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Determination of water-cement ratio in cement paste by atomic absorption spectrometry

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ABSTRACT

Title of Thesis: Determination of Water-cement Ratio of Cement Paste by Using Atomic Absorption Spectrometry and Fluorescence Fluorometer

Jiong Zhao, Master of Science, 1991

Thesis Directed by: Farhad Ansari, Assosiate Professor
Civil Engineering Department

As one of the important characteristics of concrete, water-cement ratio controls porosity and thus strength and corrosion resistance of hardened concrete.

This paper presents a laboratory observation for determination of water-cement ratio of fresh concrete for quality control and quality assurance. The atomic absorption spectrophotometer and the flouresence spectrophtometer were used to determine the calcium concentration in cement solution of various water-cement ratio. The level of water-cement ratio investigated ranged from 0.4 to 0.55 which covers the most range of water-cement ratios in present practice. The result of lab experiments shows an immediate relation between the water-cement ratio and the calcium concentration in fresh concrete. Furthermore, the results were studied and analyzed using computer programming based on different types of cements.

The aim of these laboratory experiments were to develop a new method for rapid(15 minutes or less) determination of water-cement ratio in the paste.

Determination of Water-cement Ratio in Cement Paste
By Atomic Absorption Spectrometry

by

Jiong Zhao

A thesis submitted to the faculty of the
Graduate School of New Jersey Institute of Technology
in partial fulfillment of the requirements for the degree of

Master of Science Civil Engineering
May 1991

APPROVAL SHEET

TITIL OF THESIS: Determination of Water-Cement Ratio in Cement Paste by Atomic Absorption Spectrometry

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Dedicated to

My dear husband Henry Wu
My dear and respectful parents
Jin-chai Fu and Tu- geng Zhao
My sister Xuan and my brother Hua
and all my relatives and friends in China

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Chapter 1
Introduction

1-1 General

The water-cement ratio is one of the most significant characteristics of concrete. It controls porosity and thus strength and corrosion resistance of hardened concrete. If the water-cement ratio is within the specification limits, then the concrete quality is also likely to be within the appropriate range.

Much of today's construction is very rapid. Usually by the time we learn that the concrete quality for a project is inferior, it may be too late. If we have been fortunate and the structure has not collapsed, we may still find that the inferior concrete is buried deep inside the structure where it is very difficult or practically impossible to replace.

In today's world of modern technology and rapid construction, it is becoming more and more important to be able to determine the composition and strength of fresh concrete as soon as possible. The water-cement ratio is the key factor in determining the quality of concrete, and at the same time is the most difficult parameter to measure. It would be ideal to analyze concrete before it is placed in the forms. By analyzing the water-cement ratio of concrete at a very early stage, we could determine whether or not the concrete meets the jobs specifications. We could also check the uniformity of the concrete and possibly estimate the concrete strength potential. Therefore, a method which would allow reliable and rapid determination of water-cement ratio in freshly mixed concrete on the construction site would be a useful tool for the quality control of the construction project.

1-2 Existing Methods and Survey of Literature

There are several existing test methods for determination of the composition of concrete mixture. The two values of greatest interest are the cement content and water content.

The existing standardized test is that prescribed by British Standards [1]. The water content is determined by drying the sample over a heater. Hence, the mix proportions can be calculated. The test has to be commenced virtually as soon as the concrete has been discharged from the mixer because loss of water can occur; even if evaporation is prevented, an unknown amount of hydration will take place during any period of delay. The analysis of the concrete has to be supplemented by test on the fine and coarse fractions of the aggregate. This information is essential in the calculation of the quantity of the solid constituents of the mix. The weights of fine and coarse aggregate are determined by weighing in water, and the weight of cement is obtained as a difference between the weight in water of the concrete and of the aggregate.

A slightly different method for the determination of water content in fresh concrete was suggested by Nischer [2]. A sample of such concrete is mixed with 10 per cent of its weight of alcohol and the mixture is burnt while being stirred. The process is repeated till the concrete has lost all cohesion and has a uniform color. The loss in weight gives the water content.

Several other approaches have been proposed to obtain an accurate determination of the cement content. Turton [3] suggested a modification of the method given by the British Standards [1]. In his method, he collects the washed very fine material is collected into a container, and the weight of cement is obtained directly rather than as a difference. The calculation of the weight of cement has to include a correction for the silt and dust in the aggregate as determined by a sieve analysis on the aggregate sample. In a separate research, the material smaller than 150 micrometer (No.100 sieve) is separated out by filtering and the residue is pressed dry [4], the weight of cement is taken as the weight of this fraction corrected for aggregate finer than 150 micrometer (No.100 sieve) in the material as batched. In a more recent work, cement is separated by flotation [5].

Another method [6] of determining the cement content of fresh concrete consists of the measurement of electrical conductivity of an aqueous suspension of the material. The test is based on the fact that the hydration of cement produces salt whose concentration is proportional to the quantity of cement so that there is a definite relation between the cement content and electrical conductivity. The test must be performed within an hour of mixing but the limitations of the test conditions are such that the determination cannot be made on site.

Head et al [7] surveyed the technical literature, and suggested the Kelly Vail procedure as one providing good results in a time period of a quarter-hour or more. The Kelly Vail procedure was first introduced in 1968 [8] and was extensively investigated by Howdyshell and co-workers at the CERL laboratories of the Corps of Engineers [9, 10, 11,12]. The Kelly Vail procedures for cement content are given in ASTM C1078 [13], and for water content in ASTM C1079 [14].

Similarly, as developed in England, a device known as the Rapid Analysis Machine (RAM), has had extensive mention in the literature. This procedure was developed by Forrester et al in 1974 [15]. The apparatus has found extensive use in England. The equipment has been commercialized and usage of the RAM method is now extending into the United States and Canada. The method requires about 15 minutes, may suffer from interference due to fines, and is only applicable to cement analyses.

Head et al in 1983 [16], Howdyshell in 1977 [17], and Arrand and Butler [18] also reviewed published procedures and developed methods for water and cement content. Hime and Willis in 1955 [19] reviewed the literature for cement content and developed a procedure based on density that has found acceptance for cement content and mixer efficiency tests. Nuclear procedures such as described by Howdyshell [17] and Iddings et al [20] can be very rapid but the instrumentation is not applicable to general usage.

Naik and Ramme [21] has performed laboratory and field tests using the microwave method to determine the water content of fresh concrete. Basically the test consists of weighing a fresh sample of concrete, removing the water through heating in a microwave oven for less than an hour (usually about 15 or 20 minutes), and weighing the dried sample. The weight difference between the fresh sample of concrete and the dried one is the water content of the sample. This method has produced satisfactory results and it was used in our experiments for comparison.

As the survey of technical literature indicates, a significant amount of research has been performed in determining either the water-cement ratio, or the cement and water content. However, none of the previously mentioned techniques has been able to introduce a rapid, reliable method for determination of water-cement ratio.

1-3 Objective

In the effort of developing new methods which would lead to the rapid determination of water-cement ratio of fresh concrete in a short period of time by comparatively simple means, a series of lab experiments have been conducted in our laboratory at NJIT. These experiments involve the use of Atomic Absorption Spectroscopy, and fluorescence spectroscopy (AA, and FS) in the determination of water-cement ratio in fresh concrete. Our objective is to develop a rapid, accurate test method for the determination of water-cement ratio in freshly mixed concrete.

Chapter 2

Theory, Instrumentation and Application of AAS and FS

2-1.1 Principle and Theory of Atomic Absorption

Atomic absorption spectroscopy involves the study and measurement of radiant energy by free atoms in gaseous state. The data obtained by studying this absorption provide spectroscopic information and analytical information. The spectroscopic information includes the measurement of atomic energy levels, the determination of oscillator strengths, the population of atoms in various energy levels, atoms lifetimes, and so on. The analytical information revealed includes qualitative and quantitative determination of elements, particularly the metallic elements of the periodic table.

The analytical process involves the conversion of molecules or ions into free atoms and then the measurement of absorption of radiation by these free atoms. The absorption of energy by atoms follows well-known physical laws and appears to be predictable, thus providing us with a basis for quantitative analytical chemistry. The radiant energy absorbed by the atoms is generally in the form of very narrow absorption lines with wavelengths in the visible or ultraviolet region of the radiant energy spectrum. During the absorption process the outer valence electrons of the atoms jump to a higher orbital and the atom is said to become excited. The simple relationship between excited and unexcited atoms is illustrated in Fig 2.1, which illustrates the equilibrium between an excited atom and an unexcited atom plus a photon. The unexcited atom is said to be in the ground state.

The generation of a ground-state atom plus a photon from an excited atom is the basis of emission spectroscopy. The reverse process of absorbing a photon by a ground-state atom to become an excited atom is the basis of atomic absorption spectroscopy.

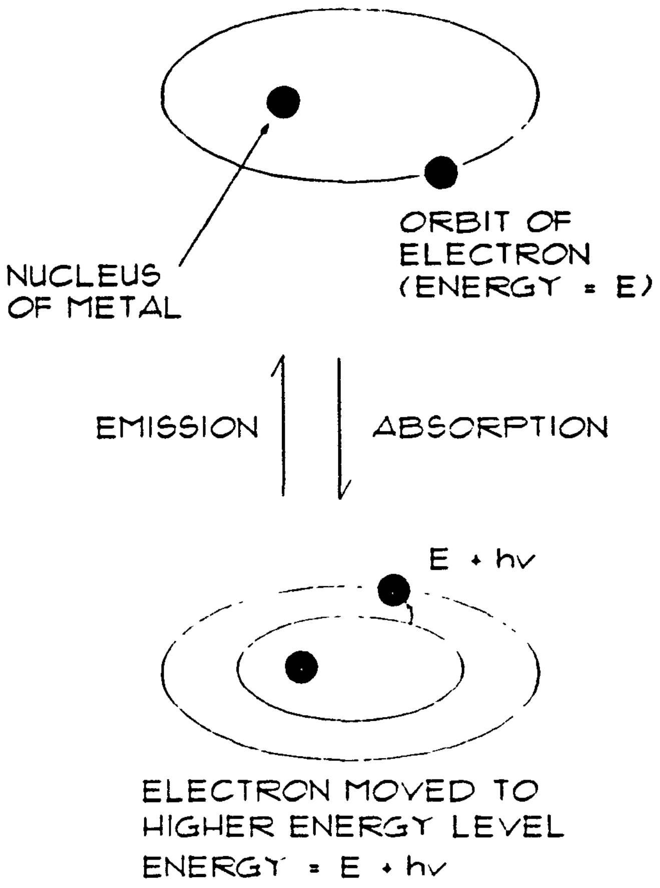


Fig 2.1 The Relationship between Atomic-Absorption and Atomic-Emission Spectroscopy.

One of the most basic and most important radiationless in spectroscopy is given in Eq. (2.1),

$$E = hv \tag{2.1}$$

where

E = energy difference between two energy levels in an atom (or molecule) between which transition occurs

h = Planck's constant

v = frequency of radiation

Also,

$$v = c/w \qquad (2.2)$$

where

c = speed of light

w = wavelength of radiation

In atomic absorption spectroscopy, if an atom changes from a ground state to a higher excited state, its energy increases. This energy E comes from the absorption of a photon (energy hv), whose energy is equal to the energy required to cause excitation in the atom. As an illustration, if an atom has two energy levels of E_x and E_y electron volts, respectively, then the difference between these energy levels equals E_x-E_y electron volts.

It has been known that only certain energy levels are permitted in atoms (or molecules). This means that the atom can exist for extended periods only at permitted energy levels; all other energy levels are unstable and can be ignored in this branch of spectroscopy.

Since only certain energy levels are permitted, the energy difference between these levels is well-defined and thus only certain wavelengths of radiation can be emitted or absorbed by an atom. Consequently, the emission spectrum of an atom is characteristic of a particular element, and similarly only certain radiation frequencies can be absorbed by any particular element. Those two properties provide us with the specificity necessary to make atomic absorption spectrography a useful, reproducible analytic tool. If an atom such as calcium is found to absorb radiation at a wavelength of 4226 Angstrom (A), then we can be assured that it will always absorb at 4226 A because the energy levels associated with the absorption of this wavelength of energy are a physical property of calcium.

The degree of absorption in atomic absorption is given by

$$\int_0^\infty K \nu \, d\nu = \frac{\pi e_2}{m c_2} N f \qquad (2.3)$$

where

K = absorption coefficient at frequency v

e_2= change of an electron

m = mass of an electron

N = number of absorbing atoms

c = speed of light

f = oscillator strength of the absorption line

The oscillator strength of a line is the probability of a transition between the ground state and excited state involved.

The number of atoms in the light path is in a state of dynamic equilibrium with the sample solution and with the products of combustion. The number of free atoms is in turn proportional to the concentration of the metal being determined in the sample. We can therefore construct calibration curves relating the degree of absorption and concentration of a solution.

2-1.2 Atomic absorption instrumentation

The atomic absorption spectrophotometry (Fig 2.2) consists basically of :

(a) A light source which emits the sharp-line spectrum of the element to be determined.

(b) A method to produce atomic vapor of the sample to be analyzed.

(c) A wavelength selector to isolate the resonance lines.

(d) A detector, amplifier, and readout system.

Light Source. The hollow cathode lamp is the most common and satisfactory source for atomic absorption spectroscopy. Fig 2.3 is a schematic diagram of a typical source unit. A hollow cathode tube consists of an anode and a hollow cylindrical

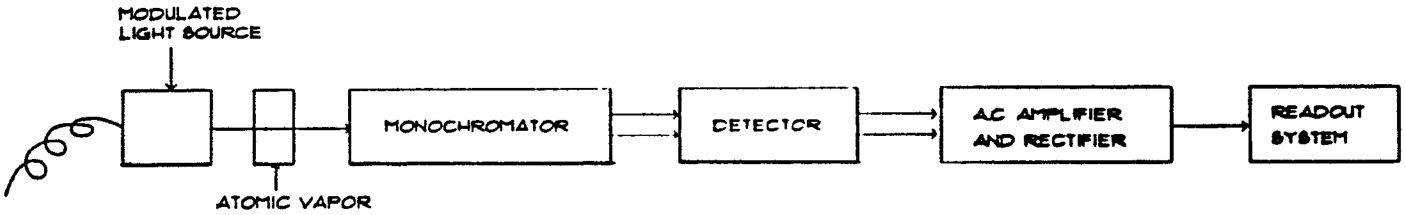


Fig 2.2 Schematic Diagram of Major Components Making up An Atomic Absorption Spectrophotometry

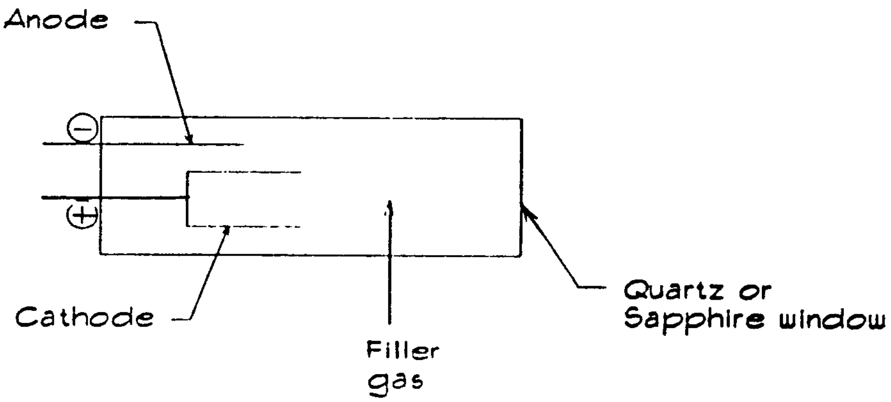


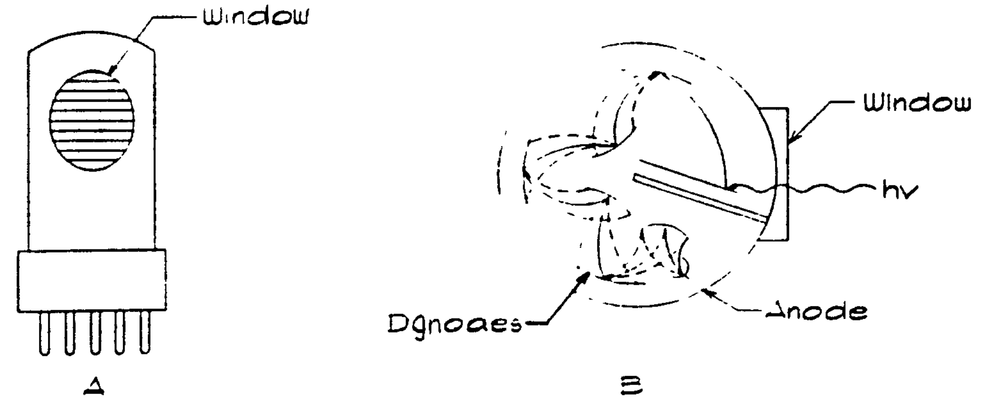
Fig 2.3 Schematic Diagram of a Typical Source

cathod containing, or lined width, the metal whose spectrum is desired. These electrodes are in a sealed tube, with a glass or quartz window, and filled with one of the inert gases at low pressure. The tube is connected to a source of electrical current. The discharge take place within the hollow cathode, and bombardment by the inert gas atoms are excited by collision with the inert gas atoms and emit the desired sharp-line spectrum.

