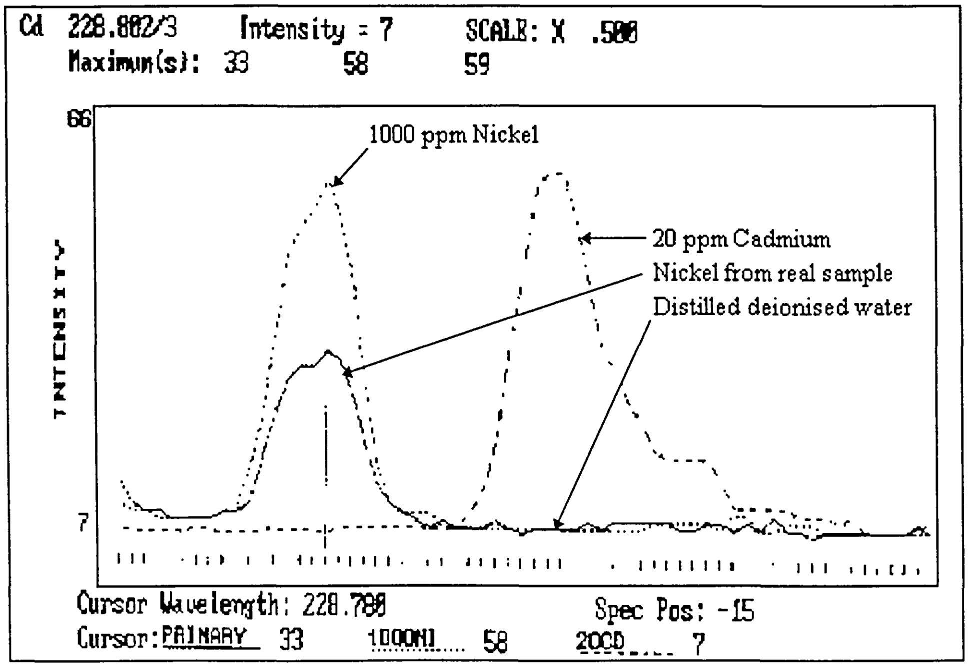


Figure 5. *Wavelength scan of cadmium, nickel and distilled deionised water at cadmium analytical channel.*



From the wavelength scans, the information about the new analytical lines and the spectrum shifter positions were recorded and the data added into the analytical programme in the computer under 'element information'. This will allow the computer to measure the intensities at the correct wavelengths and spectrum positions. The list of analytical lines for analysis of steel and cement is thus summarized in Table 1.

Table 1. *Analytical lines for analysis of steel and cement*

Element	Analytical Line, nm	
	Steel	Cement
1. Nickel, Ni	228.780	
2. Copper, Cu	324.754	
3. Molybdenum, Mo	189.983	
4. Manganese, Mn	257.610	
5. Chromium, Cr	267.716	
6. Phosphorus, P	766.504	213.620
7. Aluminium, Al	308.215	308.215
8. Silicon, Si	288.158	251.61
9. Potassium, K		766.490
10. Sodium, Na		589.592
11. Magnesium, Mg		285.213
12. Calcium, Ca		317.933
13. Iron, Fe		259.940

3.2 Instrumental Operating Parameters

During the preliminary study, it was found that the analyte emission signal was dependent on several instrument operating parameters, particularly the nebuliser pressure, the observation height, the carrier gas flow rate, the sample uptake rate and the radio frequency forward power. However, the analyte emission signals are somewhat less dependent on auxiliary and coolant gas flow rate. Therefore, each analytical line of the inductively coupled plasma atomic emission spectrometer was optimised to achieve the optimum signal-to-background ratio (SBR). The optimisation was carried out by adjusting the parameter under study whilst the other parameters were kept constant. The parameters included in the optimisation procedure were the forward power, the gas flow rates, observation height, nebuliser pressure and sample uptake rate.

The main effect of the nebulizer pressure setting is on the fraction of the nebulized sample reaching the plasma. Crystallisation or deposition of sample, especially at high salt content, corrosion and wear of the nebulizer may lead to a decrease in efficiency and increasing instability. This will caused fluctuation in emission intensity. The quantity of the element reaching the plasma and thus the emission measured, depends on the rate of aspiration and the fraction of the nebulized sample which is carried forward into the plasma. Consequently, all the physical properties involved, such as nebulizer pressure, surface tension and viscosity should be matched as far as possible, for the calibration and analyte solutions.

The carrier gas flow-rate influences the residence time of the particles in the plasma [124]. Too low a flow-rate means less particles are delivered while too high a flow-rate will reduce the residence time of the particles in the plasma so that the aerosol does not have enough time for the ionisation processes to occur efficiently [125]. A decreasing residence time for the particles thus causes a depressant effect on the analyte emission signal.

Auxiliary and coolant gases appear to play a different role. Auxiliary gas is used to sustain the plasma just above the central tube of the torch. Adjustment of the auxiliary gas flow-rate will alter the plasma vertical position, and hence change the SBR. During the optimisation procedure, it was observed that lowering the auxiliary gas flow rate below 0.7 l min^{-1} in the Jarrel-Ash-ICP and by 30 arbitrary units in Spectroflame-ICP brought the plasma down to touch the central tube of the torch. If this happened, it caused the torch to start melting. Additionally, the coolant and aerosol gas flow rates were adjusted so that a toroidal plasma is formed. This shape of the plasma greatly facilitated the entry of the cold aerosol into the plasma [126]. It was observed that a change in coolant gas flow rate did not alter the plasma vertical position, hence there was no significant change in SBR value. In addition, coolant gas may act to prevent the plasma from contacting the inner side of the outer tube of the torch.

It was observed that the best SBRs for sodium and potassium were obtained at high observation heights and low radio frequency forward power. The rest of the analytes were found to give their best SBRs at medium observation height and at 1.3 kW and 1.1 kW each in 'Spectroflame-ICP' and 'Jarrel-Ash-ICP', respectively. A compromise set of operating conditions for spectrometer used for the analysis of both cement and steels is summerised in Table 2 and Table 3.

Table 2. *Compromise operating parameters of 'Spectroflame-ICP' for analysis of ordinary Portland cement*

RF Forward Power	1.3 kW
Observation Height	14 mm
Nebuliser	Cross flow
Spray Chamber	Scott-type Double pass
Nebuliser Pressure	35 psi
Gas Flow Rates:	
Auxiliary	40 arbitrary unit
Coolant	80 arbitrary unit
Pump Tubing	1.42 mm i.d.
Sample Uptake Rate	1.2 ml min^{-1}
Integration Time	3 s
Output Mode	Intensity

Table 3. *Compromise operating parameters of 'Jarrel-Ash-ICP' for analysis of steel sample*

RF Forward Power	1.1 kW
Observation Height	14 mm
Nebuliser	Cross flow
Spray Chamber	Scott-type Double pass
Nebuliser Pressure	30 psi
Gas Flow Rates:	
Auxiliary	1.1 l pm
Coolant	18 l pm
Carrier	0.5 l pm
Pump Tubing	1.42 mm i. d.
Sample Uptake Rate	1.1 ml min^{-1}
Integration Time	3 s
Output Mode	Concentration

3.3 Inter-Element Interferences

Unfortunately, all the technical advantages of inductively coupled plasma (see Chapter One) were accompanied by spectral interferences. Although the analytical line has been optimised, spectral interferences cannot always be avoided. Spectral interferences, which are often apparent, occur when a matrix element present in the sample gives an emission line very close to the wavelength used for analyte element. The measured amount of analyte element then will be erroneously high because the spectrometer will record the emission from both analyte and interfering element but ascribe the total only to analyte element. Thus, spectral interferences must be identified and eliminated or corrected for. The inter-element correction factor, however, can only be used when 'concentration' mode is chosen as the output mode. Because of this, correction could only be carried out with the Jarrel-Ash-ICP.

Table 4. *Interfering element and inter-element correction factor*

Element	Interfering Element	Inter-element Correction Factor
Aluminium	Cobalt	0.00107
	Molybdenum	0.00149
	Nickel	0.00117
	Silicon	0.00254
	Phosphorus	0.00095
	Iron	0.00067
Molybdenum	Aluminium	0.01923
	Iron	0.01603
Silicon	Aluminium	0.00577
	Chromium	0.00720
	Molybdenum	0.02353
	Nickel	0.00779
	Phosphorus	0.00233
Chromium	Cobalt	0.00052
	Iron	0.00105
	Molybdenum	0.00182
	Nickel	0.00088
	Silicon	0.00123
	Phosphorus	0.00105
Copper	Iron	0.00020
Manganese	Iron	0.00014
Phosphorus	Copper	0.00005
	Molybdenum	0.00027
	Nickel	0.00027
Nickel	Molybdenum	0.00052
	Silicon	0.00116
	Phosphorus	0.00057
	Iron	0.00041
	Aluminium	0.00014

(n = 3)

From the results, it was found necessary to make a correction even though the spectral overlap was minimal because the concentration of interfering elements especially iron was variable. The interfering element and the relevent inter-element correction factors are presented in Table 4. Values presented in Table 4 show that the interfering element and the interelement correction factor obtained from the experiments were significant up to five decimal places. The same Table also shows that the interfering element may appear in many analytical lines especially for a spectrally rich element. For example, silicon appears at 308.215 nm, 267.716 nm and 228.802 nm, which are used for analysis of aluminium, chromium and cobalt respectively. Molybdenum also gives an inter-element interference to aluminium, silicon, chromium, phosphorus and cobalt. The appearance of spectral interferences in these analytical lines, is often due to the tail of a broadened peak but may also be due to a peak for a weak line. This type of interferences must be compensated for in order to achieve good results. The calculated inter-element correction factors were then stored in the computer.

The effectiveness of the inter-element correction applied in this study is shown in Table 5 and Table 6. In this work, a solution containing a known analyte element, at 5 $\mu g\ ml^{-1}$, was added with various concentrations of interfering element. The solutions were then analysed by two different analytical programs which were developed earlier, employing corrected and uncorrected inter-element interference factors.

Table 5. *Effect of iron as an interfering element on recovery of copper and manganese in corrected and uncorrected system*

Amount of iron added into the solution, μg ml^{-1}	Recovery, μg ml^{-1}			
	Copper		Manganese	
	Uncorrected	Corrected	Uncorrected	Corrected
0	5.03	5.01	5.01	4.98
10	5.01	5.01	5.02	5.01
100	5.03	5.0	5.15	5.0
1000	5.61	4.99	6.05	5.01
5000	7.90	5.01	8.25	4.97

Table 6. *Effect of multi-interfering elements on recovery of aluminium in corrected and uncorrected system*

Amount of interfering elements added into the solution, μg ml^{-1}					Recovery, μg ml^{-1}	
Fe	Mo	Ni	Si	P	Uncorrected	Corrected
0	0	0	0	0	5.01	5.0
10	10	10	0	0	5.03	5.01
100	50	50	100	10	5.35	5.02
200	100	100	200	10	5.61	5.015
200	100	100	100	50	5.41	5.02

Data from Table 5 and Table 6 demonstrates that the use of interelement interference correction factors gives excellent recovery results. Data from both Table 5 and Table 6 shows that the inter-element corrections can be made over a wide concentration range of interferent and are also applicable for multi-inter-element interferences.