Sample Vaporization. In an atomic absorption analysis the elements in the sample must be reduced to neutral atomic particles, vaporized, and dispersed in the radiation beam in such a manner that their numbers are reproducibly related to their concentrations in the sample. In our experiments flame and burner device for forming atomic vapors has been used.

Wavelength Selector. The basic requirement for a wavelength selector is separation of the desired resonance line form the other emission lines of the source. The most useful selector is a monochromator which can be set to pass any wavelength between calcium 1,930 and 9,000 A. A larger bandpass causes the absorbance curve to flatten. A smaller bandpass causes a decrease of the signal/noise ratio.

Detector. The most common detector used in atomic absorption spectrophotometer is a photomultiplier tube. Fig 2.4 shows a schematic diagram of a phtomultiplier tube. photomultiplier tubes require a source of negative high voltage, so a suitable power supply must be employed.



A. Side view

B Top view showing configuration of dynodes and collector

Fig 2.4 Schematic Diagram of Photomultiplier Tube

Amplifier. The Amplifier used to amplify the signal from the detector is usually a simple AC amplifier, that is, one that detects any regular intermittent signal.

2-1.3 The Use of Atomic Absorption in Determination of Water-Cement Ratio

Generally, cement consists mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products. Four compounds are usually regarded as the major constituents of cement: Tricalcium silicate, Dicalcium silicate, Tricalcium aluminate, Tetracalcium aluminoferrite. Their abbreviated symbols used by cement chemists are listed in Table 2.1.

The reactions by virtue of which cement becomes a bonding agent take place in a water-cement paste. In other words, in the presence of water, the silicates and aluminates form products of hydration, which in time produce a firm and hard mass,the hardened cement paste.

The time of hydration of cement is usually regarded as three stages: The early hydration period, the middle hydration period and the later hydration period. Table 2.2 shows a standard sequence of hydration of cement.

Table 2.1

Main Compounds of Portland Cement

Name of Compound	Oxide Compound	Abbreviation
Tricalcium Silicate	$3\ CaO.SiO_2$	C_3S
Dicalcium Silicate	$2\ CaO.SiO_2$	C_2S
Tricalcium Aluminate	$3\ CaO.Al_2O_3$	C_3A
Tetracalcium Aluminoferite	$4CaO.Al_2O_3Fe_2O_3$	C_4AF

Table 2.2

Sequence of Hydration of Cement

Period	Reaction stage	Chemical processes	Overall kinetic behaviour
Early	I. Pre-induction period	initial hydrolysis; release of ions	Very rapid Chemical slow control
	II. induction period	Continued dissolution; formation of early CSH	Nucleation or diffusion control
Middle	III. acceleration (post-induction period)	Initial growth of permanent hydration products	Rapid Chemical control
	IV. Deceleration	Continued growth of hydration products; development of microstructure	moderate chemical and diffusion control
Late	V. Diffusion period (steady-state Period)	Gradual densification of microstructure	Very slow Diffusion control

Within the first stage release of ions takes place. It is a very short period, and it lasts for only a few minutes. During this period, a large number of calcium ions (Ca^{2+}) release into the solution, and reach to a saturation level rapidly. The following chemical formulas represent the reaction during the first hydration period:

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3Ca(OH)_2$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + Ca(OH)_2$$

$$Ca(OH)_2 \Longleftrightarrow Ca^{2+} + 2OH^{-1}$$

Several other experiment observations have discovered higher concentrations of calcium ions at higher water cement ratios [22]. That is mainly because the Ca^{2+} reach over saturation levels very rapidly. Therefore, existence of more water in the solution, promote more reaction. In other words, higher water-cement ratio means more concentration of calcium ions in the paste.

Considering the capability of atomic absorption spectroscopy in providing means for determination of calcium ions concentrations, then it is possible to use AAS for prediction of water-cement ratio in cement pastes.

Portland cement is an excellent sample material for use in AAS due to the following reasons: It is easily put into solution; it consists essentially of elemental oxides for which atomic absorption is particularly applicable; it is of relatively consistent composition; and the Ca^{2+} released during the hydration is well suited within the measurement range of atomic absorption technique. One important fact we have to point out here is that to determine the high concentration of Ca^{2+} which ranges from 10 to 70% in the fresh concrete, large dilutions have to be made to bring them into highly sensitive range of present-day atomic absorption method. The determining factor for the achievable accuracy, however, is the availability of excellent cement manufacturing standards.

2-2.1 Principle and Theory of Fluorescence

Many chemical systems are photoluminescent; that is, they can be excited by electromagnetic radiation and, as a consequence, eremite radiation either of the same wavelength or of a modified wavelength. one of the most common manifestations of photoluminescence is fluorescence.

Taking an organic molecule as an example, Fig 2.5 illustrates the processes where a substance absorbs light and then emits light. At ground state, the molecule absorbs light and transits to the excited state. The molecule loses a portion of the exciting energy as vibrational energy, etc., transits to a lower vibration level with no radiation emitted and then returns to the ground state while emitting a kind of optical energy. This is called " fluorescence ".

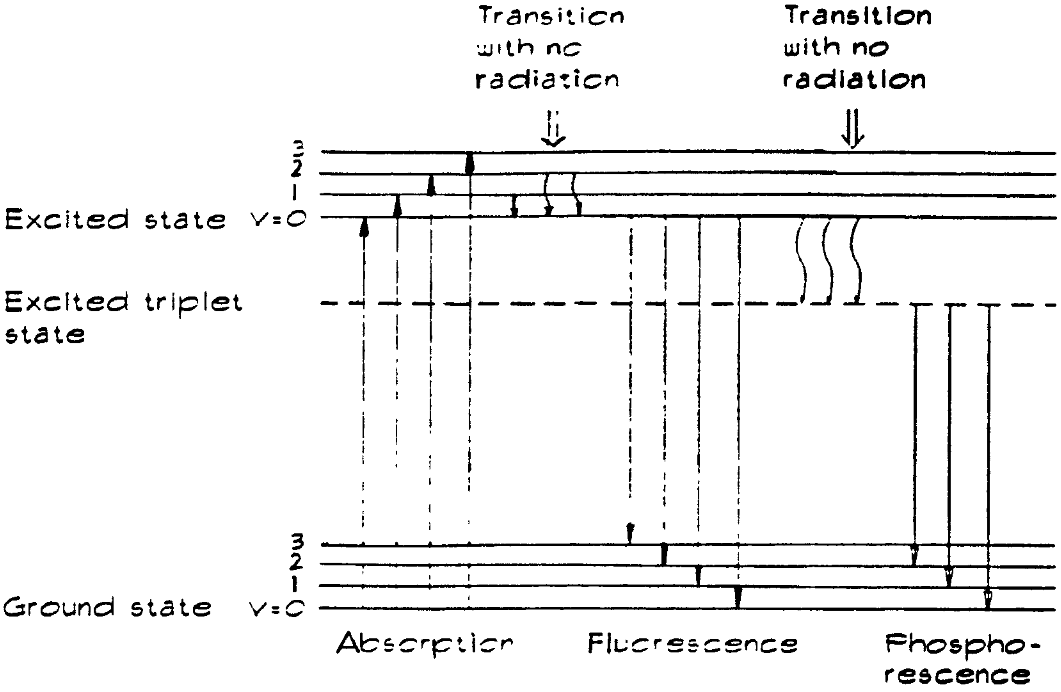


Fig 2.5 Energy Levels of Typical Organic Molecule

Since a portion of the light absorbed by a substance is lost by vibrational relaxation, etc., the fluorescence emitted from the substance has a longer wavelength than the excitation light (Stokes' law).

The ratio of the optical energy absorbed by a substance relative to the total fluorescence energy emitted from the substance is called " quantum efficiency ". It can generally be said that a substance having higher quantum efficiency is more fluorescent. The intensity of the fluorescence emitted from the substance is proportional to the optical energy absorbed.

When diluted solutions are measured as samples, therefore, it is possible to represent the fluorescence intensity by the following formula:

$$F = KI_0ClEt$$

where F = Fluorescence intensity

K = Instrumental constant

I_0 = Intensity of excitation beam

C = Concentration of sample

l = Effective optical path length of cell

E = Molar absorptivity

t = Quantum efficiency

Measurement of fluorescent intensity permits the quantitative determination of traces of many inorganic and organic species; many useful fluorometric methods exist, particularly for biological systems.

2-2.2 Instrumentation of FS

A variety of instruments for fluorescent measurement have been described, and a dozen or more designs are produced commercially.

Fig 2.6 shows a typical arrangement of components of fluorometer and spectrofluorometer. Radiation from a suitable source is passed through a monochromator or filter which serves to transmit that part of the beam which will excite fluorescence but exclude wavelengths that are subsequently produced by the irradiated sample. Fluorescence radiation is emitted by the sample in all directions but is most conveniently observed at right angles to the excitation beam; at other angles increased scattering from the solution and the cell walls is likely to result in large errors in the measurement of fluorescent intensity. The emitted radiation reaches a photoelectric detector after passing through a second filter or monochromator system that isolates the fluorescent peak. The output of the detector is amplified and displayed on a meter, a recorder, or an oscilloscope.

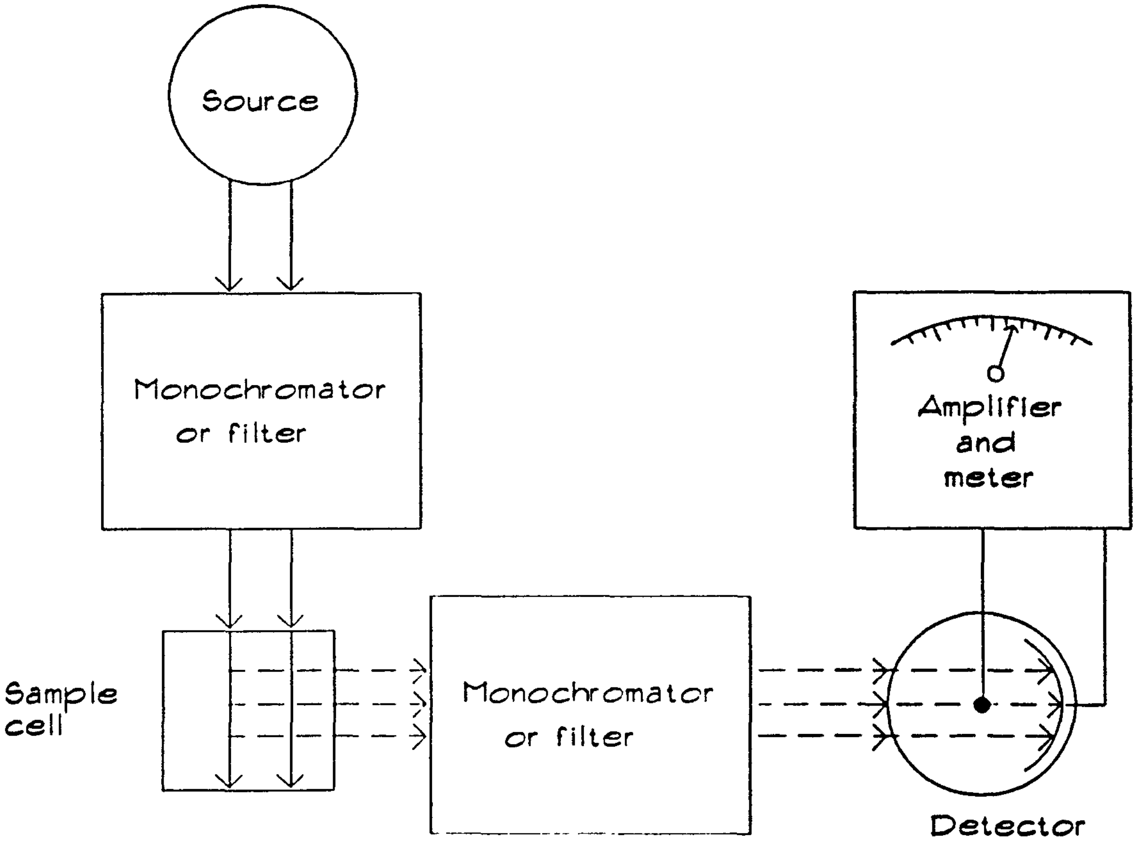


Fig 2.6 Components of fluorometer or spectrofluorometer

Sources. In most applications a more intense source is needed than the tungsten or hydrogen lamp employed for the measurement of absorption. A mercury or xenon arc lamp is commonly employed.

The xenon arc lamp produces intense radiation by the passage of current through an atmosphere of xenon. The spectrum is continuous over the range between about 250 and 600 nm, with the peak intensity occurring at about 470 nm.

Mercury arc lamps produce an intense line spectrum. High-pressure lamps (8 atmospheres) give lines at 365, 398, 436, 546, 579, 690, and 734 nm. Low-pressure lamps, equipped with a silica envelope, additionally provide intense radiation at 254 nm. In as much as fluorescent behavior can be induced in most fluorescing compounds by a variety of wavelengths, at least one of the mercury lines ordinarily proves suitable.

Filters and Monochromators. Both interference and absorption filters have been employed on fluorometers. Most spectrofluorometers are equipped with grating monochromators.

Detectors. The typical fluorescent signal is of low intensity; large amplification factors are thus required for its measurement. Photomultiplier tubes have come into widespread use as detectors in sensitive fluorescence instruments.

Cell and Cell Compartments. Both cylindrical and rectangular cells constructed of glass or silica are employed in fluorescence measurements. Care must be taken in the design of the cell compartment to reduce the amount of scattered radiation reaching the detector. Baffles are often introduce into the compartment for this purpose.

2-2.3 The Use of FS in determination of w/c Ratio

As we discussed in the previous section, we have learned the fact that the concentration of calcium ions is the key fact in determination of water-cement ratio in the freshly mixed concrete. Fluorometric methods have been successfully applied for the determination of ionic concentrations. Therefore, it was decided to also use fluorescence spectrometry for the determination of the water-cement ratio in freshly mixed concrete.

There are two things we have to point out here before we continue on to detailed procedure:

In order to increase sensitivity, the intensity of the calcium ion fluorescence has to be increased by a suitable reagent. In general, reagent and the substance to be tested will form a complex compound which will have stronger fluorescent and therefore the sensitivity of the fluorometry will increase. Survey of technical literature [23, ASTM] indicated the suitability of morin and calcein as flourometric reagents for use with calcium.

Unlike Atomic Absorption Spectrometry, Fluorescence Spectrometry can determine the ionic concentrations in dilute solutions as well as paste form. Therefore, we did not need to dilute the cement pastes after mixing, and they were directly employed in FS analysis.