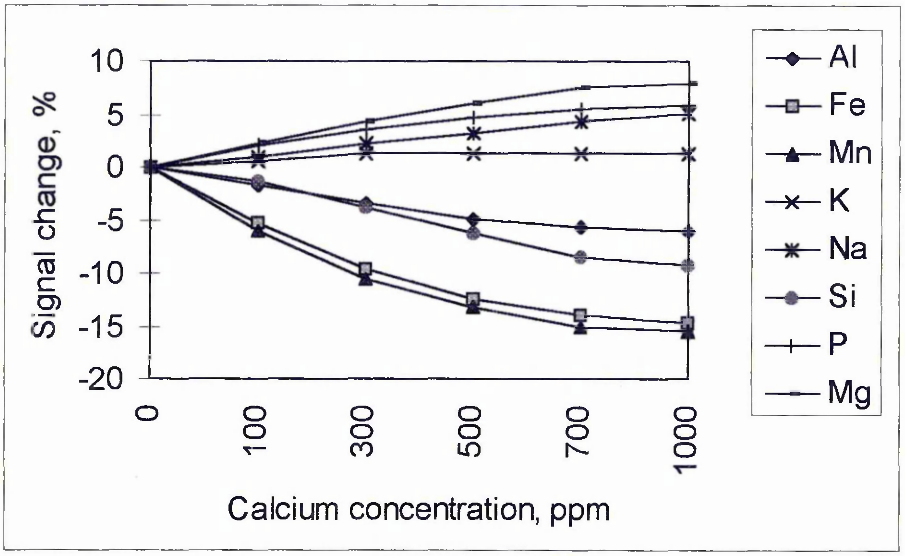
3.4 Matrix Effects

As reported by Niedermier and co-workers [127], the presence of a matrix element in a sample analysed by emission spectroscopy may affect analyte spectral line intensity. Therefore, in this study, the effect brought about by matrix elements on the analyte sensitivity was evaluated for use in guidelines for the preparation of standard solutions.

3.4.1 Effect Of Major Elements On Analyte Emission Intensities

In this study, the magnitudes of matrix effects brought about by calcium and silicon (as major elements in cement), iron, nickel and chromium (as major elements in steel) and acids as the media, on selected analytes, were evaluated. The effect of calcium on the intensity of emission signal for aluminium, iron, manganese, magnesium, potassium, sodium, silicon and phosphorus is illustrated in Figure 6. Here, analyte concentration was kept constant at 5 $\mu g\ ml^{-1}$ and the emission intensities were measured in the presence of various concentrations of calcium and the percentage of matrix effect due to calcium was calculated.

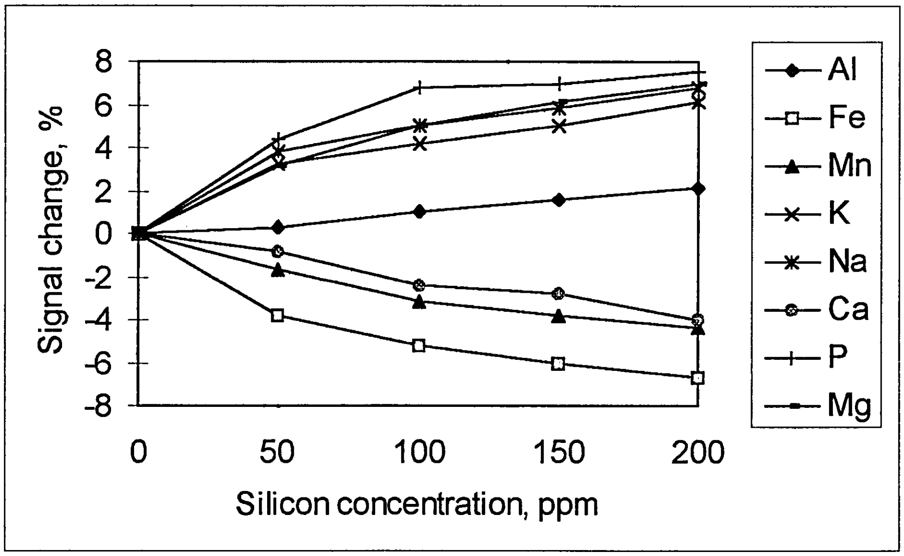
Figure 6. *Effect of calcium on analyte emission intensities.*



In general, the presence of calcium will change the analytical emission signal significantly and these changes are manifested as suppression as well as enhancement of the analyte emission signal. For potassium and phosphorus, the emission intensities increased with increasing calcium concentration and the increased was significant up to 300 μg ml^{-1} and 500 μg ml^{-1} of calcium added into the solution, respectively. Meanwhile, the emission signal for magnesium and sodium appeared to increase constantly up to 700 μg ml^{-1} of calcium. At the same time, the intensity of aluminium, silicon, iron and manganese decreased with increasing of calcium concentration. The decrease was significant up to 700 μg ml^{-1} of calcium for silicon and up to 500 μg ml^{-1} for iron, manganese and aluminium. The emission intensities of iron and manganese were badly affected by the presence of calcium in the solution. The effect of calcium on potassium emission signal is relatively small when compared with other elements. The presence of 1000 μg ml^{-1} of calcium in the solution only caused the potassium emission signal to increase about 2 %. However, calcium was found to induce a larger depressant effect on the signal for iron and manganese and as little as 100 μg/ml of calcium caused the signal decrease for both analytes to exceed 5 %. On the other hand, the depressant effect for silicon and aluminium were relatively small in magnitude and only exceeded 5 % at calcium concentrations of 400 μg ml^{-1} and 500 μg ml^{-1}, respectively.

The effect of silicon on analyte emission signal is illustrated in Figure 7. All analyte concentrations were kept constant at 5 μg ml^{-1} except for calcium, which was 100 μg ml^{-1}. It is evident that increasing the silicon concentration changed all the analyte emission signals. The signals for phosphorus, magnesium, potassium, aluminium and sodium were enhanced while those for calcium, manganese and iron experienced a decrease in their emission signal intensity. The effect of silicon on the aluminium emission signal is relatively small when compared to other elements. The presence of 200 μg ml^{-1} of silicon in the solution only caused the aluminium emission signal to increase about 2 %. The emission intensities of phosphorus, magnesium, potassium and sodium and iron were all badly affected by presence of silicon in the solution.

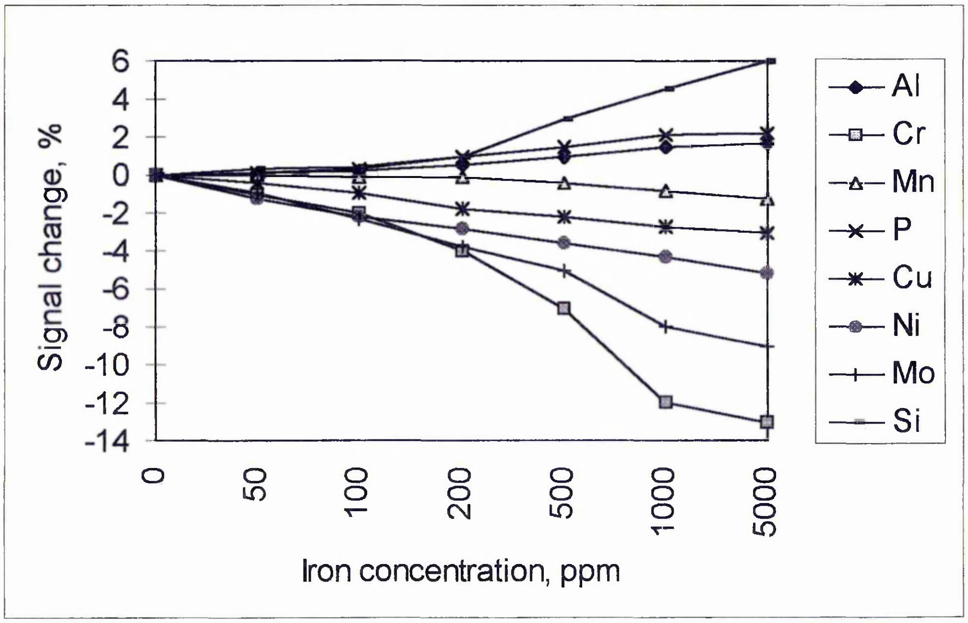
Figure 7. *Effect of silicon on analyte emission intensities*



In steel, iron is the base metal and it represents as much as not less than 95 % in a low alloyed steel. In highly alloyed steel, depending on the properties of the steel required, one or more alloying elements are included. In stainless steel, the common alloying elements added are chromium and nickel. The purpose of both elements is to prevent the material from rusting. However, in analytical work, the presence of high concentrations of base or alloying elements in the solution may affect the analyte emission intensities. The effect of iron, chromium and nickel on analyte emission signal are illustrated in Figure 8, Figure 9 and Figure 10, respectively.

Figure 8 shows how the presence of iron in the solution changes the intensity of the analyte emission signals. The intensities of the emission signal for aluminium, phosphorus and silicon were increased with the concentration of iron in the solution. Meanwhile, the intensities of the emission signals for chromium, copper, nickel, manganese and molybdenum were depressed.

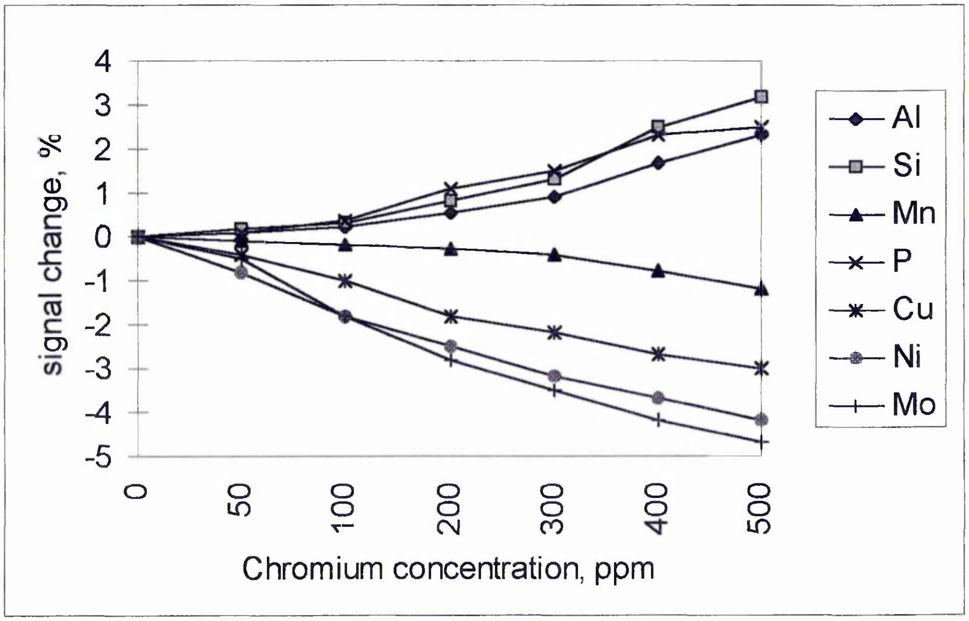
Figure 8. *Effect of iron on analyte emission intensities.*



The effect of iron on phosphorus, aluminium and manganese emission intensities were relatively smaller in magnitude and only exceeded 1 % at iron concentration of 500 μg ml^{-1}. With the presence of iron in the solution, only silicon, phosphorus and aluminium have their emission signals enhanced while the other analytes were depressed. Note the difference in response curve shape over previous elements e.g. Figure 6 and Figure 7.

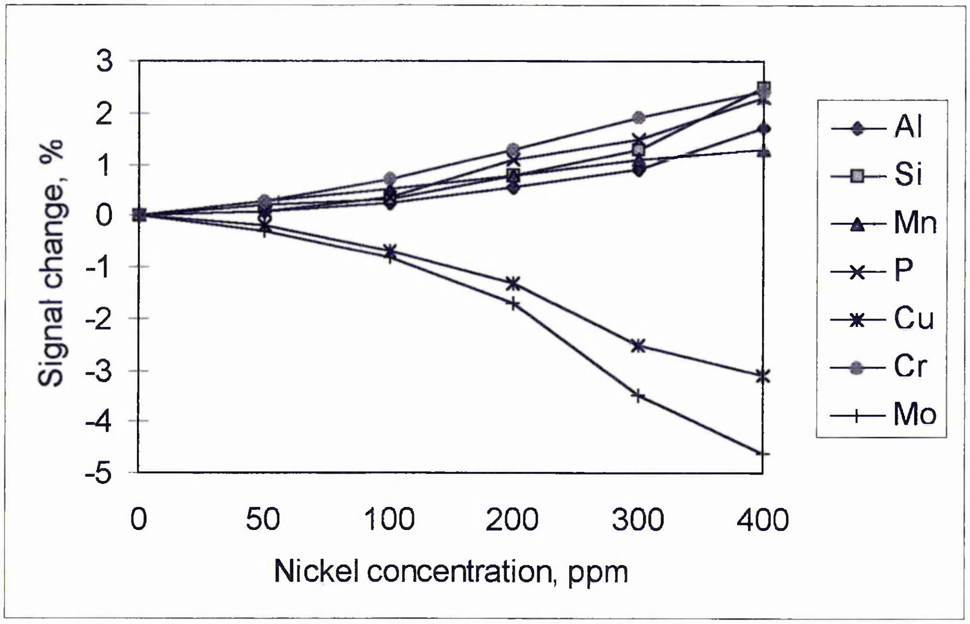
Figure 9 shows that the presence of chromium in the solution caused the emission intensities of silicon, phosphorus and aluminium to increase. At the same time, the emission intensities for nickel, molybdenum, copper and manganese were depressed.

Figure 9. *Effect of chromium on analyte emission intensities.*



As presented in Figure 10, nickel was observed to have an effect on analyte emission intensities. Except for molybdenum and copper, the emission signals for the rest of the analytes were enhanced. However, the enhancement of these signals was not very significant. At a nickel concentration of 400 μg ml^{-1}, the signals were enhanced about 2 % or less. In contrast, the emission signals for copper and molybdenum were depressed by about 3 % and 4.5 %, respectively.

Figure 10. *Effect of nickel on analyte emission intensities.*



Generally, it was observed that the analyte emission intensities changed with the presence of a matrix element. The matrix effect on the analyte emission signal is probably a complicated function of many parameters such as operating conditions, number of particles in the plasma, ionisation potential of the various elements and, total excitation potential of the analytical lines [3].

Enhancements or depression in emission intensity of analytical lines was observed when emission signals with and without the presence of matrix elements were compared. As suggested by Blades and Horlicks [128], the observations have been rationalised on the basis of a shift in the equilibrium for analyte atom (A), ion (A^+) and electron (e^-):

$$A \longrightarrow A^+ + e^- \qquad \text{Eq. 13}$$

In some cases, the addition of a matrix element may cause the electron density in the plasma to increase. This means that the equilibrium will be shifted toward the neutral atom species causing enhancement in atomic emission. If ionisation equilibrium shifts explain the enhancement in emission intensity, then the degree to which the emission intensity will change is dependent on the number of electrons in the plasma which is changed by introduction of the matrix element.

Veillon and Marghoshes [129] suggested that the enhancement in emission intensity may be due to an increase of collision rate due to the increase in electron density. This means that the greater the kinetic energy of the electron, the more likely it is that an ion-electron collision will result in excitation rather than recombination. Thus, the outcome of an increase in electron density will depend on kinetic energies of the electrons. Alternatively, the degree of ionisation also be depressed by charge transfer reactions between matrix atom (M) and analyte ion (A^+) in the following manner [130]:

$$A^+ + M \longrightarrow M^+ + A \qquad \text{Eq. 14}$$

3.4.2 Effect Of Acid On Analyte Emission Intensities

Because all the samples are to be decomposed by mean of combination of various concentrations of acids under a microwave-assisted digestion system treatment, the effect of acid on selected analyte emission intensity has been evaluated and the results are presented in Figure 11 and Figure 12. All the analytes showed a depressant effect dependent upon on acid concentration. These phenomena could be due to the change in the transport efficiency. The process of nebulization, although simple in concept, may provide a mechanism through which an acid can affect the analyte emission intensity. The depression in analyte emission intensity, as presented in both Figure 11 and Figure 12, can be related to the change in solution viscosity. An increase in the concentration of a dissolved salt can cause an increase in the viscosity of the solution, which in turn will decrease the sample uptake rate of analyte solution [2]. A decrease in sample uptake rate, of whatever magnitude, will result in a decrease of the amount of analyte being transported to the plasma and this will cause the analyte emission intensity to be depressed.

Figure 11. *Effect of hydrochloric acid on analyte emission intensity*

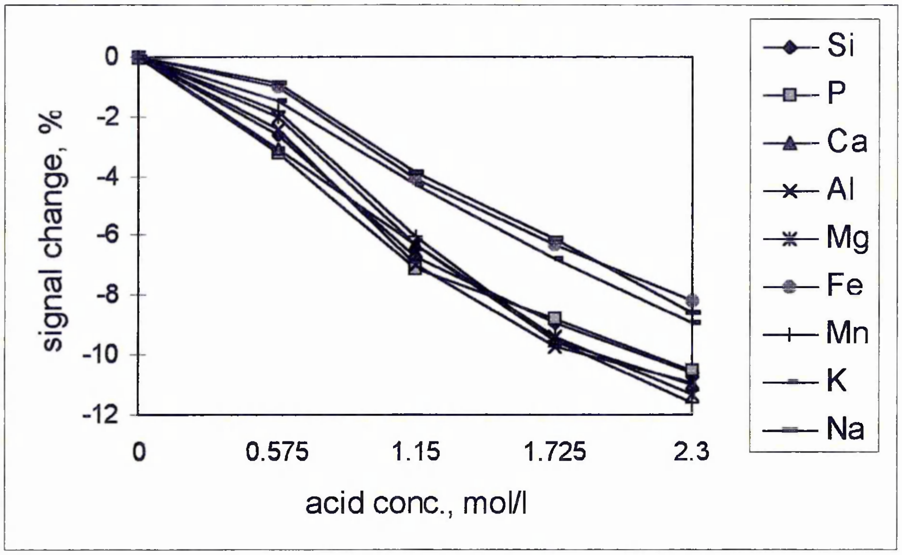
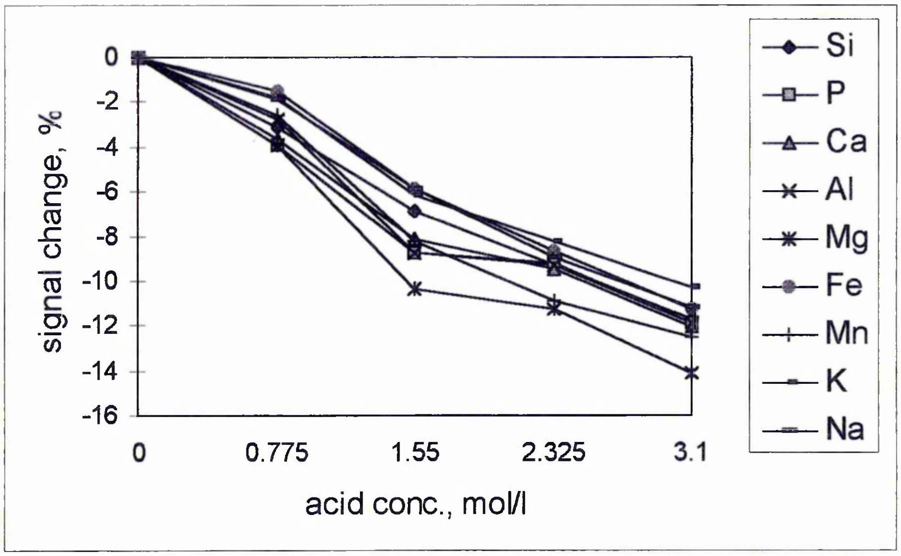


Figure 12. *Effect of nitric acid on analyte emission intensity*



Whether an increase or a decrease in the emission intensities is observed, the effect of matrix constituents on analyte elements cannot be ignored and must be allowed for in order to achieved reliable results. Information about the matrix effect has to be taken into consideration during preparation of the synthetic calibration solutions. Failure to add the appropriate amount of matrix affecting element will lead to an erroneous analytical results.

CHAPTER 4 - APPLICATIONS

4.0 Introduction

This chapter will be divided into two sections. Section 4.1 is concerned with development of a suitable decomposition procedure, the preparation of calibration solutions, the generation of results, and discussion, of the analysis of Ordinary Portland cement. Section 4.2 is concerned with the development of a decomposition procedure, the preparation of calibration solutions, the generation of results, and discussion, of the analysis of low and high alloy steel samples.