Chapter 3
Experimental Program : I-Atomic Absorption

3.1 Laboratory Apparatus

(1) The Instrument used for this study was Thermo Jarrell-Ash, Smith-Hieftje 12, model 875 atomic absorption spectrophotometer. The instrument is presented in Fig 3.1 and Fig 3.2

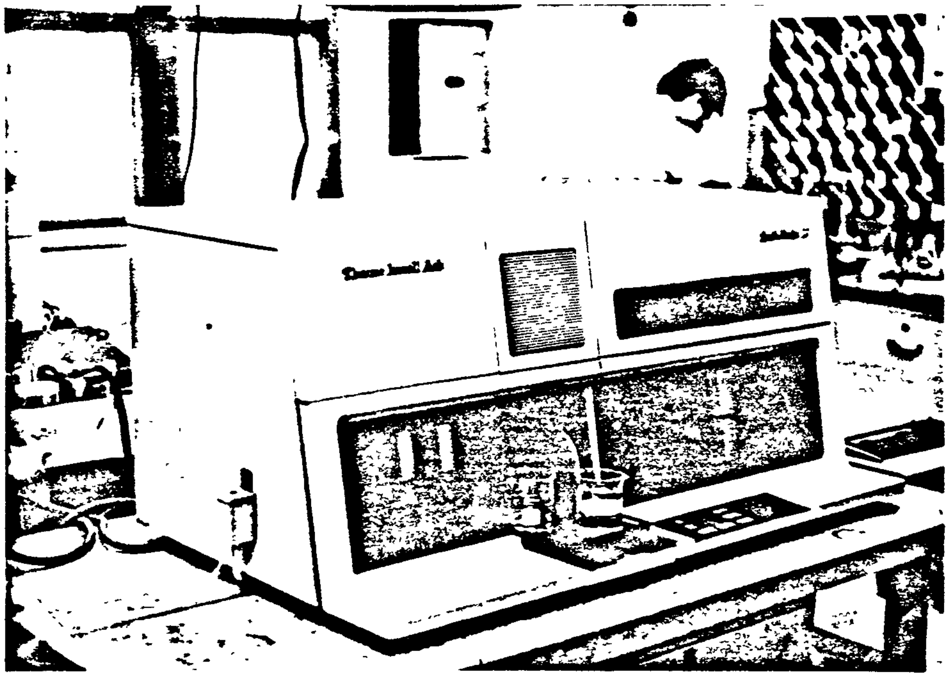


Fig 3.1 Jarrell-Ash Atomic Absorption Spectrometer

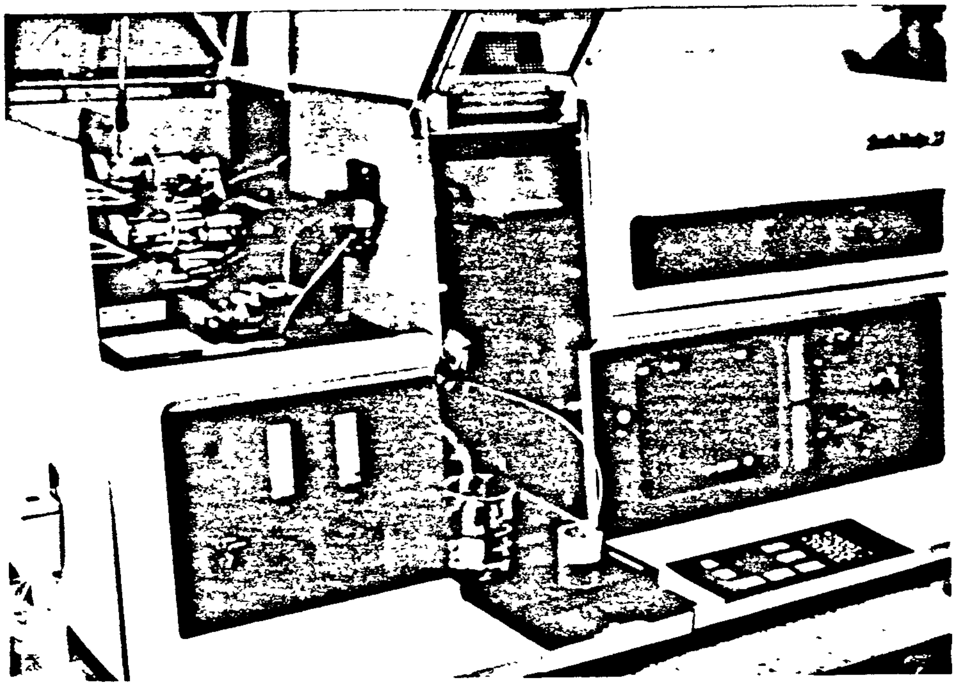


Fig 3.2 Internal View of Atomic Absorption

(2) Balance, having a minimum capacity of 1000 g and a sensitivity of at least 0.001 g.
(3) Shovels, hand scoops and rubber gloves as required.
(4) Stirrer or spatula for stirring the fresh concrete and water.
(5) a number of 25 ml volumetric flasks and one 1000 ml volumetric flask for 500 ml standard solution
(6) Pipet, 100 ul, 200 ul and 1000 ul respectively
(7) Glass fiber filter Paper 1.2 um pore, 2.1 cm diameter filter paper.
(8) Filtration funnel.
(9) Gooch crucible (ceramic filter holder).
(10) Suction flask.

3.2 Materials

(1) **Cement.** Three different brands of portland cement were employed, namely: Lone Star (typeI), Lone Star (typeII), Hercules (typeII) and Atlantic (typeII). The chemical composition of these cement types are presented in table 3.1.

Table 3.1

Standard Compositions of typical Portland Cement (Type II)

Typical Oxide Composition percent

CaO	63.0
SiO_3	20.0
Al_2O_3	6.0
Fe_2O_3	3.0
MgO	1.5
SO_3	2.0
K_2+Na_2O	1.0
Other	1.0
Loss on ignition	2.0
Insoluble residue	0.5

Calculated Compound Composition percent

C_3A	10.8
C_3S	54.1
C_2S	16.6
C_4AF	9.1
Minor Compounds	-

(2) **Water.** Pure Laboratory water was employed in the present study.

(3) **Reagent.** Lanthanum chloride is used in our study.

3.3 Preparation of Calibration Curve

The instrument has to be calibrated before the sample is analyzed. This is done so as the absorbance values obtained from the instrument can be directly related to the calcium concentration in parts per million (ppm) in the sample.

The calibration curve was made by standard solutions of different concentrations which are 1 ppm (ug/ml), 2 ppm and 3 ppm respectively in our study. Calcium standard of 500 ppm was prepared as follow : 50 ml deionized water is added to 1.249 g of primary standard calcium carbonate, $CaCO_3$. Add drop by drop a minimum volume of HCl (approx 10 ml) to effect complete dissolution of $CaCO_3$. Dilute to 1 liter with deionized water.

For preparation of 1 ppm standard calibration solution, 0.2 ml solution was taken from 500 ppm standard solution, 0.1% lanthanum chloride was added to avoid interference from other elements, and then diluted with 100 ml deionized water. Similarly, For 2 ppm and 3 ppm standard solutions, 0.4 ml and 0.6 ml respectively were taken from 500 ppm standard solution. Fig 3.3 illustrates a typical calibration curve for calcium at linear concentration.

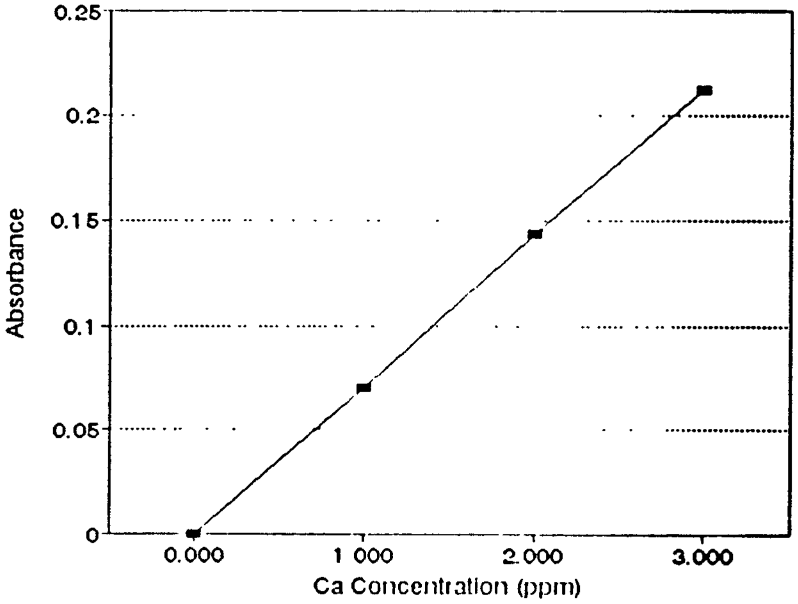


Fig 3.3 Typical Linear Calibration Curve For Calcium

3.4 Preparation of Sample

Each sample is prepared by the following procedure, except that for different water-cement ratios different weights of water are added. For example to prepare a sample with water-cement ratio of 0.4 by weight:

(1) Weigh 30 g cement and 12 g pure Water.

(2) Mix cement with water and stir continuously for exactly 10 minutes.

(3) Put glass fiber filter paper on the bottom of the gooch crucible. Cement paste is then transferred to the supernatent gooch crucible. Fig 3.4 shows the supernatent systems.

(4) Turn on the vacuum aspirator for extracting supernatant, the solution is separated into supernatent flask from the cement paste. This whole process takes exactly 2 minutes.

(5) Take 71.25 nl solution from supernatant flask, dilute with 25 ml pure water.

(6) Add 0.1% lanthanum chloride ($LaCl_3$-ZH_2O) to avoid interferences by aluminum and phosphorus. The resulting solution is required sample.

(7) Shake the flask of sample make it completely uniform.

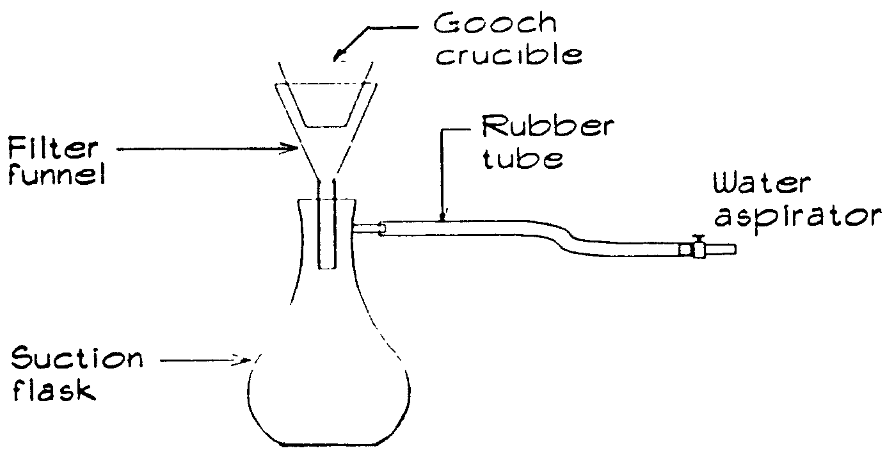


Fig 3.4 Supernatent Systems

3.5 Operating Procedures

(1) The source and detector power is switched on, and the source power is set to the manufacturers' recommended parameters which for the determination of Ca are given in Table 3.2. With modern hollow- cathode lamp and photomultiplier-amplifer systems very little warm up time is required.

Table 3.2

Operating Parameter for Calcium

	Ca
Wavelength	4227A
Bandwidth	1 nm
Burner	5-cm slot
Fuel	C_2H_2
Oxidant	Air
Sensitivity	0.04 ppm
Analytical Range	0.2-7 ppm
AA Lamp Current	7
High Voltage	380

(2) The source position and optical system are adjusted so that the source radiation in atomic absorption spectroscope is incident upon the monochromator slit; the analytical line and spectral slit-width to be employed are selected at the monochromator.

(3) The flame is ignited and the fuel : oxidant flow rate ratio adjusted to recommended settings 10:4.

(4) The burner is allowed to warm up while solvent is nebulized.

(5) The absorption of calcium is dependent on the fuel-to-air ratio and the height of the light beam above the burner. The fuel flow should be adjusted to yield maximum absorption for a calcium standard before beginning the analysis.

(6) The standard, sample and blank (for zero calibration) solutions are aspirated directly into the flame sequentially and absorbance reading is noted for each. Each solution should be aspirated for sufficient time to enable the analytical signal to reach a steady value that can be measured with confidence.

(7) The nebulizer and burner assembly would better be washed by aspiration of pure solvent between each sample solution measured. This is particularly important when liquid of high dissolved solid content are dealt with in order to minimize clogging of the burner head or nebulizer capillary.

(8) The concentration of Calcium in solution per milliliter is determined by referring to a standard curve where calcium concentration is plotted versus absorbance. The final calculation of total calcium concentration in the sample is determined by taking into account dilution factors and size of the analyzed aliquot.

(9) After experiment all glassware should be soaked in mild detergent solution to remove gross contamination. Before use, each piece is cleaned with concentrated (1:1) HCl three times then rinse with tap water, then soaked in (1:1) nitric acid, followed by singly and doubly distilled water.

Chapter 4

Experimental Program : II-Fluorescence Spectrometry

4.1 Laboratory Apparatus

(1) The instrument used for this experiment was HITACHI model F-3010 Fluorescence spectrophotometer. The instrument is presented in Fig 4.1. A block diagram of the instruments components are given in Fig 4.2.

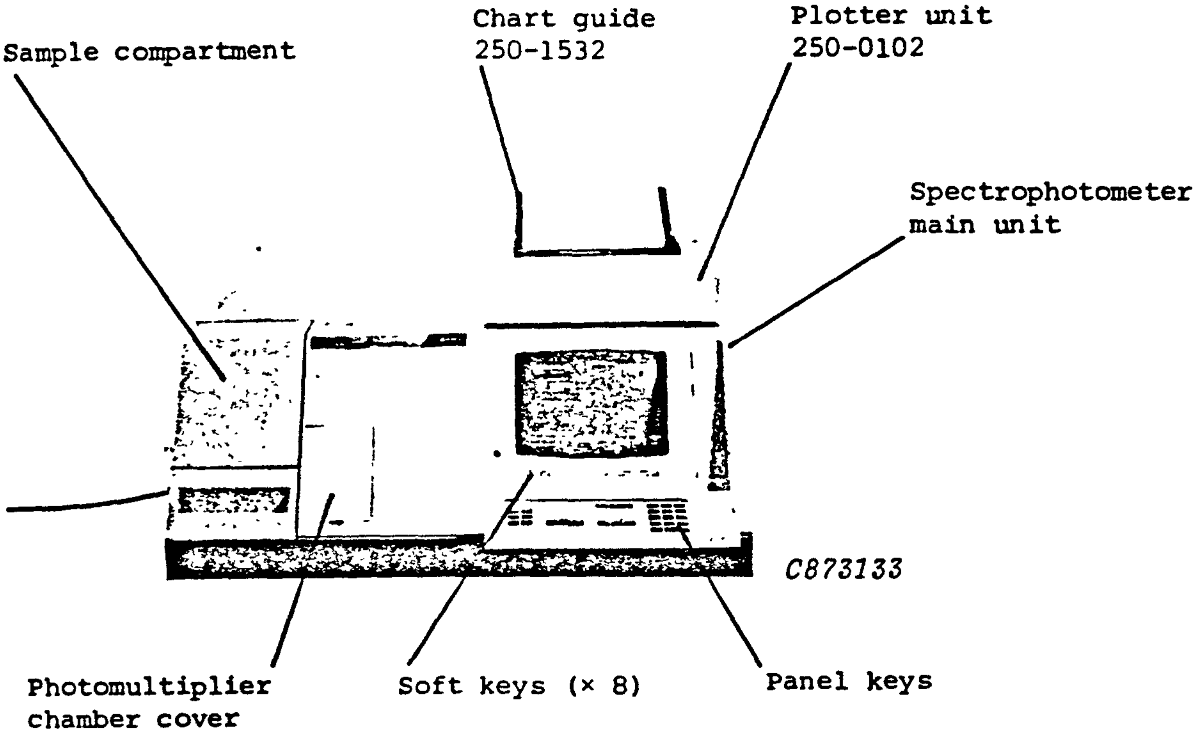


Fig 4.1 External View of Model F-3010

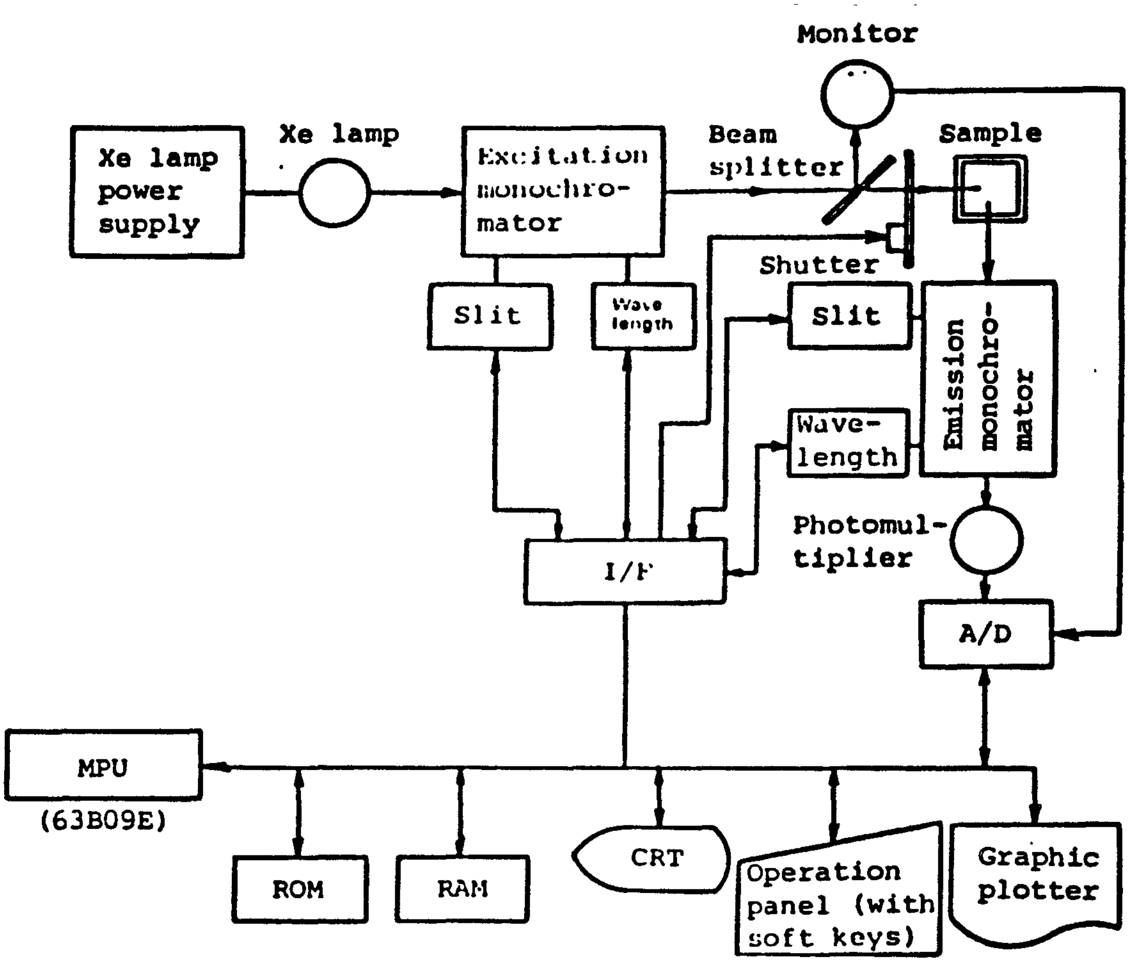


Fig 4.2 Functional Block Diagram

(2) Balance, Having a minimum capacity of 1000 g and a sensitivity of at least 0.001 g.

(3) Shovels, Hand scoops and rubber gloves as required.

(4) Stirrer or spatula for stirring the fresh concrete and water.

4.2 Materials

(1) **Cement.** Lone Star (type I) was used in this experiment.

(2) **Water.** Pure Laboratory water was employed

(3) **Reagent.** Morin and calcein were used as fluorescence reagent.

4.3 Preparation of Sample

All the samples were prepared according to the following procedure, with the exception in variations given to the amount of water added for various water-cement ratios, and amounts of added reagent for each test. For example to prepare a sample with water-cement ratio of 0.4 by weight:

(1) Weigh 10 g cement, 4 g water and 0.005 g reagent. (morin or calcein)

(2) Mix cement, water and reagent together and stir continuously for exactly 10 minutes.

(3) Weigh 1 g cement paste from the mixture. Transfer it to a solid sample hold for testing (Fig 4.3).

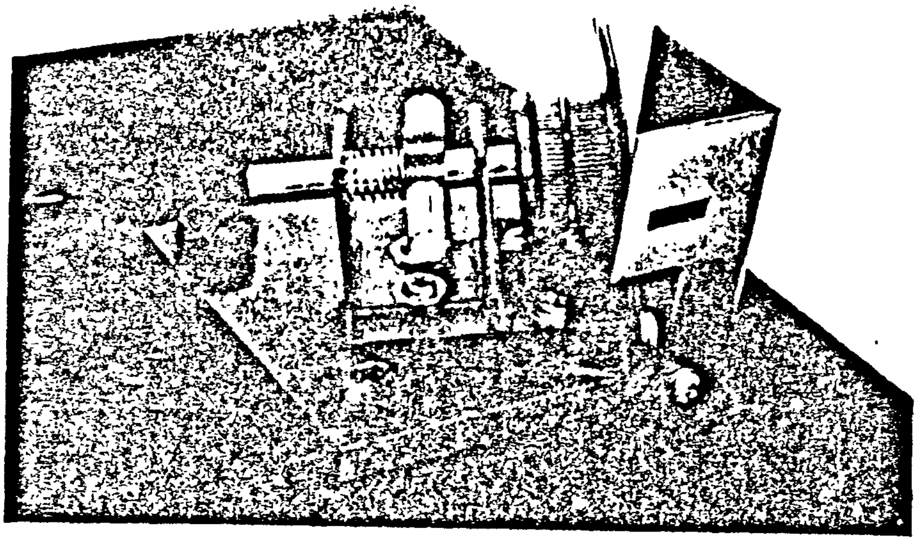


Fig 4.3 Analysis of cement paste sample

4.4 Operating Procedure

(1) Turn on the power switch. Make sure that lamp cooling fan is operating and that air is exhausted from the instrument.

(2) About ten seconds later, depress the Xe lamp start button to ignite the Xe lamp, the Xe lamp cannot be ignited while the computer switch is turn on. This is necessary to protect the built-in computer from shock at ignition of the Xe lamp.

(3) Turn on the computer switch.

(4) Set the following machine operating parameters on the computer:

Table 4.1

Operating Parameter

For testing calcium-morin complex

Excitation wavelength	425 nm
Emission wavelength	450-700 nm
Scan speed	60 nm/sec
Excitation bandpass	5 nm
Emission bandpass	5 nm
Total scan time	2 minutes

The excitation and emission wavelengths were chosen according to a previous scan for obtaining optimum peaks.

(5) Scan the emission wavelength, wavelength peak value which is optimum intensity for fluorescence complex.

Chapter 5
The Microwave Method

5-1 Introduction and Laboratory Apparatus

The microwave method is one of the methods for determining the water content of fresh concrete. Basically the test consists of weighing a fresh sample of concrete (cement paste in our case), removing the water through heating in a microwave oven for less than an hour (usually about 15 to 20 minutes), and weighing the dried sample. The difference is the water content of the sample.

The following equipment is required to perform a test for the water content of fresh concrete by the microwave method.

1. 1000 g capacity scale with 0.001 g readings and accuracy.
2. 18 cm (7 in) microwave resistant ceramic plate.
3. Microwave oven.
4. Putty knife to break up and stir sample.
5. 0.001 m^3 (0.25 gal) air tight plastic container.
6. Scoop or trowel to place the fresh concrete sample in the ceramic plate.

5-2 Materials and Experimental procedure

Three different brands of cement used in this method were the same as those used in atomic absorption method. Tap water at room temperature was used in preparing the cement paste samples.

The test is performed in six steps:

1. Weigh and mix approximately 100 gm cement paste in different water-cement ratios, Ranging from 0.4 to 0.55 at 0.025 interval. Then place the cement paste in an air tight container to help avoid any water loss due to evaporation.
2. Level and balance the scale and determine the weight of the ceramic plate.
3. Measure 45 g cement Paste as our representative sample onto the microwave resistant ceramic plate , and then spread it out evenly.
4. Place the cement paste sample and ceramic plate into the microwave oven and set the desired heating level.
5. Dry to a constant weight, stopping every few minutes to break- up and stir the sample. This helps to relieve any entrapped water. When the sample appears dry, weigh it after stirring each time to determine constant weight.
6. Subtract the final weight from the initial weight to obtain " water dried out in the microwave oven." This value can be easily converted to percent water content in the sample.

Chapter 6

Experimental Results and Discussion

6-1 Atomic Absorption (AA) Experiments

A series of tests by employing the AA technique were conducted during the course of this study. The main objective of this investigation was to study the effect of w/c ratio on the concentration of calcium ions in the cement paste system. The experimental program is outlined in table 6.1

Table 6.1

Experimental Program

w/c Ratio Studied	Cement Type Studied	Number of Test
0.400 0.425 0.450 0.475 0.500 0.525 0.550	Lone Star (typeII) Atlantic (typeII) Hercules (typeII) Lone Star (type I)	Three tests per type and per w/c ratio

Tables 6.2 through 6.5 represent test results based on experiments performed on Lone Star (typeII), Atlantic (typeII), Hercules (typeII) and Lone Star (typeI). These tables indicated the actual water-cement ratio and the corresponding calcium concentration results from the AA method. Fig 6.1, Fig 6.3, Fig 6.5 and Fig 6.7 represent the calibration curves based on the experiments indicated in tables 6.2 through 6.5.

Data shown in each one of the tables 6.2 through 6.5 were analyzed using linear regression. Results are depicted in Fig 6.2, Fig 6.4, Fig 6.6 and Fig 6.8.

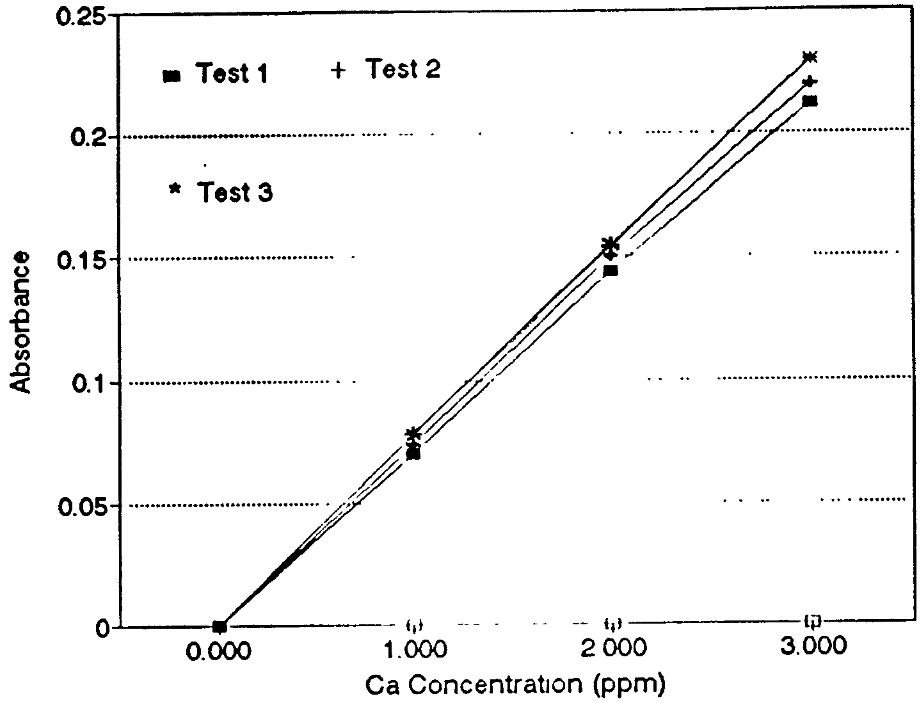


Fig 6.1 Standard Calibration curves for Test Results Shown in Table 6.2

Table 6.2

AA Results Obtained from Tests with Lone Star (TypeII) Cement

w/c Ratio	Calcium Concentration (ppm)		
	Test 1	Test 2	Test 3
0.400	1.820	1.848	1.923
0.425	1.905	1.928	2.032
0.450	2.108	2.178	2.095
0.475	2.278	2.210	2.285
0.500	2.374	2.365	2.407
0.525	2.415	2.456	2.535
0.550	2.585	2.513	2.587

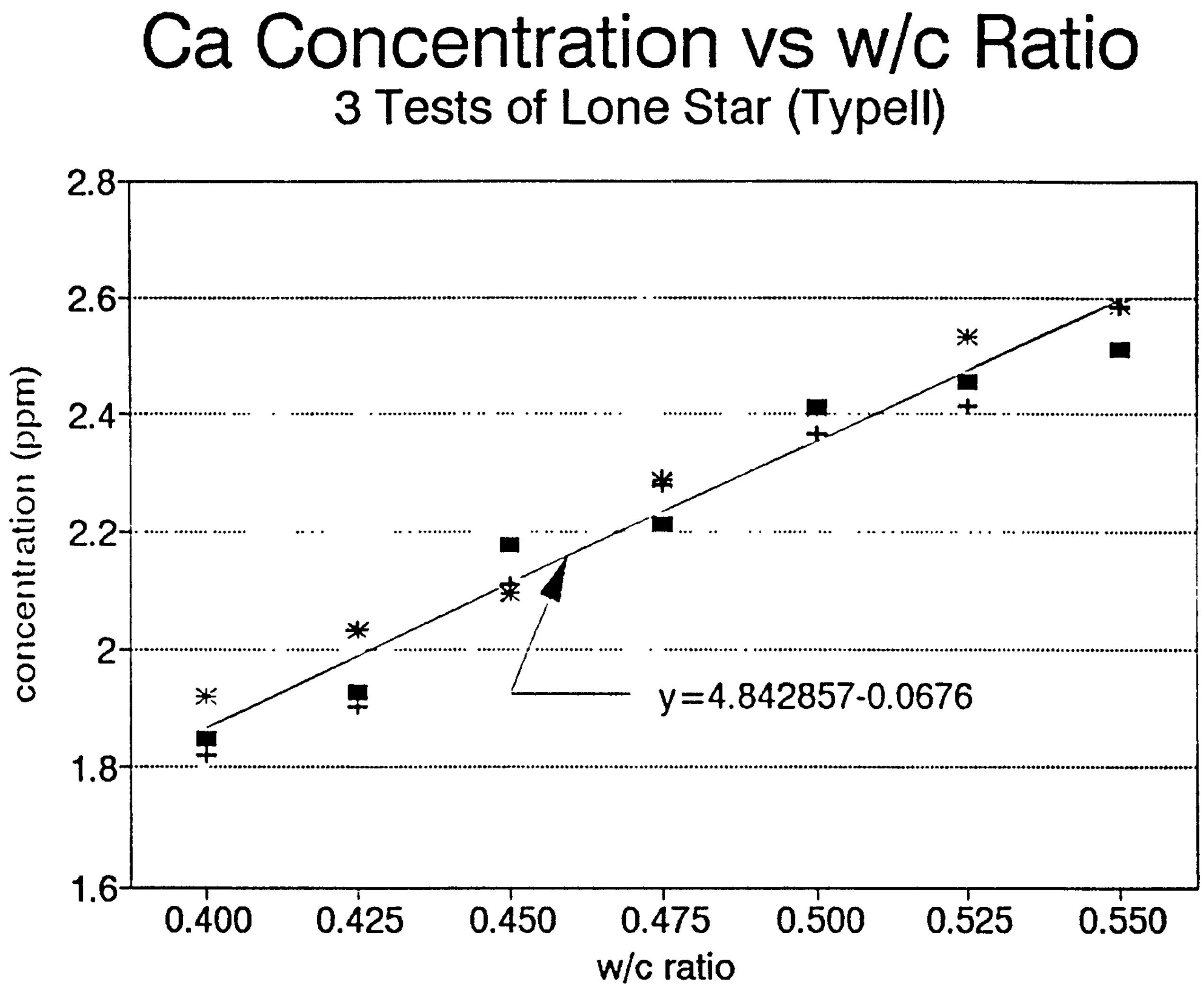


Fig 6.2 Linear Regression Curve for Determination of W/C Ratio of Lone Star (Type II) Cement