4.1 Analysis Of Portland Cement

4.1.1 Development Of The Decomposition Technique For Analysis Of Cement Samples

In simultaneous analysis, it is desirable to apply to a sample a single dissolution, which enables the total recovery and determination of a wide range of elements. However, at the early stage of the development of the decomposition technique for the analysis of cement samples, it was found that a combination of pressure and temperature from the microwave-assisted digestion system was unable to digest the sample completely. After the sample had been treated with a mixture of nitric acid, hydrochloric acid and hydrofluoric acid proportions and digested, it was always found that there was precipitate at the bottom of the digestion vessel. The same observation was still made even when the sample weight was reduced to 100 milligrams and variations of acid concentration, coupled with variation of the operational parameters of the microwave-assisted digestion system, were tried. The precipitate was always white in colour and the use of sulphuric acid to dissolved the precipitate caused the solution to become milky white possibly due to the formation of either colloidal sulphur or calcium fluoride. The same problem has been experienced by Kemp *et al*. [131] when they used the same technique to digest carbonate rock samples for chemical analysis. They had analysed the white precipitate by using x-ray diffraction and it was then identified as calcium fluoride. It was then considered that a pressure equilibrium in the sealed system that they used had prevented the complete dissolution of the carbonate material. Subsequently, calcium fluoride was formed by the reaction of the remaining carbonate with hydrofluoric acid. To overcome the problem, they decided to introduce an earlier stage into the procedure. Thus a reaction with ethanoic acid in an open system to allow the evolution of the carbon dioxide, thereby preventing a pressure equilibrium in the subsequent sealed system was introduced. In this study, a different approach has been used to overcome the precipitation problem.

Realising that some metal elements, especially calcium, are capable of reacting with excess hydrofluoric acid during the decomposition process to form metal fluorides which are difficult to decompose, it was considered necessary to separate all the metallic elements from the hydrofluoric acid.

This can be achieved by utilising a decomposition procedure which involves two sequential stages. In the first stage, all metal elements were dissolved by using a combination of hydrochloric acid and nitric acid with the aid of a microwave-assisted digestion system. This solution was then passed through a filtration process where, by rinsing with distilled water, all the dissolved metal elements were separated from acid insoluble silicates and were collected in a volumetric flask. The residue, which consisted of acid insoluble silicates, was transferred into a Teflon flask. Hydrofluoric acid was added to digest this residue followed by addition of boric acid to neutralised the excess hydrofluoric acid which remained in the solution, thus forming tetrafluoroboric acid. This mixture was then treated in the microwave-assisted digestion system to produce a clear solution. It was observed that there was no white precipitate present at any stage of this procedure.

Acid reaction between insoluble silicates and hydrofluoric acid is shown in the following equation:

$$SiO_2 + 4HF \longrightarrow 2H_2O + SiF_4 \qquad \text{Eq. 15}$$

The purpose of the addition of boric acid into the mixture of hydrofluoric acid, distilled water and insoluble silicates is to neutralise the excess hydrofluoric acid in the solution. Neutralisation of the hydrofluoric acid will also prevent the acid from reacting with borosilicate glass, the nebuliser, spray chamber or torch within the ICP-AES which will lead to erroneous readings for silicon concentration as well as damage to the equipment. The neutralisation process may occur as in the following equations, as suggested by Bernas [132]:

$$H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O \qquad \text{Eq. 16}$$

$$HBF_3OH + HF \longrightarrow HBF_4 + H_2O \qquad \text{Eq. 17}$$

Thus it seems that combination of equation 16 and equation 17 can be simplified as:

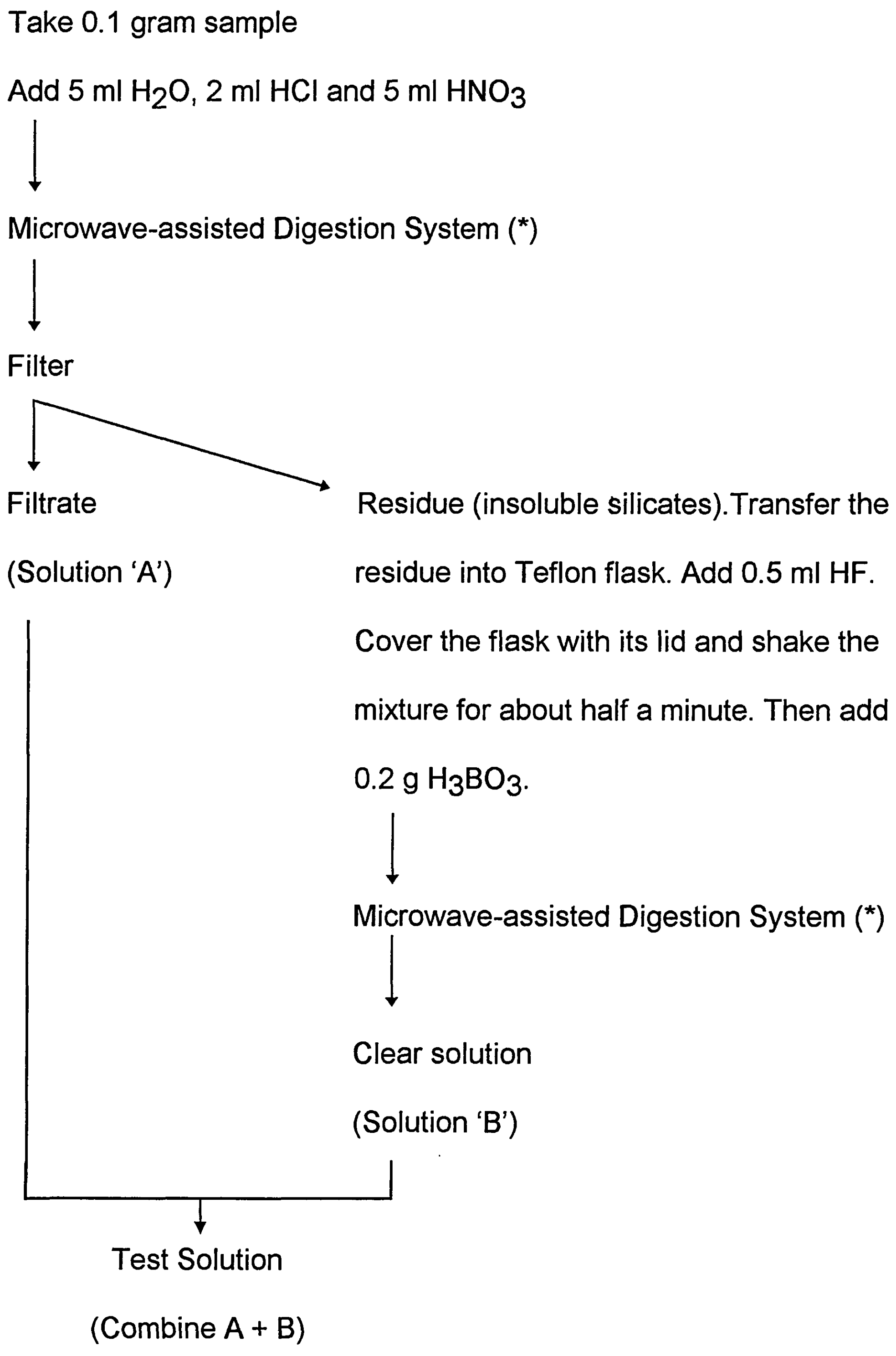
$$H_3BO_3 + 4HF \longrightarrow HBF_4 + 3H_2O \qquad \text{Eq. 18}$$

The complete protocol for the preparation of the test solution is described in subsection 4.1.2.

4.1.2 Preparation Of A Test Solution

0.1 Gram of the test sample was placed in the 100 ml Teflon flask. Sequentially with stirring, 5 ml of distilled water, 2 ml of hydrochloric acid and 5 ml of nitric acid were added, any gritty particles were broken up with the end of the stirring rod. The glass rod was rinsed down. The acid additions were done carefully to avoid spillage. The flask was covered and placed in the carousel and the microwave-assisted digestion system run with the programme operating parameters as in Figure 13. When the digestion programme was complete, the carousel was cooled under running water for about 10 minutes and the solution filtered. The filtrate was collected in a 100 ml volumetric flask. The filter was washed with distilled water, and the washings were collected in the same volumetric flask, but taking care to leave sufficient room for the silicate solution, about 30 ml, to be added later. The filtrate was stored. The filtered residue was transferred into the Teflon flask, 2 ml of water was added together with 0.5 ml of hydrofluoric acid. The flask was covered and carefully shaken for about half a minute. About 0.2 gram of boric acid was added and the flask covered again. The flask was placed in the carousel and the microwave-assisted digestion system run with similar programmed operating conditions. The carousel was cooled under running water for about 20 minutes to allow all volatile material, if any, to redissolve or condense. The resulting clear solution was transferred to the reserved filtrate in the 100 ml volumetric flask, made up to the mark with distilled water and mixed by shaking. This sample solution was to be used for determination of all the elements, including silicon, which are present in the cement sample.

The following chart represents the sample dissolution procedure used in this study:



Take 0.1 gram sample

Add 5 ml H_2O, 2 ml HCl and 5 ml HNO_3

Microwave-assisted Digestion System (*)

Filter

Filtrate

(Solution ‘A’)

Residue (insoluble silicates).Transfer the residue into Teflon flask. Add 0.5 ml HF. Cover the flask with its lid and shake the mixture for about half a minute. Then add 0.2 g H_3BO_3.

Microwave-assisted Digestion System (*)

Clear solution

(Solution ‘B’)

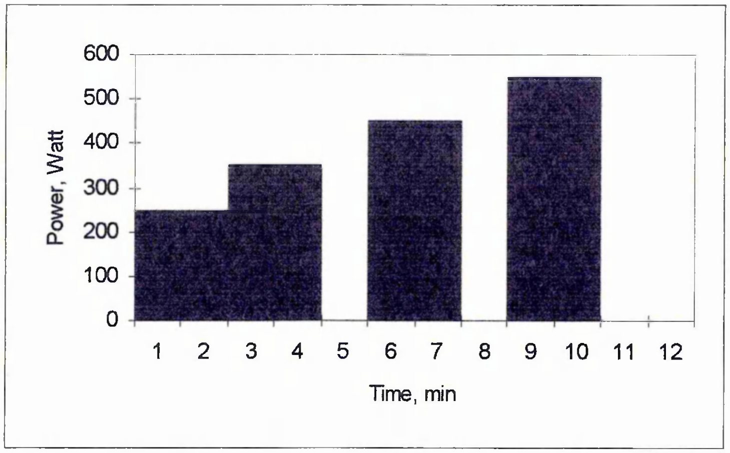
Test Solution

(Combine A + B)

(*) Microwave-assisted digestion system operating conditions are as in Figure 13

From the above chart, one can see that after diluting to the mark with distilled water, solution 'A' could be used for determination of all metal elements in the cement sample. However, if silicon is to be determined at the same time, solution 'B' must be added into solution 'A' before dilution up to the mark. Total time taken for the whole decomposition process is about one hour, and since the carousel can handle 10 flasks at one time, so 10 cement samples can be decomposed in a single run. A second batch of samples can be treated whilst the first one is in the cooling process, providing there is an extra set of flasks and a second carousel. Five batches per day are readily processed giving 50 samples per day for analysis, excluding quality control and blank samples.