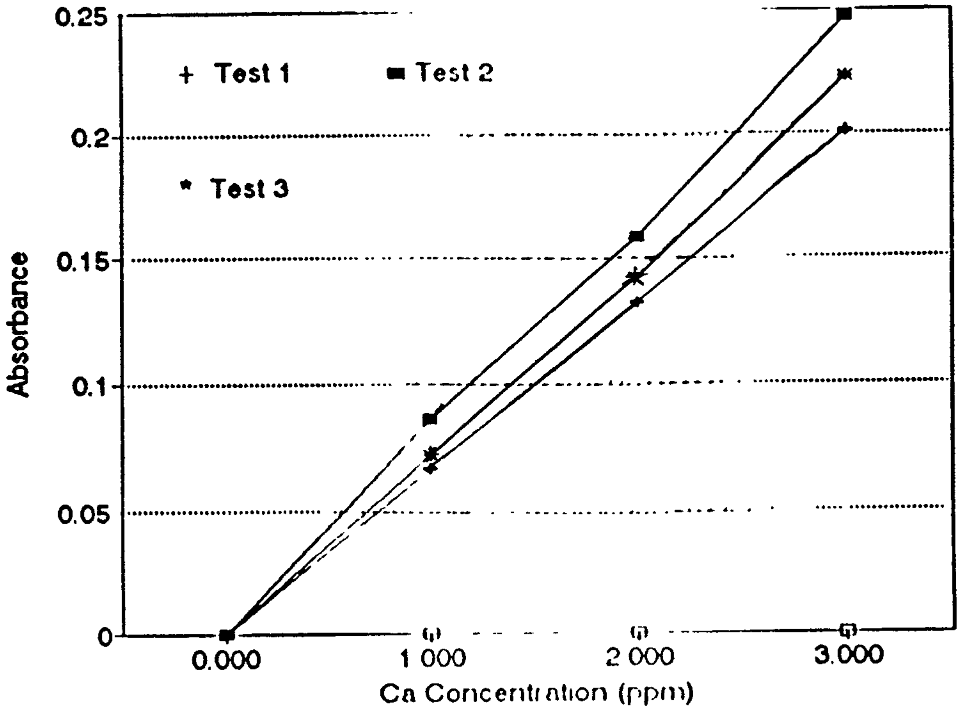


Fig 6.3 Standard Calibration Curves for Test Results Shown in Table 6.3

Table 6.3

AA Results Obtained from Tests with Atlantic (TypeII) Cement

W/C	Calcium Concentration (ppm)		
Ratio	Test 1	Test 2	Test 3
0.400	2.389	2.524	2.474
0.425	2.481	2.678	2.553
0.450	2.601	2.723	2.532
0.475	2.663	2.903	2.704
0.500	2.895	2.923	2.825
0.525	2.900	2.906	2.902
0.550	3.003	3.097	3.020

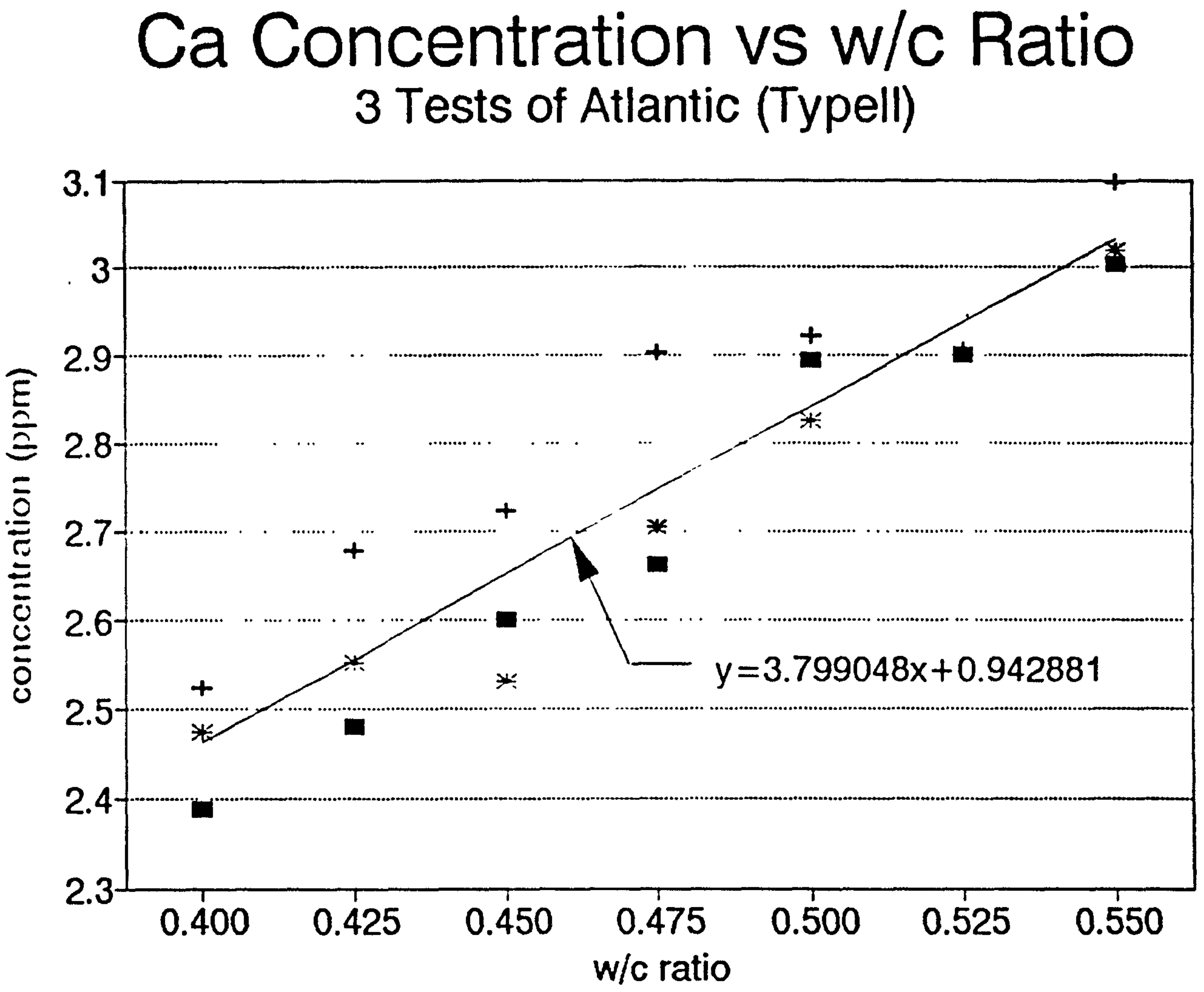


Fig 6.4 Linear Regression Curve for Determination of W/C Ratio of Atlantic (Type II) Cement

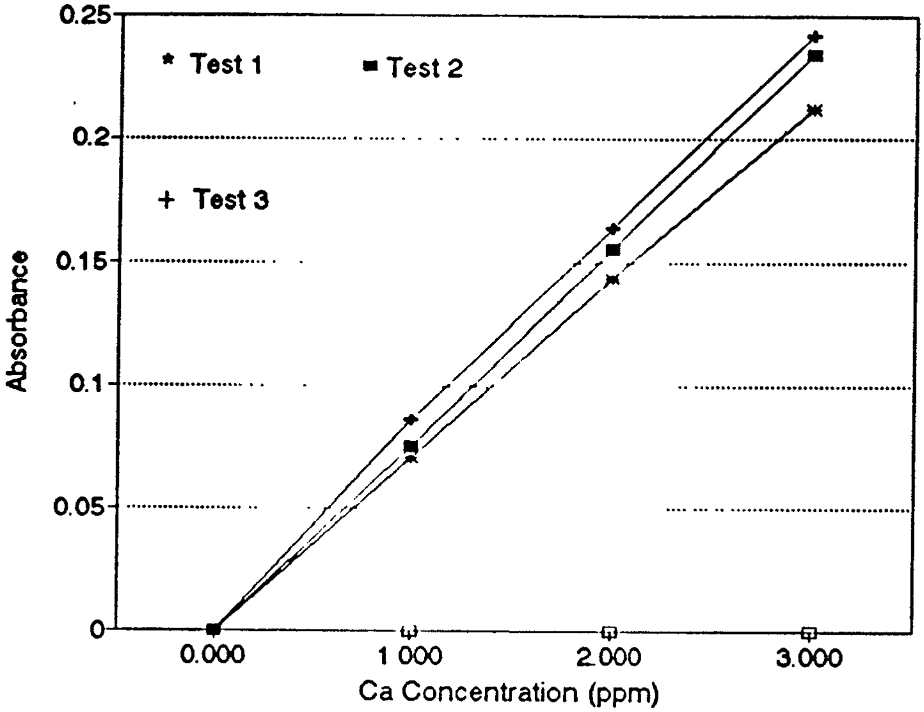


Fig 6.5 Standard Calibration Curves for Test Results Shown in Table 6.4

Table 6.4

AA Results Obtained from Tests with Hercules (Type II) Cement

w/c Ratio	Calcium Concentration (ppm)		
	Test 1	Test 2	Test 3
0.400	2.117	2.147	2.230
0.425	2.256	2.335	2.423
0.450	2.445	2.622	2.550
0.475	2.538	2.706	2.786
0.500	2.875	2.738	2.835
0.525	2.814	2.828	2.942
0.550	3.085	2.955	3.123

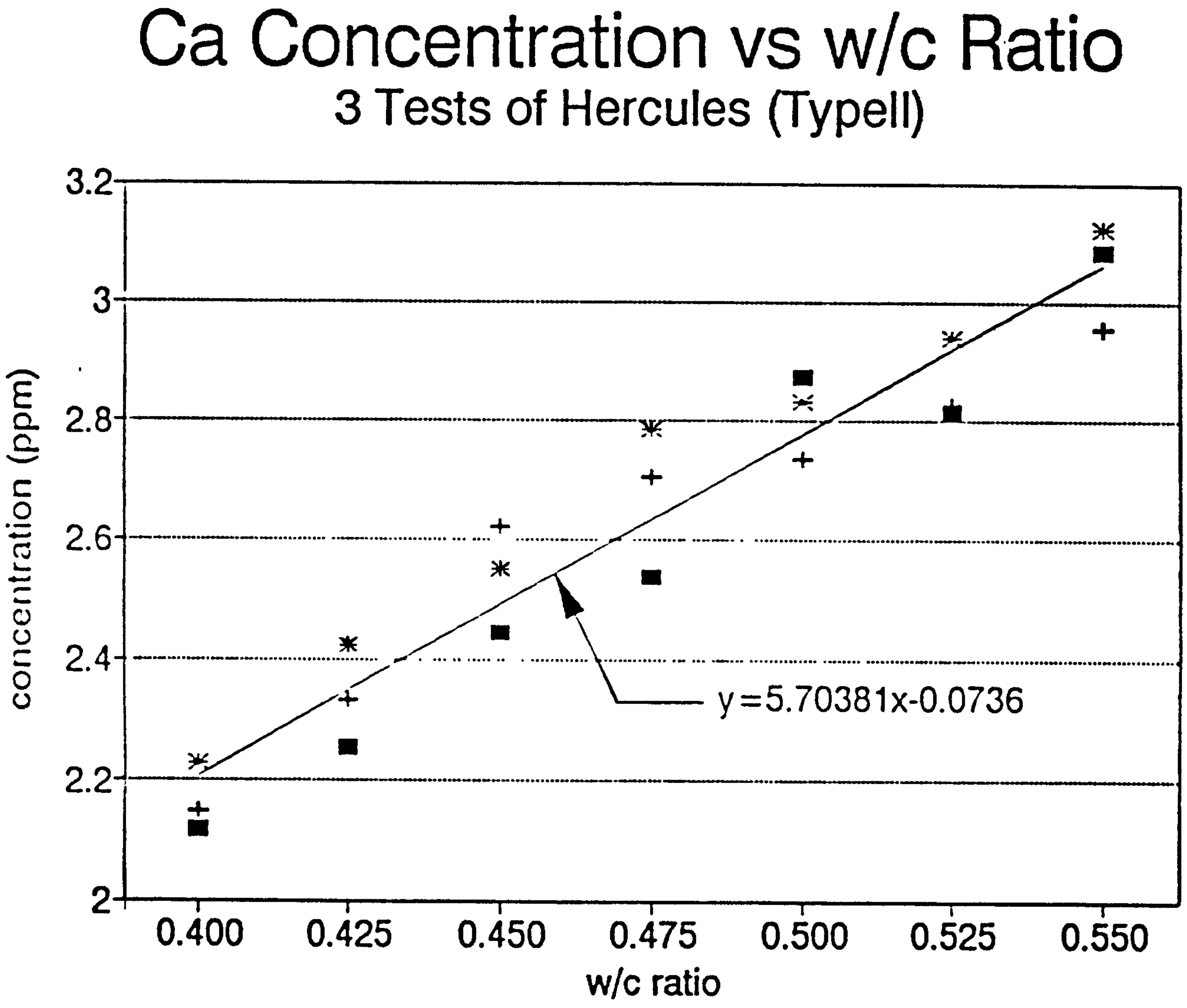


Fig 6.6 Linear Regression Curve for Determination of W/C Ratio of Hercules (Type II) Cement

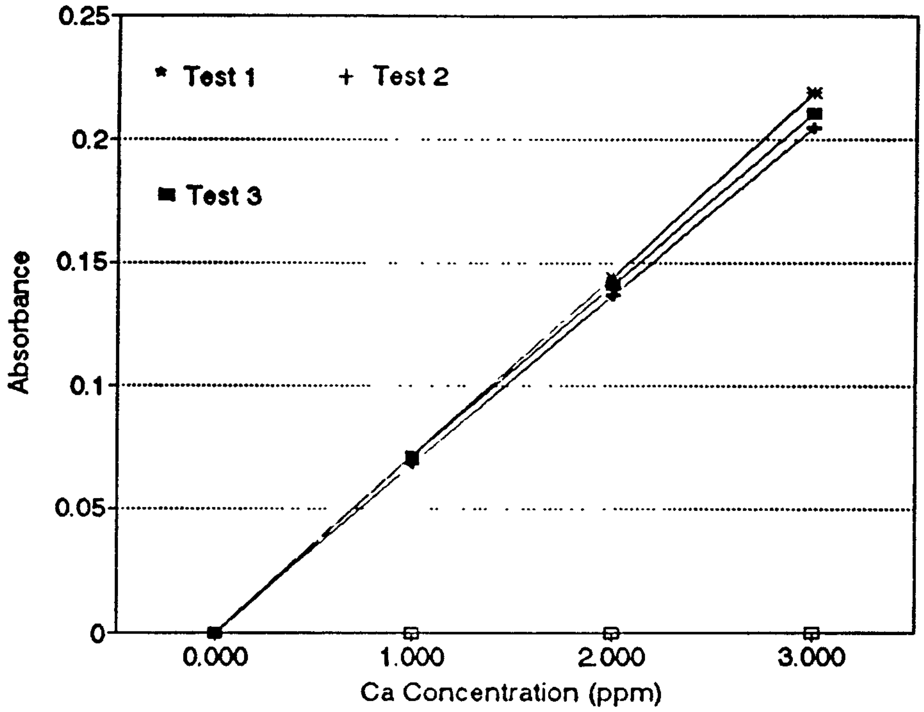


Fig 6.7 Standard Calibration Curves for Test Results Shown in Table 6.5

Table 6.5

AA Results obtained from Tests with Lone Star (type I) Cement

w/c Ratio	Calcium Concentration (ppm)		
	Test 1	Test 2	Test 3
0.400	4.720	4.600	4.480
0.425	5.060	5.200	4.840
0.450	5.500	5.200	5.200
0.475	5.300	5.400	5.500
0.500	6.020	5.600	5.640

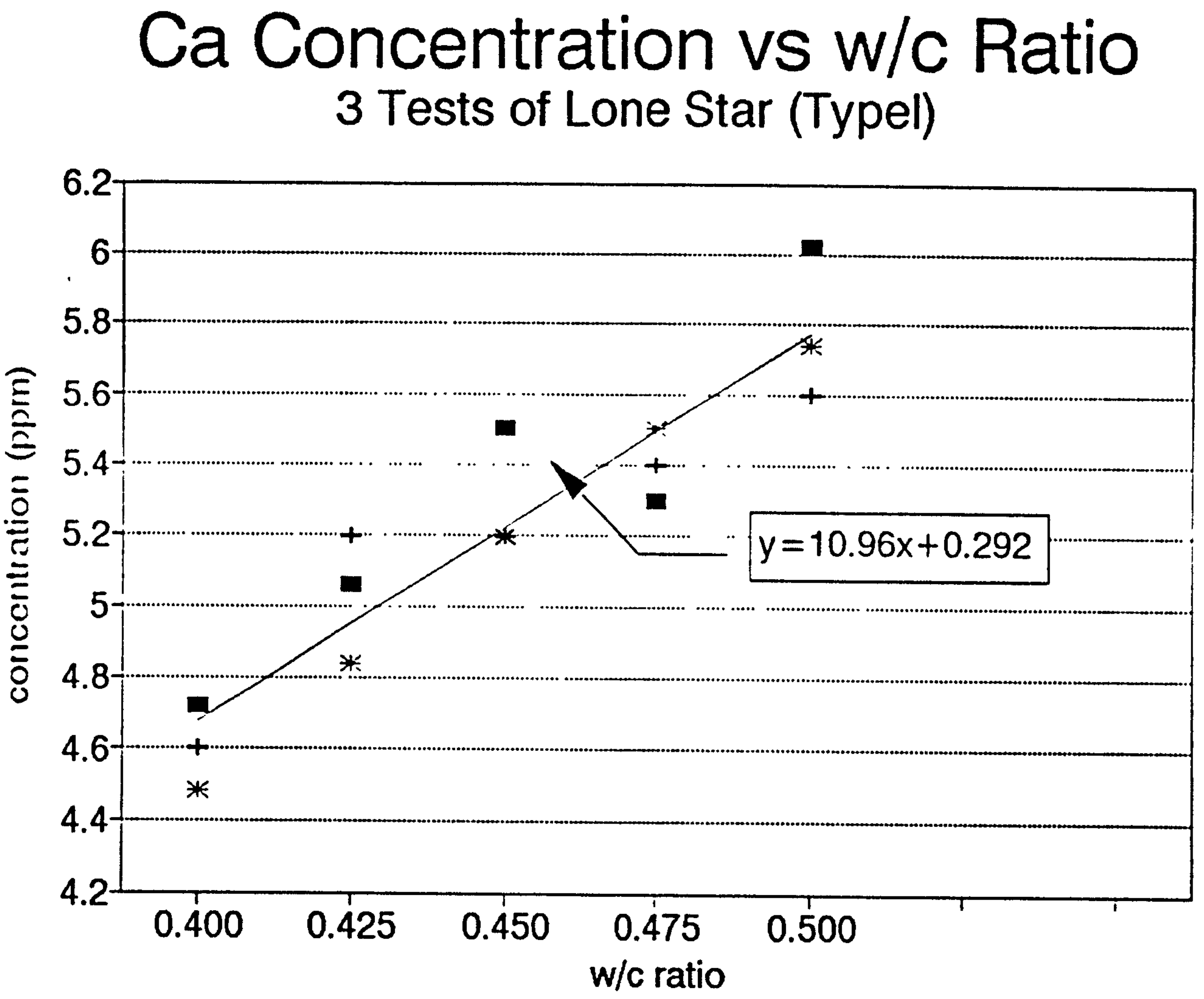


Fig 6.8 Linear Regression Curve for Determination of W/C Ratio of Lone Star (Type I) Cement

Table 6.6 represents correlation relationships obtained from the regression analysis performed on data from Lone star (typeII) cement experiments. The table includes percent of error and difference. Tables 6.7 through 6.9 represent the same for the Atlantic (typeII), Hercules (typeII) and Lone star (typeI) cements respectively.

Table 6.6

Max. Positive & Negative Error of AA Method (Lone star II)

actual w/c ratio	value from R.C A (ppm)	Max value from test B (ppm)	Min value from test C (ppm)	difference A-B (ppm)	Max +ve error percent	difference A-C (ppm)	Max -ve error percent
0.400	1.864	1.820	1.923	0.044	2.36%	-0.059	-0.317%
0.425	1.955	1.905	2.038	0.050	2.56%	-0.077	-3.940%
0.450	2.127	2.095	2.178	0.032	1.50%	-0.051	-2.260%
0.475	2.258	2.210	2.285	0.048	2.12%	-0.027	-1.200%
0.500	2.396	2.365	2.413	0.031	1.29%	-0.017	-0.710%
0.525	2.469	2.415	2.535	0.054	2.19%	-0.066	-2.670%
0.550	2.567	2.513	2.587	0.049	1.91%	-0.025	-0.980%

Table 6.7

Max. Positive & Negative Error of AA method (Atlantic II)

actual w/c ratio	value from R.C A (ppm)	Max value from test B (ppm)	Min value from test C (ppm)	difference A-B (ppm)	Max +ve error percent	difference A-C (ppm)	Max -ve error percent
0.400	2.451	2.389	2.524	0.071	2.890%	-0.064	-2.590%
0.425	2.561	2.481	2.678	0.080	3.124%	-0.117	-4.569%
0.450	2.658	2.601	2.725	0.057	2.140%	-0.067	-2.515%
0.475	2.759	2.663	2.903	0.096	3.480%	-0.144	-5.219%
0.500	2.855	2.825	2.924	0.030	1.050%	-0.069	-2.420%
0.525	2.956	2.900	2.906	0.056	1.894%	+0.050	+1.691%
0.550	3.052	3.003	3.097	0.049	1.610%	-0.045	-1.474%

Table 6.8

Max. Positive & Negative Error of AA Method (Hercules II)

actual w/c ratio	value from R.C A (ppm)	Max value from test B (ppm)	Min value from test C (ppm)	difference A-B (ppm)	Max +ve error percent	difference A-C (ppm)	Max -ve error percent
0.400	2.207	2.117	2.230	0.090	4.060%	-0.023	-0.106%
0.425	2.350	2.256	2.423	0.094	4.000%	-0.073	-3.106%
0.450	2.494	2.445	2.622	0.049	1.960%	-0.128	-4.600%
0.475	2.638	2.538	2.706	0.100	3.791%	-0.068	-2.578%
0.500	2.781	2.738	2.875	0.044	1.560%	-0.094	-3.360%
0.525	2.925	2.814	2.942	0.111	3.795%	-0.017	-0.581%
0.550	3.069	2.955	3.123	0.114	3.720%	-0.054	-1.760%

Table 6.9

Max. Positive & Negative Error of AA Method (Lone Star I)

actual w/c ratio	value from R.C A (ppm)	Max value from test B (ppm)	Min value from test C (ppm)	difference A-B (ppm)	Max +ve error percent	difference A-C (ppm)	Max -ve error percent
0.400	4.636	4.480	4.720	0.156	3.360%	-0.084	-1.810%
0.425	4.932	4.840	5.060	0.092	1.865%	-0.128	-2.595%
0.450	5.229	5.200	5.500	0.029	0.550%	-0.271	-5.180%
0.475	5.526	5.300	5.500	0.226	4.089%	+0.026	+0.471%
0.500	5.822	5.600	6.020	0.222	3.800%	-0.198	-3.400%

As we can see from these tables, the 0.025 increment for water-cement ratio seems too small to show a clear relation between each consecutive tests. (Except the one for Lone Star typeII cement) For this reason, we chose four points based on 0.05 increments in w/c for each group. Therefore, the water-cement ratio of 0.4, 0.45, 0.50 and 0.55 were chosen for analysis. (Fig 6.9 through Fig 6.12)

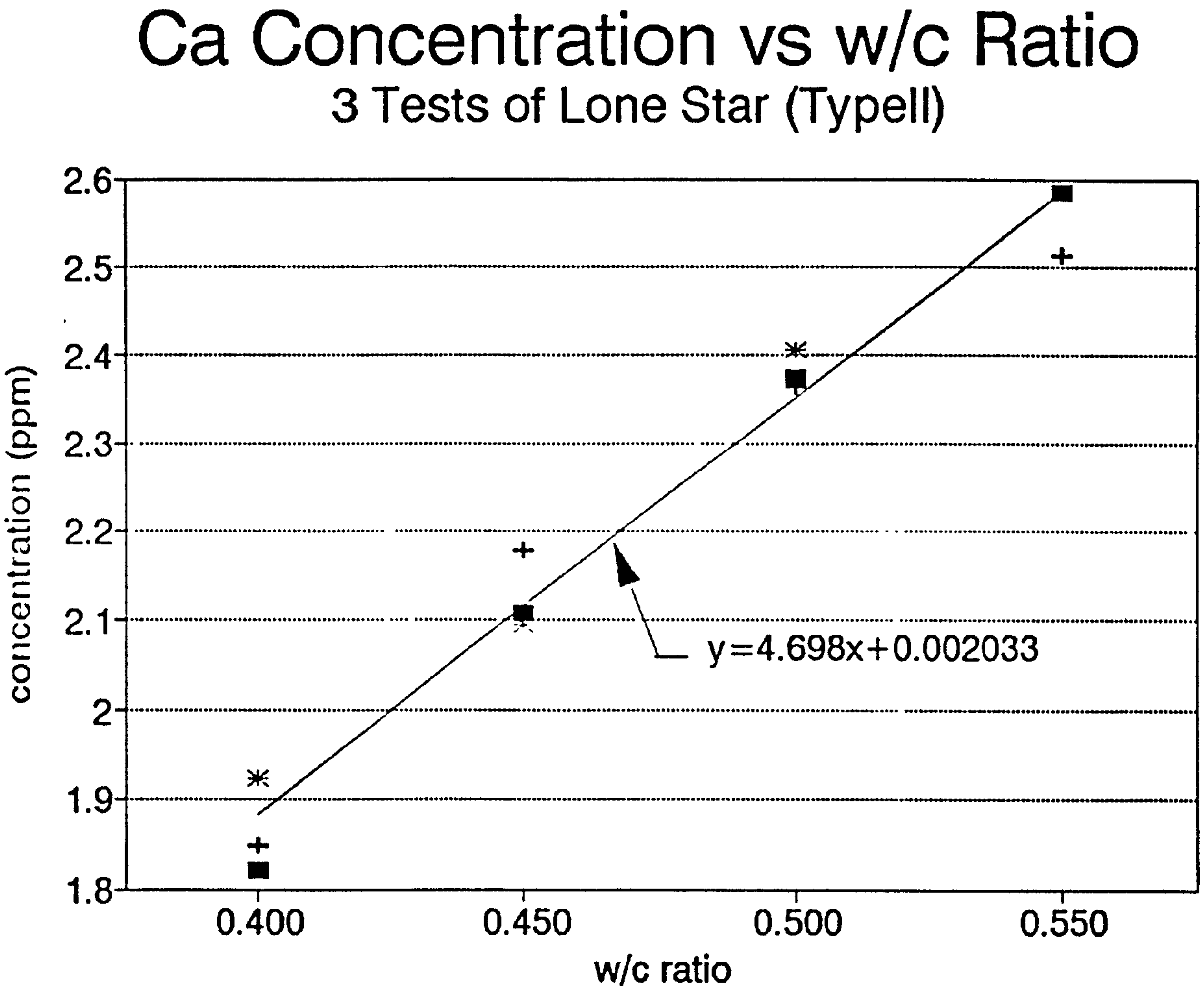


Fig 6.9 Linear Regression Curve Based on Four Points for Determination w/c Ratio of Lone Star (typeII) Cement

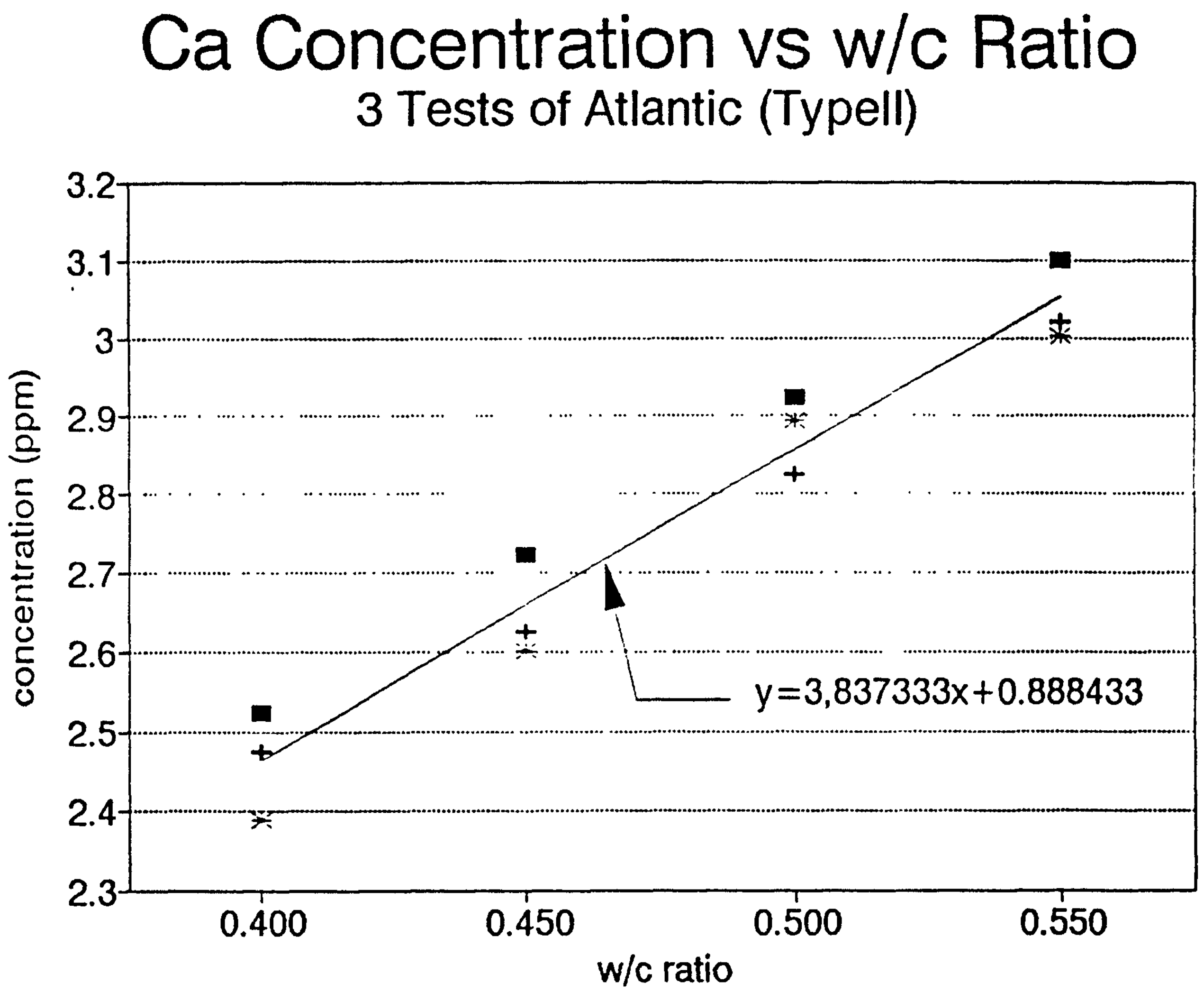


Fig 6.10 Linear Regression Curve Based on Four Points for Determination w/c Ratio of Atlantic (typeII) Cement