Figure 13. *Microwave-assisted digestion system operating conditions used for decomposition of cement sample.*



As shown in Figure 13, the microwave power was ramped and was interrupted twice with one minute cooling breaks to avoid an overheating problem in the vessel. Approximately 50 cement samples can be decomposed by employing the above decomposition technique in one working day by one operator. This method offers considerable advantages of sample throughput and total digestion over the classical fusion method. Moreover, only a small amount of sample and reduced reagent volumes are required. Hence the analysis can be performed at low operating unit cost compared with the traditional approach.

4.1.3 Elemental Volatility Study

It was necessary to check the volatility of various elements when the sample is treated under microwave-assisted digestion system, especially when hydrofluoric acid was used. This is necessary because silicon, as SiF_4, is relatively easy to volatise in this environment. In this work, a set of experiments was carried out in which a known amount of each analyte element in the solution was treated as for dissolution of a cement sample. The resulting solution was transferred into a 100 ml volumetric flask and diluted to the mark before analysis by inductively coupled plasma atomic emission spectrometry, employing the same operating conditions as for the actual sample. Results in Table 7 show that the recovery of some elements such as silicon, aluminium, magnesium, sodium and manganese are about 0.2 % to 0.4 % lower than was spiked into the solution. However, the recoveries of iron, calcium and potassium were observed to be 0.2 % higher. This, however, does not give a significant amount of loss or gain in the recovery results. Thus the method was considered acceptable for use for the analysis of cement.

Table 7. *Recovery study on typical elements in a cement sample after being treated with HF in microwave-assisted digestion system.*

Element	Amount Added, μg ml^{-1}	Found, μg ml^{-1}	Deviation, %
Silicon	5	4.98	-0.4
Aluminium	5	4.98	-0.4
Iron	5	5.01	0.2
Calcium	5	5.01	0.2
Magnesium	5	4.99	-0.2
Sodium	5	4.98	-0.4
Potassium	5	5.01	0.2
Manganese	5	4.98	-0.4

4.1.4 Preflush Time

An appropriate preflush time for the instrument system prior to measurement of analyte signal intensities, must be taken into consideration. Any measurement made before the signal reaches a steady state condition will generate repeatability errors and hence poor results will be obtained. In this study, an actual test solution was aspirated into the sample introduction system and the intensity was recorded every 15 seconds, starting from the time when the sample uptake tube was introduced into the solution. Two sets of experiments were carried out in order to research the preflush time. First, a sample solution was aspirated at a sample uptake rate of 1.3 mlmin^{-1}; secondly, sample solution was aspirated at 'high speed' mode for 30 seconds before the speed was put back at 1.3 ml min^{-1}. The reason for re-setting the sample uptake rate back to 1.3 ml min^{-1} in the second experiment is that the signal intensities are depressed at a high sample uptake rate. Figure 14 and Figure 15 shows the preflush profile from the sample solution being aspirated by utilising both sets of experimental conditions. The time required for the emission signals to reach their steady state condition in both sample uptake rates is summarized in Table 8. In both Figure 14 and Figure 15, there is an initial rapid increase between 15 and 30 seconds. The increase becomes significantly slower after some 30 seconds until the signal reach their highest value after 150 seconds at 1.3 ml min^{-1}. This phenomena could be caused by the formation of droplets of blank solution, which was aspirated before the sample solution, on the inner side of the spray chamber. So, when an aerosol of sample solution is introduced, it will mix with the blank solution droplets and, as a result, the concentration of the analyte was diluted.

Figure 14. *Time required for the analyte emission signal to reach the steady state condition at a liquid flow rate of 1.3 ml min^{-1}.*

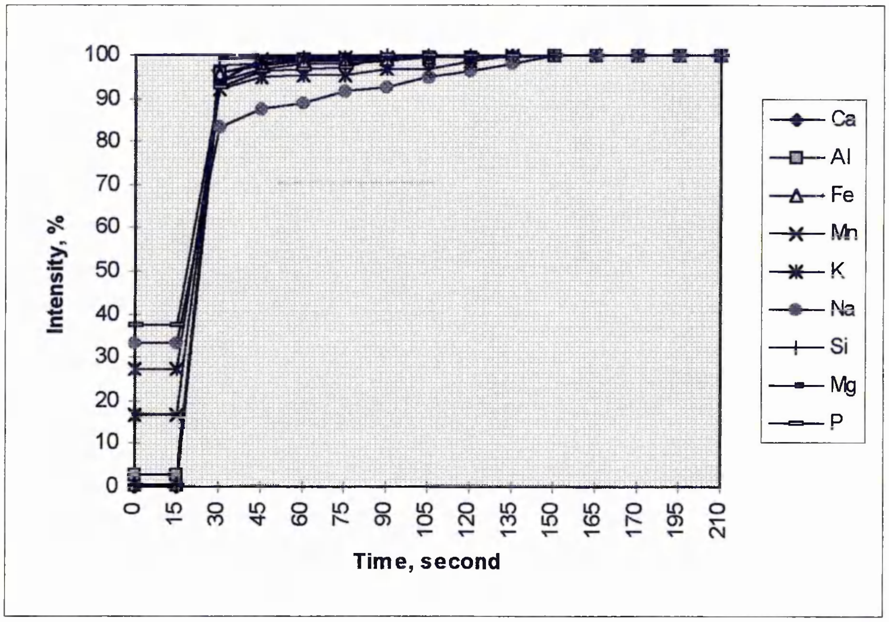
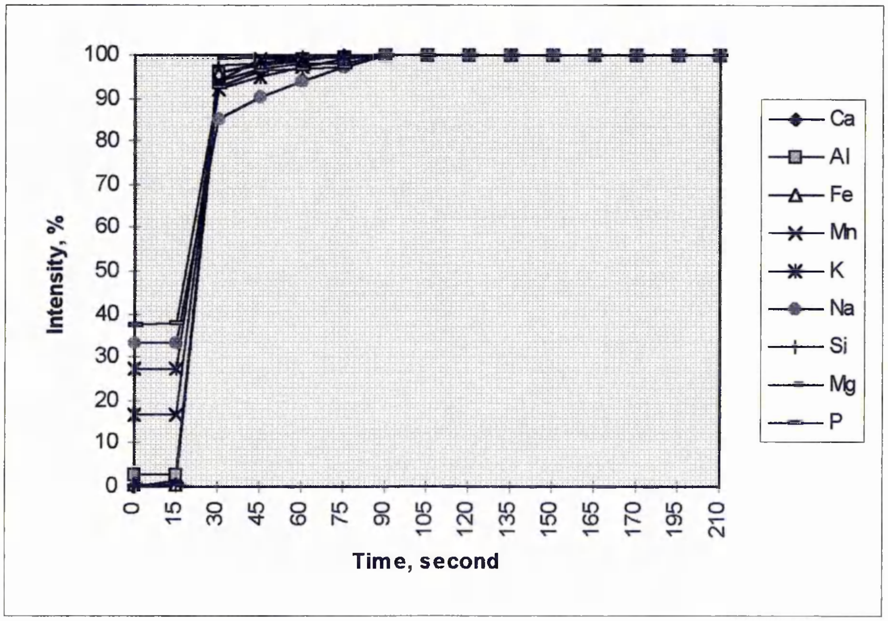


Figure 15. *Time required for the analyte emission signal to reach a steady state condition at 'High Speed' mode flow rate.*



The preflush time required for all elements to reach steady state condition is between 150 seconds and 165 seconds at 1.3 ml min^{-1}. The relative standard deviations of ten emission intensities measured after 165 seconds for all analytes were between 0.29 % to 0.68 %, except for phosphorus which gave a value of 2.28 %. By pressing 'High Speed' mode for about 30 seconds from the sample solution being aspirated, the preflush time was shortened to some 105 seconds. After this new preflush time, the relative standard deviation of ten emission signals measured were between 0.31 % to 0.65 %, except phosphorus which was 2.36 %. For analysis purposes, the preflush time is fixed at 110 seconds after the sample solution is introduced at 'High Speed' mode.

Table 8. *Time required for the analyte emission signal to reach steady state condition.*

Element	Time required, second	
	Flow rate of 1.3 ml min^{-1}	'High Speed' mode
Calcium	150	105
Aluminium	150	105
Iron	150	90
Manganese	150	105
Potassium	150	90
Sodium	150	90
Silicon	150	105
Magnesium	165	105
Phosphorus	150	105

.4.1.5 Memory Effects

For routine purposes, it is preferable to develop a method for the analysis of all the elements in cement samples in the shortest possible time. To accomplished this, it is required that no persistent memory effects remain from the previous sample and the time taken to clean the sample introduction system are appropriate. Figure 16 shows a memory effect profile from the blank solution being aspirated. It shows that there are no changes in the signal emission within the first 15 seconds because the blank washing solution has not yet reach the plasma. There is an initial faster decrease between 15 seconds and 30 seconds and it then becomes significantly slower until the emission signals reach background value. Only manganese and calcium need shorter times for their emission signal to reach the background, taking 75 seconds and 90 seconds, respectively. The rest of the analytes require from 120 seconds to 180 seconds for their respective emission signals to reach background. This long memory effect is probably caused by the sample solution being deposited along the sample introduction system, especially on the inner side of the spray chamber, when the sample solution is being transported as an aerosol. Droplets formed on the side of the spray chamber will contain analyte from the previous sample, and, depending on the aerosol production rate, may stay in the chamber for quite some time [133]. When this does occur, it will cause a carry-over of the previous sample emission signal to the following sample. This is known as a 'memory effect'. In order to minimise wash-out time, the

Figure 16. *Time required to wash out the sample introduction system after analysis of cement at liquid flow rates of 1.3 ml min^{-1}.*