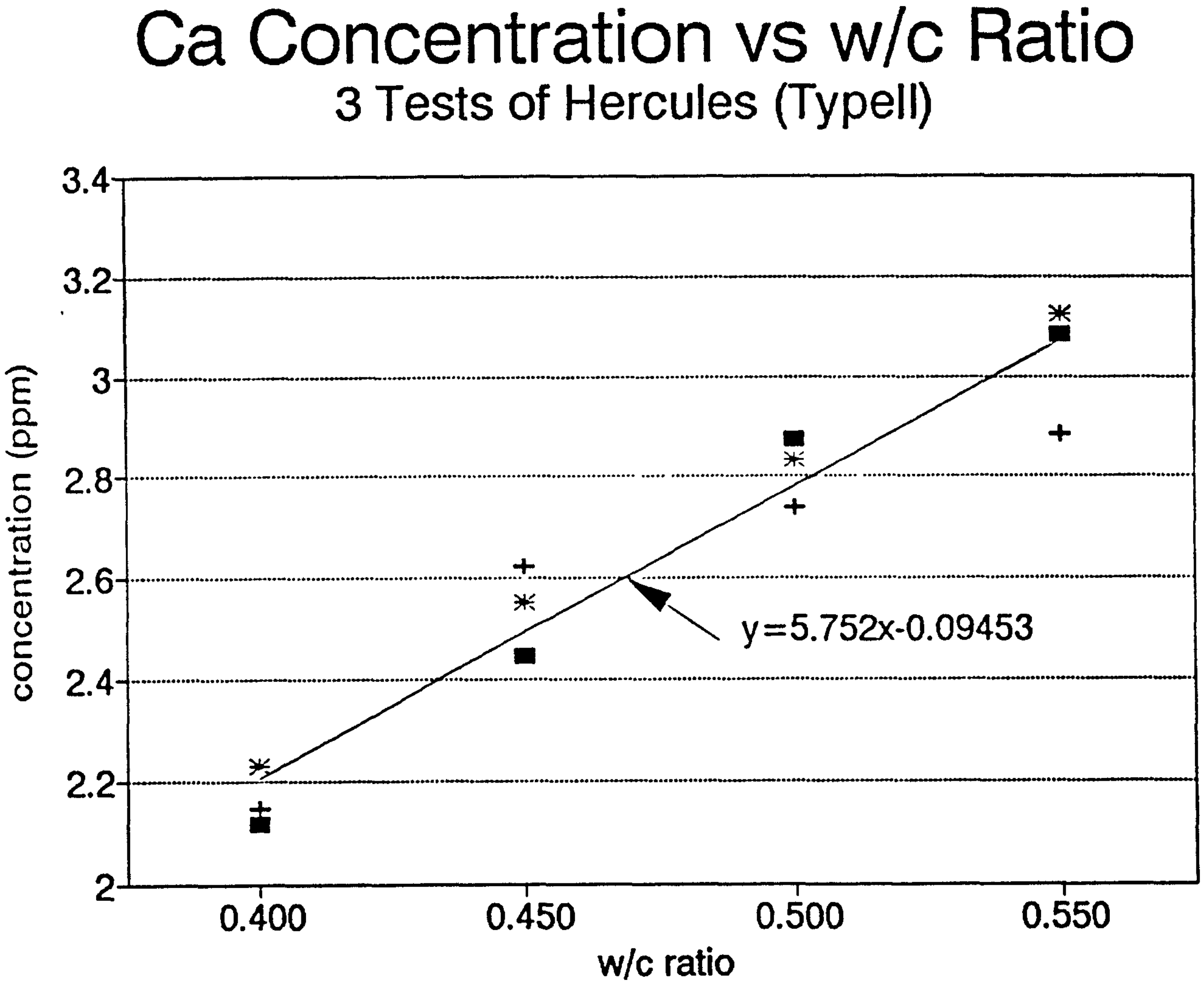


Fig 6.11 Linear Regression Curve Based on Four Points for Determination w/c Ratio of Hercules (typeII) Cement

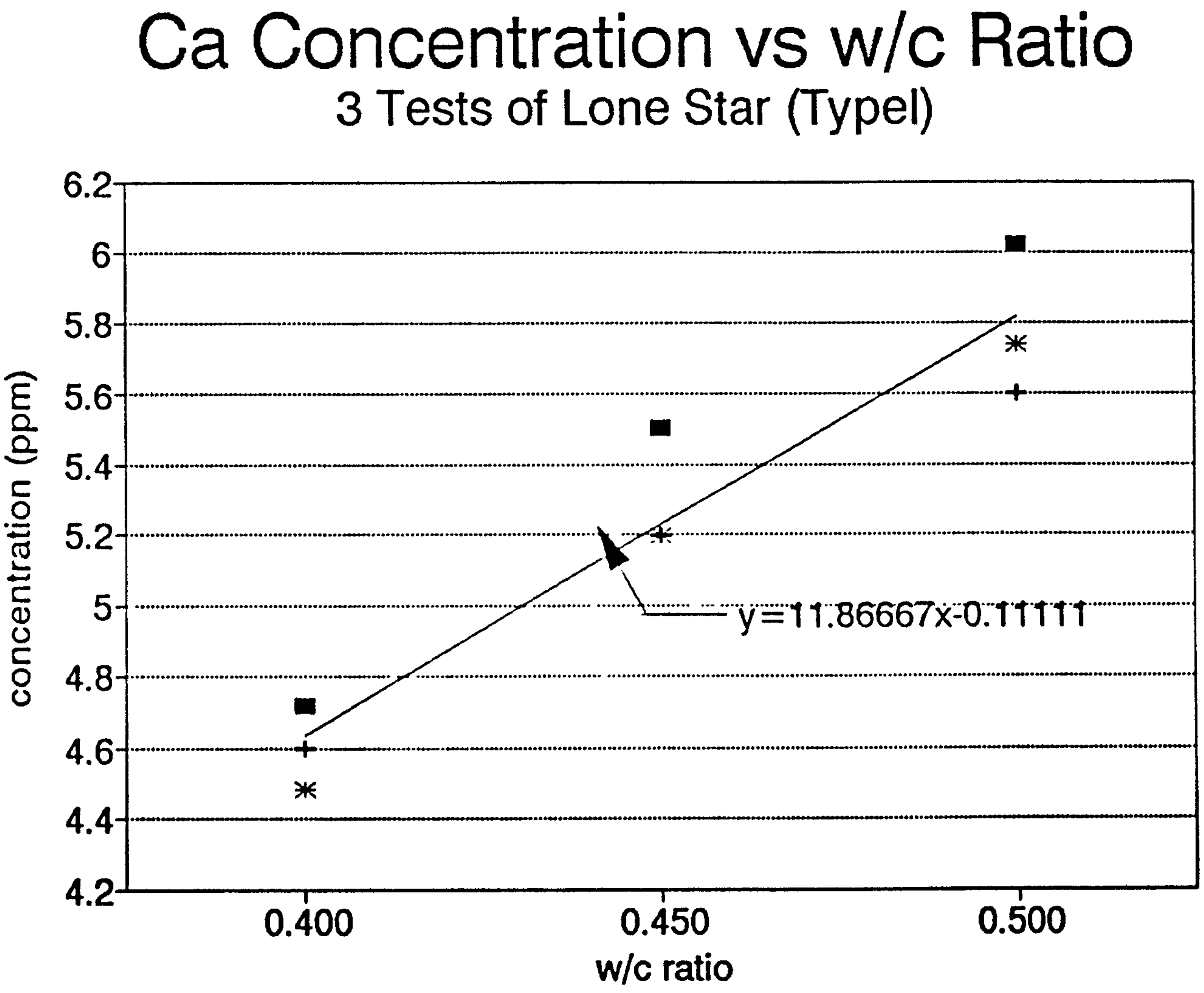


Fig 6.12 Linear Regression Curve Based on Four Points for Determination w/c Ratio of Lone Star (typeI) Cement

Using the regression curve, water-cement ratio can be estimated from the concentration values obtained by AA.

Table 6.10

Results in terms of w/c Ratio

w/c	Lone Star II w/c by: y=4.698*x+0.0020			Atlantic II w/c by: y=3.937*x+0.8884			Hercules II w/c by: y=5.752*x+0.0945		
	No.1	No.2	No.3	No.1	No.2	No.3	No.1	No.2	No.3
0.40	0.387	0.393	0.409	0.381	0.415	0.403	0.384	0.390	0.404
0.45	0.448	0.463	0.446	0.435	0.466	0.417	0.442	0.472	0.460
0.50	0.505	0.503	0.512	0.510	0.517	0.492	0.516	0.493	0.510
0.55	0.550	0.534	0.550	0.537	0.561	0.541	0.553	0.530	0.560

Where x = water-cement ratio; y = concentration

There are several facts we should point out here based on the experience we have had and the results we obtained from this investigation:

(1) For the range of water-cement ratios studied here (0.4-0.55), a linear relationship exists between the water-cement ratio and the concentration of calcium ions. This result further prove the finding of previous studies.

(2) Our experiments indicated that, with AA the scatter in data prevent us from using this technique for water-cement ratio with increments less than 0.05. For example, the percent scatter in calcium ion concentration was between 5% to 6%. The percent increment { (0.425-0.40) X 100%/0.40 } was within the same range as the 6% error. For this reason the water-cement ratio increments were changed to 0.05. This will produce a percent increment of: (0.45-0.40) X 100%/0.40=12.5%.

(3) It is also believed that the scatter in results may be due to the variations one may obtain from the standard calibration curve for the AA instrument in the

beginning of each test. For instance our experimental results showed an increase in the calcium concentration for standard calibration curves which were shifted higher during calibration. Calibration is a machine property which changes with temperature, and moisture condition.

(4) To achieve good results, all the samples should be tested during the same time period. Slight differences in mixing times from sample to sample affect the results tremendously. This is specially true after acquisition of the supernatent from the cement paste. Because the CO_2 in the air will react with the Ca^{2+} in the solution once the sample is exposed in the air. The Ca^{2+} and CO_2 will compose into $CaCO_3$ as solid form. This would result a lower value of Ca^{2+} concentration of the test sample.

(5) From Fig 6.5 through Fig 6.12, it can be seen the effect of the cement brand, and cement type. Calcium ion concentration Quantitatively differs from one brand of cement to another.

(6) The paper we use for cleaning the container usually carries a certain amount of Ca^{2+} which would have some impact on the test result. It is suggested to use the microwave for drying the container.

6-2 Fluorescence Spectrophotometer Experiments

The amount of morin (fluorescence reagent) was varied in our experiments so as to study the effect of morin on the observed results. Figs 6.13 through Fig 6.15 represent the relation between water-cement ratio and intensity of calcium-morin complex.

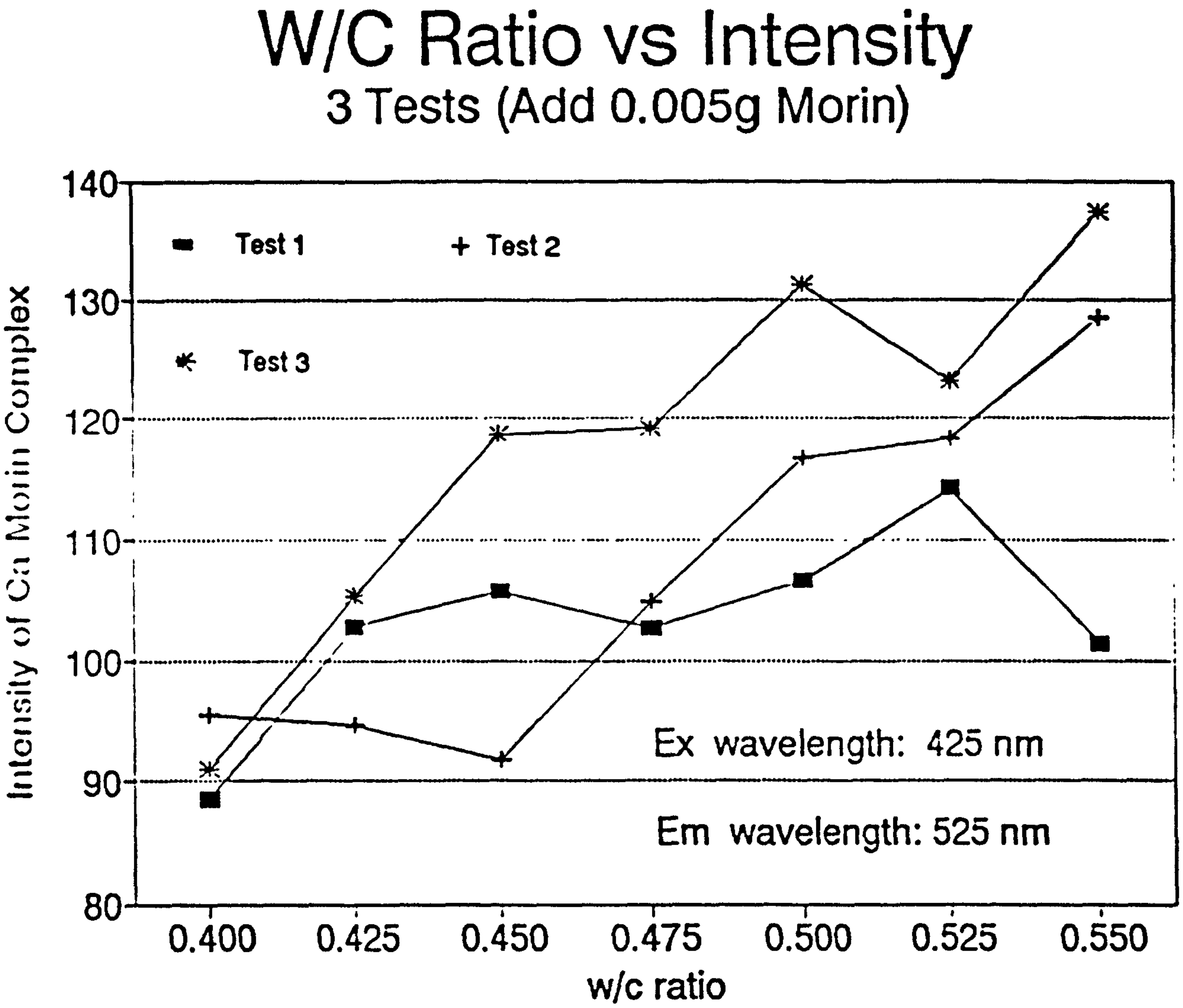


Fig 6.13 The relationship between Ca-Morin Complex and w/c Ratio by Adding 0.005 g Morin in The Samples

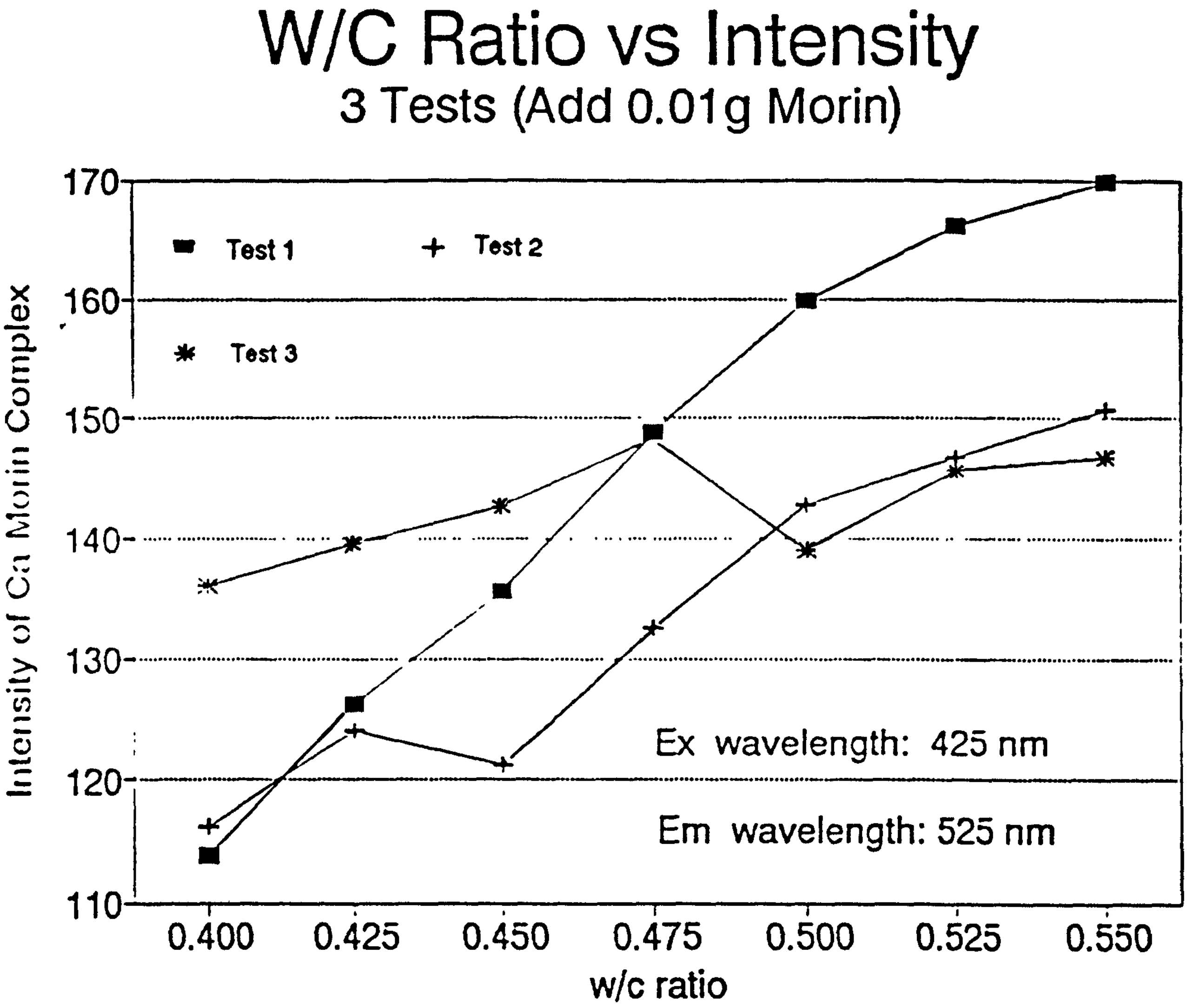


Fig 6.14 The Relationship between Ca-Morin Complex and w/c Ratio by Adding 0.01 g Morin in The Samples