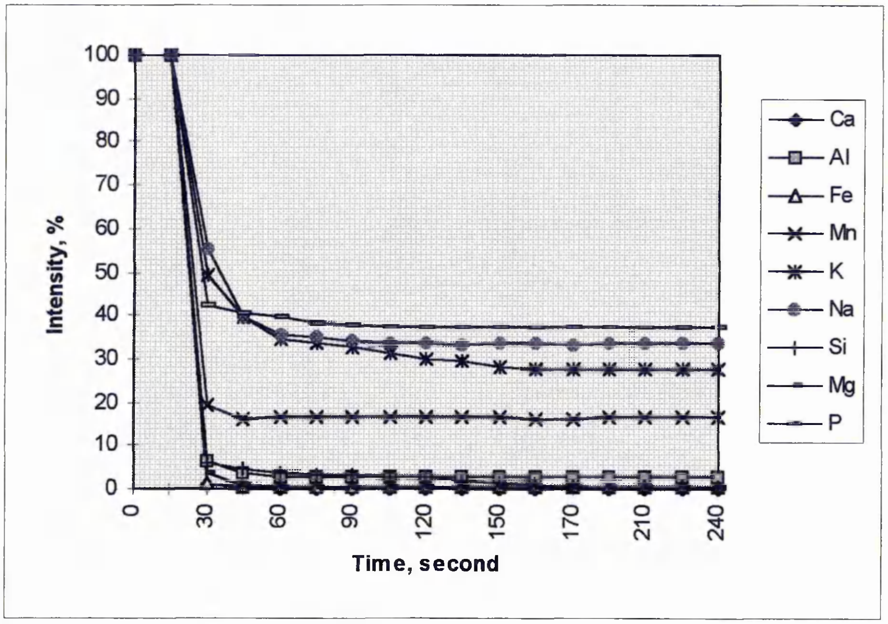
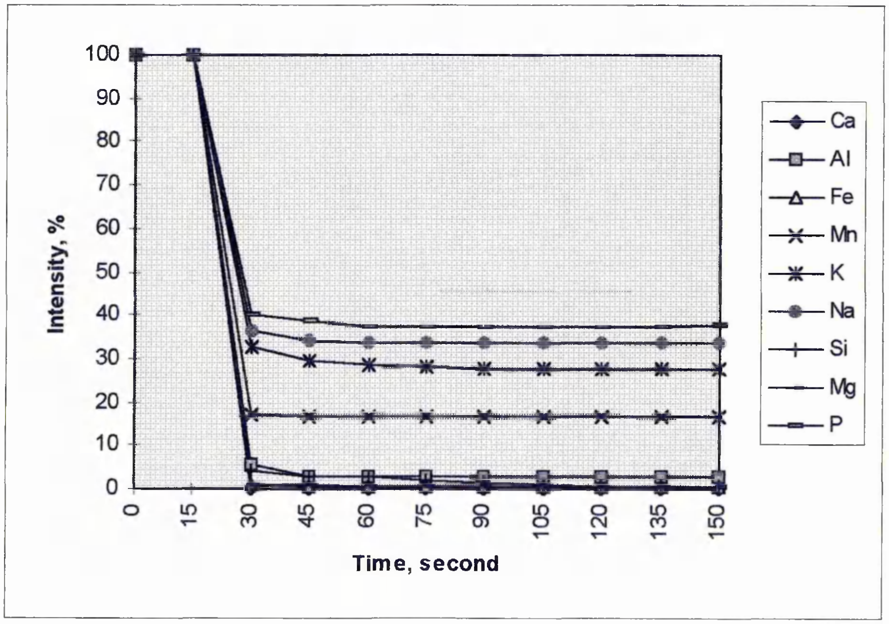


Figure 17. *Time required to wash out the sample introduction system after analysis of cement at 'High Speed' mode liquid flow rates.*



sample uptake rate was increased by utilising the 'High Speed' mode which is available within the peristaltic pump device. Figure 17 shows a memory effect profile from the samples solution being aspirated with 'High Speed' mode. The time required for the emission signals to reach background for both sample uptake speeds is summarized in Table 9. For the analysis of cement sample, 'High Speed' mode has been used to reduced the wash out time from 180 seconds to about 105 seconds. It is probable that the rise time response profile, and the memory effect fall time response profile, are the same and related to the geometry of the sample uptake path.

Table 9. *Time required to wash out the sample introduction system after analysis of cement sample.*

Element	Time required, second	
	Flow rate of 1.3 ml min^{-1}	'High Speed' mode
Calcium	90	60
Aluminium	180	105
Iron	135	75
Manganese	75	60
Potassium	165	105
Sodium	120	75
Silicon	180	120
Magnesium	135	75
Phosphorus	120	60

4.1.6 Preparation Of Calibration Solutions

As with other analytical instrumental methods, inductively coupled plasma atomic emission spectrometry does not provide directly the concentration of elements in any unknown sample [134]. A calibration procedure is required involving measurement of intensities for a series of solutions with known concentrations so as to construct a calibration graph. The idea of constructing a calibration curve is to measure the amount of an analyte in an unknown sample for quantitative purposes by interpolation on the graph [135]. Hence calibration is one of the most important steps taken during the whole analytical process. However, the preparation of the calibration solutions is not as simple as diluting an element from a stock solution into distilled water especially when the unknown sample may contain a significant range of analyte concentrations. In preliminary studies, it was found that the presence of high levels of matrix elements and acids often changed the intensity of the emission signal for an analyte being measured (see Chapter 3). Thus, the effects of matrix components on the analyte emission signal cannot be ignored for precise practical analyses. For the analysis of cement, two types of standards were used, namely 'matrix matched calibration solutions' and the method of 'standard addition'. The effectiveness of both techniques to give good results will be discussed later in this Section. During preparation of calibration solutions, information regarding the effect of matrix elements on analyte emission intensity was taken into consideration. The objective was to minimise or eliminate the matrix effect. To achieve this, the matrix matching calibration solutions were prepared to contain, with the analyte, an appropriate amount of the matrix elements so that the interference can be minimised. The 'blank' solutions also contained the matrix elements in the same proportion that pertain for the test solutions. Hence several 'blank' solutions were prepared for different elements or groups of elements.

Generally, the concentrations of calcium and silicon in Ordinary Portland cement are predictable because their content must be about 45 % and 10 %, respectively. However, in this work, the Ordinary Portland cement sample has been treated as an unknown sample. Hence, a semiquantitative analysis of the test solution was carried out in order to ascertain the approximate amount of calcium and silicon present in the sample. Later, both calcium and silicon were added to the calibration solutions for determination of the rest of the analytes. Meanwhile, a separate series of calibration solutions, inclusive of a blank solution, for the determination of the silicon in the cement sample were prepared containing only calcium at the appropriate amount. To each calibration solution, the same amounts of acids and chemicals used for the decomposition of the cement samples were added. The amount of matrix element added into each calibration solution, including the blank solution, will influence the analytical results. Too little or too much of the matrix element added will cause the calibration graphs to deviate from the correct response. Thus it was necessary to check the matrix element level in the test solution by performing semiquantitative analysis. From the preliminary tests, depending on the weight of sample being used, it was found that the concentrations of calcium and silicon were between 460 μg g^{-1} and 470μg g^{-1} and 95 μg g^{-1} and 105 μg g^{-1}, respectively. To know the proper amount of matrix adjustment to be added into the calibration solution, a recovery study has been carried out by comparing the percentage of recovery against sets of calibration solutions containing various concentrations of matrix element. Considering that both calcium and silicon are capable of causing a change in analyte emission signal (see Chapter 3), calibration solutions have to be prepared separately and each solution must be buffered with the matrix elements, acids and chemicals used for dissolution purposes. From the recovery study, it was found that the addition of 450 μg ml^{-1} of calcium and 100 μg ml^{-1} of silicon is sufficient to achieve satisfactory results for determination of aluminium, iron, magnesium, manganese, phosphorus, potassium and sodium. For determination of silicon, 450 μg ml^{-1} of calcium was added into each calibration solution. Alternatively, 100 μg ml^{-1} of silicon is required to be added into the calibration solutions for determination of calcium. However, it was difficult to identify any systematic error, which may arise due to dilution, when only two standards, and a blank, were used. Thus, in this study, we decided to use five standards for the calibration graphs and thus highlight any dilution error in any of the standards because it would be observed by reduction of the correlation coefficient.

To summarize therefore, each of the calibration solutions for the determination of aluminium, iron, magnesium, manganese, phosphorus, potassium and sodium was buffered with 100 μg ml^{-1} silicon and 450 μg ml^{-1} calcium. For determination of silicon, each of calibration solutions was buffered with 450 μg ml^{-1} of calcium, meanwhile, for determination of calcium, each of the calibration solutions was buffered with 100 μg ml^{-1} of silicon. All calibration graphs obtained in this study were found to be linear with a regression coefficient of at least 0.999.

In the standard addition technique, 20 ml of the sample solution was transferred into each of five 100 ml volumetric flasks. To each flask, a known amount of entire element set was added, except one so-called zero addition solution. Then, the solutions were made up to the mark with distilled water to give a dilution factor of 5. The resulting solutions, together with zero addition solution, were then analysed in order to give the concentration of the analyte in the sample solution.

4.1.7 Detection Limit

Commonly, two of the most frequently stated advantages of the inductively coupled plasma atomic emission spectrometer are its capability of multi-element measurement and low detection limits (see Chapter 1). Determination of detection limits becomes one of the important parts of method development in order to verify that the method developed is suitable for determination of those elements which are present at low level. In this study, the detection limit of each element is defined as three times the standard deviation of their concentration in blank solution. The blank solutions used for calibration purposes were used for determination of the detection limits.

Table 10. *Detection limit of element of interest in analysis of cement.*

Element	Detection Limit, $\mu g\ ml^{-1}$	Detection Limit, %
Silicon	0.03	0.008
Aluminium	0.03	0.01
Iron	0.006	0.001
Calcium	0.009	0.001
Magnesium	0.003	0.0003
Sodium	0.015	0.004
Potassium	0.03	0.007
Manganese	0.009	0.002
Phosphorus	0.03	0.013

To be more representative, each detection limit has been converted into the percentage of oxide compound that it presents in the real samples. The percentage values were calculated based on a sample weight of 0.1 g. As presented in Table 10, the detection limits for all analytes were found to ranged from 3 ng ml^{-1} to 0.3 $\mu g\ ml^{-1}$ (Table 10) and are adequate for determination of all elements which are present and for which a value is required.

4.1.8 Analysis Of Cement Sample

In order to test the accuracy and applicability of the proposed method to the analysis of real samples, a Certified Reference Material of Ordinary Portland cement was obtained from the Bureau Of Analysed Samples Ltd. It was analysed using the optimised conditions described above.

Table 11. *Analysis results of Ordinary Portland cement*

Compound	Certified Value, %	Result Obtained From This Study, % (n = 5)	
		Matrix Matched Calibration Solution	Standard Addition
Silicon dioxide	20.3 ± 0.2	19.9 ± 0.4	20.1 ± 0.3
Alumina	5.37 ± 0.09	5.25 ± 0.07	5.25 ± 0.05
Ferric Oxide	3.42 ± 0.03	3.51 ± 0.05	3.47 ± 0.05
Calcium Oxide	65.3 ± 0.1	64.7 ± 0.5	64.8 ± 0.3
Magnesia	1.31 ± 0.03	1.29 ± 0.03	1.28 ± 0.03
Sodium Oxide	1.10 ± 0.01	1.18 ± 0.02	1.15 ± 0.02
Potassium Oxide	0.75 ± 0.03	0.79 ± 0.03	0.77 ± 0.02
Manganese trioxide	0.074 ± 0.007	0.069 ± 0.004	0.071 ± 0.004
Phosphorus pentoxide	-	0.075 ± 0.005	0.079 ± 0.005

Earlier, the results obtained from analysis of Solution ‘A’ revealed that all the metal concentrations are in close agreement with the certified values. However, the results for Solution ‘A’ also indicate an incomplete dissolution of silicate where only 32 % of the total silicon was recovered.The analyses results presented in Table 11 show that all the results are in good agreement with the certified values. By using matrix matched calibration solutions, the RSD values for all compounds, except manganese trioxide and phosphorus pentoxide, ranged from 0.8 % to 3.8 %. Meanwhile, the RSD values obtained from standard addition technique were found to be from 0.8 % to 2.6%. Manganese trioxide and phosphorus pentoxide were found to give slightly higher RSD values for both calibration techniques which were between 5.8 % to 6.7 % in matrix matched and from 5.6 % to 6.3 % by the standard addition technique. The overall analysis of cement by the proposed method was indeed encouraging as it was able to measure all the major and minor constituents accurately in a single solution. Analysis time for each solution was approximately four and a half minutes inclusive of preflush and washout time. Compared to the matrix matched calibration approach, however, the use of a standard addition method seems to extend the sample preparation and total analysis time since there are dilution steps to be followed and more glassware is required, thus more solutions are to be measured for each sample. As long as there is no change in the operating parameters of the inductively coupled plasma atomic emission spectrometer, the same matrix matched calibration solutions can be used for analysis of many cement samples. Comparing the RSD values, the matrix matched calibration solution method was found to give acceptable results and a better sample throughput than the standard addition method.

4.2 Analysis Of Steel Samples

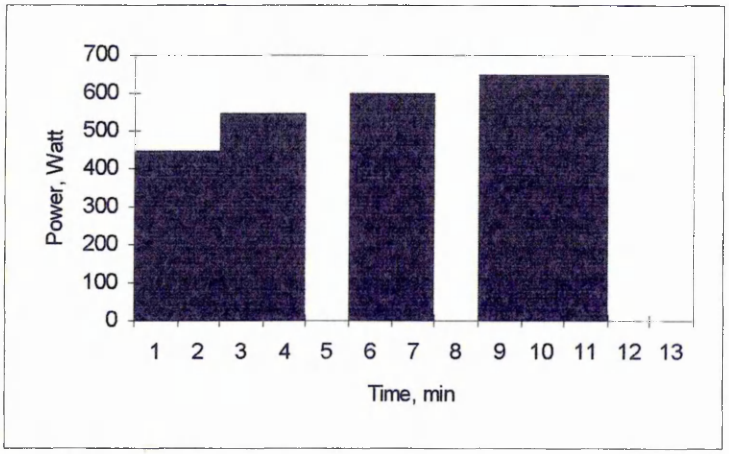
In this study, a simultaneous multi-element analysis was performed and it was important to ensure that the dissolution procedure was capable of detemining all elements in a single solution without any dilution steps. This means that samples containing approximately 1 % of silicon must be digested in a proper manner so that satisfactory results are obtained. Calibration solutions were prepared based on the presence of matrix elements in the sample being analysed. Here, the matrix elements to be considered are iron for both low and high alloy steels, and nickel and chromium for high alloy steel.

4.2.1 Development Of Sample Dissolution Procedure

Before the sample dissolution procedures and microwave-assisted digestion operating parameters, as presented in Figure 18, were chosen, several sets of experiments were carried out. These involved different volumes and ratios of acids and also variation of the combination of power and time of the microwave-assisted digestion system. The capability of each set of experiments to produce acceptable results was based on the recovery of aluminium and silicon where the values of both elements were compared to their certified value. Aluminium was chosen for recovery study to verify the developed method because it has been reported that there is lack of a decomposition procedure that gives a complete aluminium digestion in steel [136].

As the digestion efficiency is dependent on time and power settings, a study of this effect was carried out by keeping the sample in the microwave digestion system for different times and power setting. From the results of the preliminary experiments, it was noted that it was difficult to achieve a combination of power and digestion time for complete sample dissolution. Too high a power setting caused the internal pressure to increase whilst a low power with a longer digestion time was found to digest the sample incompletely. As a result of this study, the combination of power and digestion time, as presented in Figure 18, was found to be a practical combination for excellent recoveries and avoided excessive internal pressure.

Figure 18. *Microwave-assisted digestion system operating parameter for dissolution of low and high alloyed steel samples.*



In addition, the overall digestion time taken was about 20 minutes which is shorter than the classical wet digestion procedure. Recovery of aluminium and silicon as presented in Table 12 are the highest recoveries among all previous work. Thus, the dissolution procedure and the combination of power and digestion time (Figure 18) were adopted for these analyses.

The microwave-assisted digestion parameters presented in Figure 18 were applicable to the dissolution of both low and high alloy steels. The final step of Figure 18 was for cooling and ventilation purposes, where all the acid fumes, if any, were vented from the system. The percentage recoveries of aluminium and silicon in low and high alloyed steel obtained by employing the protocol developed in this study are presented in Table 12. Note that these results were obtained on a series of calibration solution made-up in distilled water, i.e. no matrix matching was performed.

Table 12. *Recovery of silicon and aluminium in low and high alloyed steel samples.*

Sample Identification	EURONORM-CRM No. 186-1		EURO-CRM No. 281-1		BCS-CRM No. 402/2		EURONORM-CRM No. 292-1
Element	Si	Al	Si	Al	Si	Al	Si
Certificate Value, %	1.72	0.014	0.929	0.015	0.111	0.161	0.402
Found, %	1.64	0.012	0.86	0.013	0.100	0.14	0.38
Recovery, %	95.3	85.7	92.6	93.3	90.1	87.0	94.5

4.2.2 Sample Dissolution Procedure For Low Alloy Steel (BCS-CRM No. 402/2 And EURONORM-CRM No. 292-1)

Approximately 250 mg of sample was weighed out and placed into a 100 ml Teflon vessel. Next, 5 ml of distilled deionised water, 8 ml of nitric acid and 1 ml of hydrochloric acid were added. The vessel was left uncovered for about half a minute and then the cover was added and the vessel placed in a carousel. The microwave-assisted digestion system was run with programme operating parameters as in Figure 18. After the digestion was completed, the carousel was cooled under running water for about 15 minutes. This was to allow volatile elements/compounds, if any, to redissolve or condense. The sample solution was transferred into a 100 ml volumetric flask. The digestion vessel was rinsed several times with distilled deionised water and the rinsing was added to the same flask. The resulting solution was diluted to the mark and mixed. The final solution was pale brown in colour and clear.

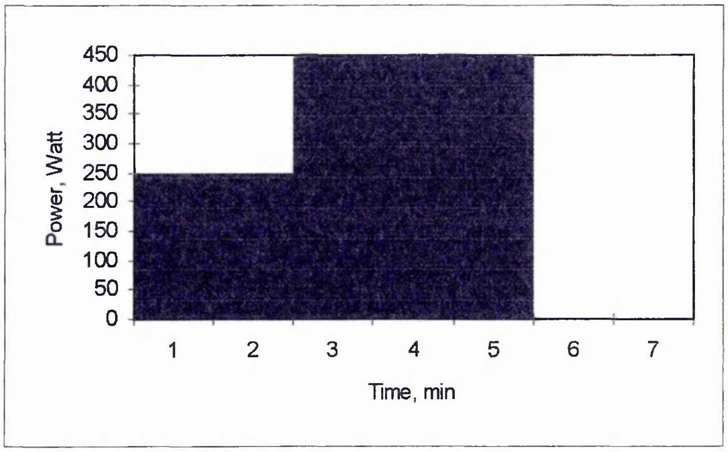
4.2.3 Sample Dissolution Procedure For High Alloy Steel (EURONORM-CRM No. 186-1 and EURO-CRM No. 281-1)

Approximately 200 mg of sample was weighed and placed into a 100 ml Teflon vessel. Then 5 ml of distilled deionised water, 10 ml of nitric acid and 4 ml of hydrochloric acid were added. The vessel was left uncovered for about one minute for gas evolution. Then the vessel was closed and placed in a carousel and the microwave-assisted digestion system was run with the operating parameters in Figure 18. After the digestion time was completed, the carousel was cooled under running water for about 15 minutes. This was done to allow volatile elements, if any, to redissolve or condense. The sample solution was transferred with filtering into a 100 ml volumetric flask. The vessel was rinsed several times with distilled deionised water and the rinsings added to the flask. The resulting solution was diluted up to the mark and mixed. The final solution should be clear and green in colour.

4.2.4 Problems Encountered

During these studies on dissolution of low and high alloyed steels by using microwave-assisted digestion system, it was found that the internal pressure of the closed vessel being used increased and this led to the release of gas fumes from the hot vessels when they were opened. This increase of internal pressure was generated by two factors. First, a vigorous reaction between the sample and the acids used produced some fumes or vapours within the vessel. Second, the heating properties of the microwave interaction. In some cases, the release of fumes was accompanied by liquid vapour or drops of sample solution leading to physical loss of sample and the potential loss of volatile analytes. When this occurs during sample preparation, it will not only cause an error in recovery and accuracy of analysis, but it will also endanger the user. In order to avoid this problem, a delay was introduced before closing the vessel of about half a minute for the low alloy steel (BCS-CRM No. 402/2 and EURONORM-CRM No. 186-1) and one minute for the high alloy steel (EURONORM-CRM No. 292-1 and EURO-CRM No. 281-1). The time required to release the gases produced in high alloy steel was longer than that required by the low alloy steel because the reaction of the acid and the high alloy steel was not so vigorous. During this period of time, the fumes produced from a reaction between the sample and acids were removed by the fumehood. As a result, less pressure was produced during sample preparation using the microwave-assisted digestion system and the internal pressure was thus much less. The strong heating of the vessels can be avoided by interrupting the microwave-assisted digestion system operating program with cooling breaks (see Figure 18). Hence, the program was interrupted twice by a one minute cooling break each time. By following the above procedures, no excess pressure was found inside the microwave-assisted digestion system on completion of the decomposition process. However, it was observed that there was a light brown particulate deposit on the inner side of the vessel after the digestion of low alloy steel. This particulate material was analysed and confirmed to contain only iron which is present as the basic element in steel. Therefore, it is essential to clean the inner side of the vessel each time after use to avoid cross-contamination to the other samples, particularly to other samples where iron is one of the elements to be determined. In this work, each vessel was cleaned by the following procedure. Firstly, the particulate material was removed with wet tissue paper and then was rinsed several times with tap water followed by distilled water. Then, 10 ml of distilled water, 5 ml hydrochloric acid and 5 ml nitric acid were added. The vessels were then covered and placed into the carousel, and with the programmed operating parameters shown in Figure 19. On the completion of the digestion reaction, the acid mixture was then poured out and the vessel was rinsed with distilled water several times. To verify that the vessel was iron free, 50 ml of a 5 μg ml^{-1} iron solution solution was added to each vessel and then was reacted in the digester with the programme operating parameters as in Figure 18. From the recovery results, (no enhancement of iron content) it was concluded that the cleaning procedure was effective.

Figure 19. *Microwave-assisted digestion system operating parameter to clean the Teflon vessel.*



4.2.5 Determination Of Preflush And Wash Out Time

Determination of preflush and wash out times were carried out prior to the analysis of steel samples and the procedure was similar to the experiment conducted for analysis of cement. As the Jarrel-Ash-ICP is equipped with 'time scan' software, determination of both parameters was easier. From the results, the preflush time for all elements was fixed at 65 seconds after the solution was introduced. Subsequently, the wash out time required was found to be 90 seconds. The preflush and washout time for Jarrel-Ash-ICP were found to be shorter than those required by the Spectroflame-ICP and this is probably due to the difference in total volume of the sample introduction system.