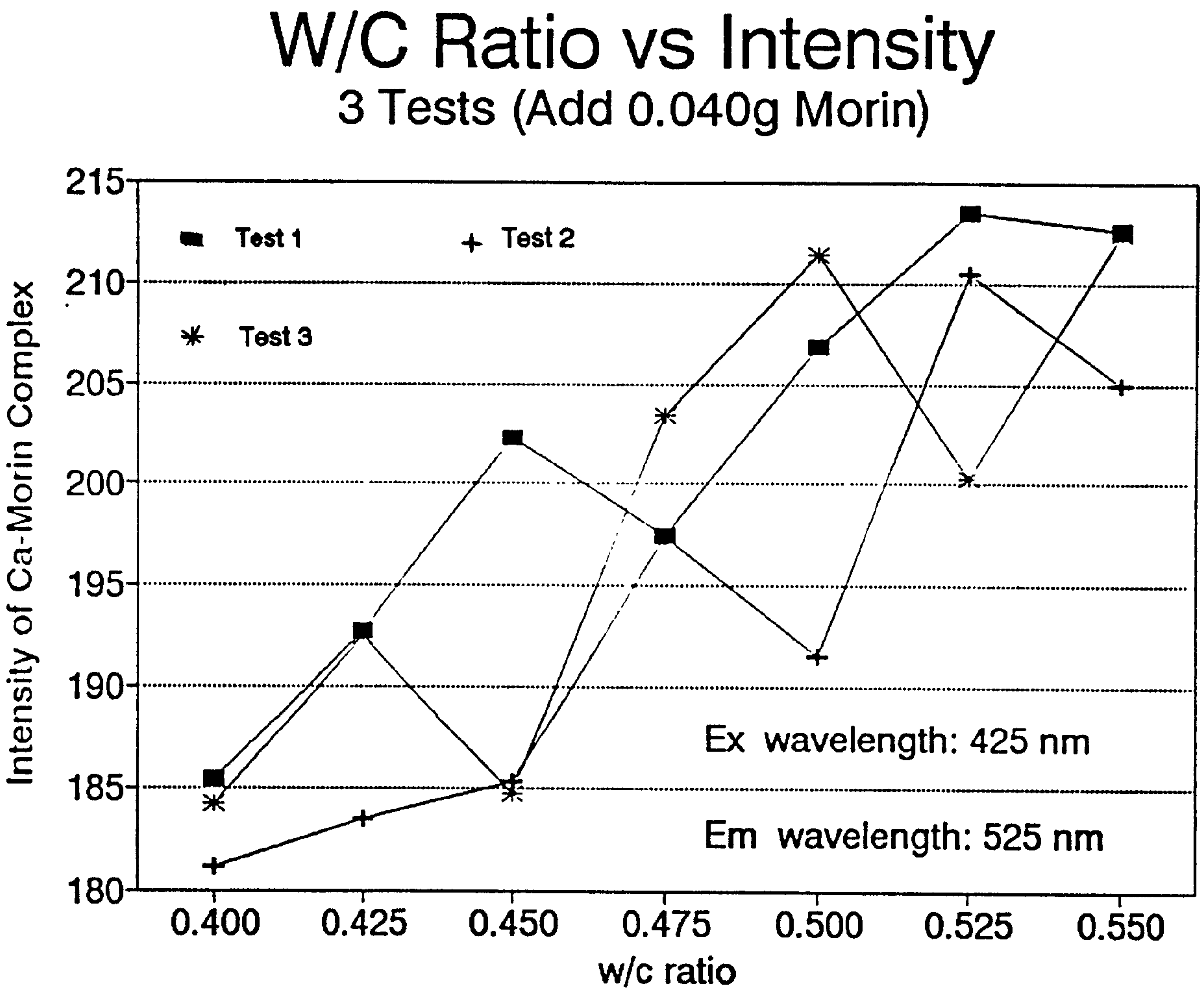


Fig 6.15 The Relationship between Ca-Morin Complex and w/c Ratio by Adding 0.04 g Morin in Samples

Figs 6.13 through 6.15 indicate that an increase in the amount of morin will result in higher intensities. Therefore, A test was performed in order to determine the least amount of morin to get maximum intensity., We used 0.5 as standard water-cement ratio and added increasing amounts of morin in different samples until the intensity of Ca-morin reached a constant level. The optimum morin level can be read from Fig 6.16.

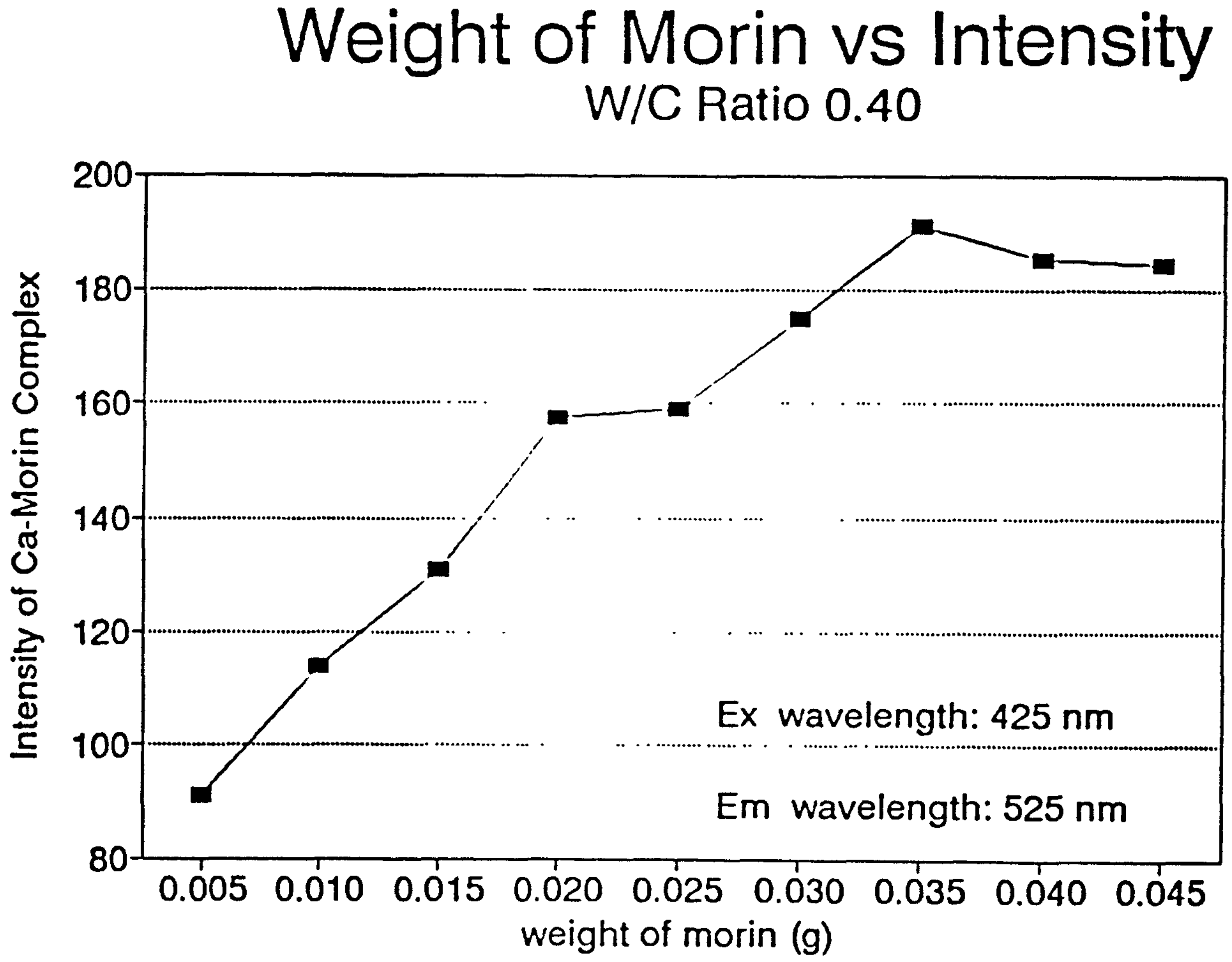


Fig 6.16 The relationship Between Ca-Morin Complex and Amount of Morin

In general, results obtained from experiments with fluorescence spectrophotometer technique were not very satisfying. The following lists some of the observations from FS experiments:

(1) Results showed a relation between water-cement ratio vs the concentration of Ca^{2+} (which here in terms of the intensity of the complex of calcium and the reagent added in) But it was not a clear linear relation.

(2) We have chosen two reagents for this experiment: morin and calcein. The results obtained from the tests using morin somehow showed a relatively stable condition of the wavelength peak form while some results from the tests using calcein showed a random condition. However, both tests were failed to show a constant linear relationship between the water-cement ratio and the intensity of the complex of Ca^{2+} and reagent. The nonlinearity results may have been caused by the interference from other metal ions in the solution which could react with both types of reagents.

6-3 Microwave Experiments

As a comparison, a series of tests were performed using microwave technique. Experimental program consisted of the same cement types used in AA test method. Each test required four minutes, during which, the heating process stopped periodically for stirring the mixture so as to reduce the lumps. Table 6.11-6.14 represent the results obtained from the results obtained by the microwave technique.

Table 6.11

Results Obtained by Microwave Method Lone Star (TypeII)

Actual w/c Ratio	weight of P&C* A	1 min dry B1	2.5 mins dry B2	4 mins dry B3	water loss W=A-B3	Cement 45-W	w/c
0.400	340.17	327.95	327.63	327.45	12.72	32.28	0.394
0.425	338.14	325.60	325.09	324.85	13.28	31.71	0.419
0.450	339.16	325.97	325.72	325.52	13.64	31.36	0.435
0.475	338.73	324.92	324.50	324.24	14.49	30.51	0.475
0.500	339.50	325.23	324.95	324.70	14.80	30.20	0.490
0.525	338.04	323.45	323.07	322.49	15.55	29.45	0.528
0.550	337.92	323.88	323.38	322.01	15.91	29.09	0.547

P&C : Ceramic plate and cement paste

B1, B2, B3 : Weight of plate and cement paste after given time dry

W : Weight of the water loss after four minutes

Cement 45-W : weight of cement paste after four minute dry

Table 6.12

Results Obtained by Microwave Method Atlantic (TypeII)

Actual w/c Ratio	Weight of P&C A	1 min Dry B1	2.5 mins Dry B2	4 mins Dry B3	Water loss W=A-B3	Cement 45-W	w/c
0.400	339.34	325.88	326.41	326.67	12.67	32.33	0.392
0.425	338.28	326.47	325.98	325.19	13.09	31.91	0.410
0.450	338.05	325.30	324.83	324.30	13.75	31.25	0.440
0.475	337.63	324.73	323.07	323.49	14.14	30.86	0.458
0.500	337.48	323.54	322.91	322.46	15.02	29 98	0.501
0.525	336.92	322.85	322.49	320.93	15.51	29.49	0.526
0.550	337.13	323.73	322.12	321.62	15.99	29.01	0.551

Table 6.13

Results Obtained by Microwave Method Hercules (TypeII)

Actual w/c Ratio	Weight of P&C A	1 min Dry B1	2.5 mins Dry B2	4 mins Dry B3	Water loss W=A-B3	Cement 45-W	w/c
0.400	338.72	326.93	326.48	326.09	12.63	32.37	0.390
0.425	338.46	326.89	325.51	325.13	13.33	31.67	0.421
0.450	338.04	324.99	324.57	324.36	13.68	31.32	0.437
0.475	337.81	324.56	323.81	323.46	14.35	30.65	0.468
0.500	337.55	323.35	323.07	322.63	14.92	30.08	0.496
0.525	337.31	322.73	321.98	321.84	15.47	29.53	0.524
0.550	336.93	321.83	321.03	320.76	16.17	28.83	0.561

Table 6.14

Results Obtained by Microwave Method Lone Star (TypeI)

Actual w/c Ratio	weight of P&C A	1 min dry B1	2.5 mins dry B2	4 mins dry B3	water loss W=A-B3	Cement 45-W	w/c
0.400	338.56	326.72	326.21	325.93	12.63	32.37	0.390
0.425	338.41	325.67	325.04	324.73	13.68	31.32	0.437
0.450	338.08	324.93	324.60	324.01	14.07	30.93	0.455
0.475	337.81	324.02	323.87	323.22	14.59	30.41	0.480
0.500	337.58	323.37	322.85	322.28	15.30	29.70	0.515

6-4 Comparison of AAS and Microwave Method

Tables 15 through 18 are a series of comparison chart which indicate the error percent of both microwave method and AA method. The different error percent between two methods are indicated also.

Table 6.15

Microwave Method and AA value Comparison (Lone Star II)

actual w/c ratio	microwave method	error percent	AA method	error percent	difference
0.400	0.394	-1.5%	0.395	-1.2%	0.25%
0.425	0.419	-1.4%	0.418	-1.6%	-0.24%
0.450	0.435	-3.3%	0.431	-4.2%	-0.83%
0.475	0.475	0.0%	0.475	0.0%	0.00%
0.500	0.490	-2.0%	0.502	0.5%	2.50%
0.525	0.528	0.6%	0.531	1.2%	0.57%
0.550	0.547	-0.6%	0.543	-1.3%	-0.73%

Table 6.16

Microwave Method and AA Value Comparison (Atlantic)

actual w/c ratio	microwave method	error percent	AA method	error percent	difference
0.400	0.392	-2.0%	0.420	+5.0%	+7.14%
0.425	0.410	-3.5%	0.442	+4.0%	+0.78%
0.450	0.440	-2.2%	0.440	-2.2%	0.00%
0.475	0.458	-3.6%	0.486	+2.3%	+6.11%
0.500	0.501	+0.2%	0.517	+3.4%	+3.19%
0.525	0.526	+0.2%	0.538	+2.5%	+2.28%
0.550	0.551	+0.2%	0.569	+3.5%	+3.27%

Table 6.17

Microwave Method and AA Value Comparison (Hercules)

actual w/c ratio	microwave method	error percent	AA method	error percent	difference
0.400	0.390	2.5%	0.389	2.75%	0.26%
0.425	0.421	0.9%	0.422	0.71%	-0.24%
0.450	0.437	2.9%	0.473	-5.11%	-8.24%
0.475	0.468	1.5%	0.486	-2.53%	-3.85%
0.500	0.496	0.8%	0.493	1.40%	0.60%
0.525	0.524	0.2%	0.509	3.05%	2.86%
0.550	0.561	-2.0%	0.531	3.45%	+5.35%

Table 6.18

Microwave Method and AA Value Comparison (Lone Star I)

actual w/c ratio	microwave method	error percent	AA method	error percent	difference
0.400	0.390	2.5%	0.382	4.50%	2.05%
0.425	0.437	-2.8%	0.415	2.35%	5.00%
0.450	0.455	-1.1%	0.448	0.44%	1.54%
0.475	0.480	-1.0%	0.470	0.00%	1.04%
0.500	0.515	-3.0%	0.488	2.40%	5.24%

Chapter 7

Conclusions

(1) A series of investigation for the rapid determination of water-cement ratio in freshly mixed cement paste is presented in this paper. Two new methods which employ the atomic absorption spectrophotometer and fluorescence spectrophotometer are introduced.

(2) The results of the experiments of AA method is relatively good and there are no particular technical difficulty encountered so far. The test takes approximately 16 minutes to complete. A quite clear linear relationship between the water-cement ratio and the concentration of calcium ions is shown in the resulting graphic chart. When compared to the standard microwave method, the difference of error percent is relatively small.

(3) For the case of using fluorescence technique which takes about 14 minutes for completion, the results are somehow unsatisfying. While the cause may vary, two major technical concern are the proper amount of reagent to be add in and the interference of other metal iron in the test samples. If these two problems can be well solved in the future research, the use of fluoresce technique would have the potential possibility to become a new valid method for the rapid determination of water-cement ratio.

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