4.2.6 Preparation Of Calibration Solutions

As for cement, the analysis of low and high alloy steel was performed utilising two types of calibration, namely, 'matrix matched calibration solutions' and 'standard addition'. The calibration solutions were prepared by diluting the stock solution and each solution, inclusive of a blank solution, was buffered with the appropriate amount of acids and matrix element. Some 2500 $\mu g\ ml^{-1}$ of iron was spiked into each calibration solution to compensate for the matrix effect during the analysis of the low alloy steel. On the other hand, for the determination of silicon, manganese, molybdenum, aluminium, copper and phosphorus in high alloy steel, 1400 μg ml^{-1} of iron, 400 μg ml^{-1} of chromium and 200 μg ml^{-1} of nickel were spiked into each calibration solution. For determination of chromium, 200 μg ml^{-1} of nickel and 400 μg ml^{-1} of iron were spiked into each calibration solution, inclusive of blank solutions. For nickel, 400 μg ml^{-1} of chromium and 1400 μg ml^{-1} of iron were spiked into each calibration solution.

4.2.7 Analysis Of Steel Samples

Four Certified Reference Materials have been analysed in order to verify the accuracy of the methods developed. All the results were obtained from five determinations and are presented in Table 13, Table 14, Table 15 and Table 16.

The analysis results for low alloy steel (BCS-CRM No. 402/2) presented in Table 13 show that all the values were in good agreement with their certified values. By using matrix matched calibration solutions, most of the analytes gaves RSD values less than 5 % except phosphorus and molybdenum, which gave RSD value of 7.2 % and 6.7 %, respectively.

Table 13. *Analysis results of Low Alloy Steel (BCS-CRM No. 402/2)*

Element	Certified value, %	Result obtained from this study, %			
		Matrix Matched		Standard Addition	
		Mean	RSD*	Mean	RSD*
Silicon	0.111 ± 0.006	0.110	4.5	0.109	3.7
Manganese	0.228 ± 0.005	0.231	1.4	0.229	1.3
Chromium	0.652 ± 0.014	0.670	3.7	0.670	3.7
Molybdenum	0.140 ± 0.009	0.133	6.7	0.135	5.1
Nickel	0.808 ± 0.009	0.812	1.2	0.810	1.1
Aluminium	0.161 ± 0.005	0.160	2.5	0.160	3.7
Copper	0.302 ± 0.007	0.290	3.5	0.290	2.7
Phosphorus	0.0161 ± 0.0009	0.015	7.2	0.014	6.9

* n = 5

A similar pattern of RSD values was also obtained using the standard addition technique. Poor RSD values were obtained for phosphorus and molybdenum in both techniques possibly due to the use of less sensitive analytical lines leading to higher noise levels.

Results obtained from analyses of silico-manganese steel (EURONORM-CRM No.186-1) showed that, by using matrix matched calibration, the RSD values for most analytes was between 1.1 % to 5.0 % (see Table 14).

Table 14. *Analysis results of Silico-Manganese Steel (EURONORM-CRM No.186-1)*

Element	Certified Value, %	Result obtained from this study, %			
		Matrix Matched		Standard Addition	
		Mean	RSD*	Mean	RSD*
Silicon	1.72 ± 0.02	1.71	1.2	1.72	0.9
Manganese	0.870 ± 0.008	0.880	1.1	0.877	1.0
Chromium	0.218 ± 0.010	0.221	3.6	0.218	3.7
Molybdenum	0.048 ± 0.003	0.050	8.0	0.050	6.0
Nickel	0.190 ± 0.006	0.210	2.8	0.205	1.4
Aluminium	0.014 ± 0.001	0.014	5.0	0.014	3.6
Copper	0.281 ± 0.009	0.275	1.8	0.280	1.8
Phosphorus	0.022 ± 0.001	0.019	5.2	0.020	5.0

* n = 5

Again, molybdenum and phosphorus gave higher RSD value which were 8.0 % and 5.2 %, respectively. By using the standard addition technique, the RSD values dropped to between 0.9 % and 3.7 %. Molybdenum and phosphorus, however, still showed RSD values of more than 5 %.

During sample preparation of low alloy steel (BCS-CRM No. 402/2) and silico-manganese steel (EURONORM-CRM No.186-1), no filtration process was required since the solution produced was clear and free from any suspended undissolved material. The resulting sample solution was directly introduced into the sample introduction system and no blockage problem was experienced.

Analysis results of highly alloyed steel (EURO-CRM No. 281-1) are presented in Table 15. Good RSD values both in matrix matched calibration solution and standard addition techniques were obtained. Except for aluminium and phosphorus, the RSD values for results obtained from both matrix matched and standard addition ranged from 0.2 % to 3.7 % and 0.2 % to 2.5 %, respectively. Chromium was found to give an RSD value of 0.2 % in both techniques. However, aluminium and phosphorus both gave higher RSD values at 6.3 % and 9.0 %, respectively.

Table 15. *Analysis results of Highly Alloyed Steel (EURO-CRM No. 281-1)*

Element	Certified Value, %	Result obtained from this study, %			
		Matrix Matched		Standard Addition	
		Mean	RSD*	Mean	RSD*
Silicon	0.929 ± 0.008	0.935	1.0	0.932	0.8
Manganese	0.786 ± 0.007	0.791	1.0	0.789	0.9
Chromium	18.17 ± 0.05	18.21	0.2	18.21	0.2
Nickel	9.37 ± 0.05	9.370	0.8	9.37	0.8
Aluminium	0.015 ± 0.001	0.016	6.3	0.016	6.3
Copper	0.076 ± 0.003	0.081	3.7	0.079	2.5
Phosphorus	0.012 ± 0.001	0.010	9.0	0.009	8.8

* n = 5

Except for phosphorus, the analysis results of Niobium Stabilised Stainless Steel (EURONORM-CRM No. 292-1) showed that all of the analytes gave RSD value of less than 5 % in both matrix matched and standard addition techniques although molybdenum was still relatively high at 4.6 % (see Table 16).

Table 16. *Analysis results of Niobium Stabilised Stainless Steel (EURONORM-CRM No. 292-1)*

Element	Certified Value, %	Result obtained from this study, %			
		Matrix Matched		Standard Addition	
		Mean	RSD*	Mean	RSD*
Silicon	0.402 ± 0.005	0.397	0.7	0.399	1.0
Manganese	1.744 ± 0.006	1.740	1.7	1.738	1.7
Chromium	18.00 ± 0.02	18.04	0.2	18.01	0.2
Molybdenum	0.0464 ± 0.0011	0.043	4.6	0.043	4.6
Nickel	10.09 ± 0.02	10.11	0.6	10.05	0.4
Copper	0.0391 ± 0.0010	0.04	1.7	0.04	1.7
Phosphorus	0.0175 ± 0.0007	0.0162	5.2	0.0168	5.0

* n = 5

The prepared solutions of high alloy steel (EURO-CRM No. 281-1) and Niobium Stabilised Stainless Steel (EURONORM-CRM No. 292-1) both needed to be passed through filteration process before it could be introduced into the spectrometer. This was necessary because of the presence of some suspended material in the solution which may cause clogging in the nebuliser. However, all the results obtained were in good agreement with the certified values. Total analysis time for each solution, including preflush and wash out time, is some 2 minutes and 50 seconds.

Comparison of the silicon and aluminium results obtained from standards made up in distilled water (see Table 12) and standards containing matrix elements of the steel sample to be analysed, has shown that the recoveries of those elements are much improved using the latter standards. Thus, for accurate analysis, the standard solutions need to be buffered with appropriate amount of matrix element and other other chemicals being used for the sample dissolution. Although the standard addition technique gave improved recoveries, it increases the sample preparation times, and the improvement is not considered sufficient to justify the increase in analysis time.

CHAPTER 5 - CONCLUSION

5.0 Conclusion

In general, users often claim that the inductively coupled plasma - atomic emission spectrometry shows interferences that are smaller in magnitude than in flame atomic emission spectrometry, flame atomic absorption spectrometry and furnace atomic absorption spectrometry. This claim, however, sometimes leads to the misconception that inductively coupled plasma spectrometry is interference-free. In fact, spectral interferences in inductively coupled plasma atomic emission spectrometry are very clear especially those caused by the presence of concomitant elements and the OH line. Thus, analytical lines have to be selected carefully.

Since the analyte emission intensities are dependent on the instrument and its many variables, sample and calibrations solutions have to be measured under identical conditions and care has to be practised in the correct setting and regular checking of the instrument. The successful application of inductively coupled plasma atomic emission spectrometry in analytical methods therefore depends on defining the operational parameters and achieving them in practice. Currently, this type of instrument is manufactured by many companies and the difference between available instruments implies that specific operational settings may vary from one to another.

The capability of inductively coupled plasma atomic emission spectrometry for the simultaneous determination of major and minor constituents in cement and steel has been demonstrated in this study. However, it was observed that all the technical advantages of inductively coupled plasma as mentioned in Chapter One were moderated by the spectral interferences, matrix effects and inter-element interferences. A spectral interference, occurs when matrix element present in the sample give an emission line very close to the wavelength used for analyte element. The measured amount of the analyte element then will be erroneously high because the spectrometer will record the emission from both analyte and interfering element but ascribe the total only to analyte element. In a sequential inductively coupled plasma system, spectral interference can be minimised, if not totally avoided, by using alternative emission lines. It is difficult to alter the emission line in a simultaneous system. Thus, those who plan to have a simultaneous inductively coupled plasma atomic emission spectrometry system need to identify and choose the wavelengths carefully to suit to their sample matrix in order to minimise those interferences, otherwise a sequential system should be used. Alternatively, if there is no way to avoid spectral interferences, then a background correction can be applied during analysis. The apparent intensity can be subtracted from the total intensity at the line where the interference occurs. In this study, the effect of matrix components on analyte emission intensities has been eliminated by buffering the standard solution with major elements in the sample to be analysed and the chemicals being use for sample dissolution.

Application of a microwave-assisted digestion system in high-pressure vessels allows the cement and steel samples to be rapidly dissolved and requires only a small volume of acid. Except for the solution transfer process, which may cause error in volume transferred, other problems associated with the use of microwave-assisted digestion system have been solved. Although complicated to develop such a method, once developed, can be utilised for the analysis of cement and steel as a routine analytical tool with high sample throughput capability.

5.1 Future Work

It is hoped that this work will be continued toward the development of simultaneous determination of trace and ultra-trace constituents in both cement and steel samples. On-line microwave-assisted sample dissolution coupled with flow injection may be able to offer considerable rapid and volume transfer error-free analysis. Another area of future research work may include the development of special columns, through which the solutions have to pass after the dissolution process so that the interfering element can be trapped to eliminate the undesired effect. Thus, calibration solutions can then be prepared in distilled water without modification.

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