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Analytical Methods For Assessing Paper Degradation In Transformers

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ABSTRACT

Power transformers are essential equipments for distributing electricity. However, maintenance of these equipments is necessary to ensure long working life and to avoid catastrophic incidents.

Insulation of the instrument is essential, and mainly consists of mineral oil and cellulosic paper.

This research work investigates and examines in a series of different experiments the compounds produced from the degradation of the cellulosic paper, known as furanic compounds.

Five furanic derivatives (5-HMF, 2-FAL, 2-ACF, 5-MEF and FOL) were examined, and it was established throughout this work that these furanic compounds degradate faster in aqueous solution, under a controlled environment, than in an organic, it is possible to produce from one furanic compound other derivatives, and finally each furanic compound distributes differently in an oil water environment, affecting the recovery of each individual.

The knowledge obtained from this research work can be used for the development of the existing method of analysis of furanic compounds, and help to provide a better diagnosis of the insulation state of the transformer.

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CHAPTER ONE

INTRODUCTION

AND

LITERATURE REVIEW

1.0 INTRODUCTION

Electricity is essential to humanity in order to provide our daily lives and working environment with essential energy, ultimately leading to a higher quality of life. Power Transformers are used world wide for the transmission and distribution of high voltage electrical energy over long distances with minimum power losses and at least cost [1]. The power transformation process involves increasing and/or decreasing voltage levels according to the need of the consumer, using a power transformer. Essentially, transformers are crucial to the transfer of electrical energy from the production point to the point where the energy will be consumed. This is achieved by using high voltages for transmission purposes, followed by stepping down of the voltage levels for distribution to the consumer.

1.1 Transformers

Generally, the operation theory of a transformer is based upon three principles:

- ✚ A voltage is delivered to the primary winding via a conductor, which generates a magnetic field within the transformer core.
- ✚ The magnetic field around the core will be producing an induction current within the secondary winding
- ✚ This secondary winding current is used as an output of the electrical energy to the transmission lines.

There are many different types of transformers including: Generator transformers; Transmission transformers; Distribution transformers; Transformers for DC converter stations; and Earthing transformers. As described above, all the transformers operate under the same principles but in general they can be divided into two major categories from the design point of view: the shell type and the core type.

In a core type transformer, the core is made of laminated magnetic steel and its role is to reduce the current drawn by the transformer from the system when it is off load. The core is surrounded with windings (high voltage or low voltage) that are cylindrical in form. The type of configuration can be as a disc, a layer or even a foil. No matter which configuration is used, the manufacturer always considers the alignment to provide the best cooling process of the system and also the better insulation by the oil. A transformer may contain from one up to three cores (in the case of a three phase transformer), with all cores connected with laminated magnetic steel, the same material used for the production of the core.

In the shell type transformer, the configuration of the laminated magnetic steel of the core is square or rectangular having slots for the windings to be arranged, which again may be of high and low voltages [2].

When it comes to the production of a transformer the designer and the engineer need to consider several factors in order to achieve a suitably long working life for the transformer. A well designed transformer will exhibit fewer faults, maximum system performance and also to be able to take heavy load whenever is required. These design aspects may include the winding connection, tappings and tap changers including the types of connection, the function of on load tap changer, the transformer impedance, the thermal design, insulation, the cooling system, the electrical and mechanical design, and finally parameters designed to protect the transformer during normal operation (moisture, overload, electrical) [2].




The insulating material of a transformer mainly consists of cellulosic paper wrapped around the conductor impregnated in mineral oil, the latter acting both as coolant and as a dielectric element. These two materials are essential for the efficient operation of the transformer and are especially important with respect to insulation. Insulation is a critical issue because it will determine the effective working lifetime of the transformer. Any fault to the system will be a result from its insulation. It is vital to monitor the insulation condition of the transformer in order to predict any malfunction and to resolve the problem before transformer failure. A single problem on a transformer can not only cause problem to the individual unit, but may cause major faults to the whole circuit, with the worst outcome being a total system

shutdown. On such occasions the treatment is significantly more costly than repair of a single transformer unit and requires more time to be resolved.

1.2 Insulating oil

Mineral oil is used for the insulation of a transformer and can be classified into two categories; the paraffinic and the naphthenic. The naphthenic oil is the crude oil used at the refinery for the production of the transformer oil, which later can be used as insulating matter to the transformer [3]. Paraffinic refined oil has low physical properties and may produce oxidation products which can lead to sludge forming in the windings and furthermore to blockage of the ducts in a transformer. Naphthenic oil will allow those oxidation products to be dissolved. Therefore, it is essential to reduce the rate of oxidation of the oil, such as by using antioxidant reagents or enhancing the existing antioxidants by 'hydrogenation'. Such approaches have been shown to confer a longer working life on the transformer [3].

The oil in the transformer, apart from its insulation properties, has other useful functions such as;

-  Cooling
-  Electrical insulation
-  Information carrier

Besides those functions (physical, chemical) the oil which will fulfill the requirements of the power transformation process, must follow certain requirements from the point of Environmental Legislation and Health and Safety. International Standards and National specifications are often listed with the minimum requirements expected from the oil. The most common standards are IEC 60296 and ASTM D3487. National specifications are often used from the transformer producers according to their own needs [2].

1.3 Insulating Paper

Solid insulation of a transformer is commonly provided by cellulosic paper which is impregnated with the oil. The paper is made by the delignification of wood pulp by the Kraft process [2, 3, and 4]. Like the insulating oil, cellulosic paper also provides useful functions to the circuit, such as;

- ✚ Electrical insulation
- ✚ Mechanical stability
- ✚ Creation of space
- ✚ Direction of oil flow

Also, cellulosic paper is used due to highly compatibility with the mineral oil, giving an overall increase in beneficial electrical and physical properties over and above that exhibited by each individual material.

Insulating paper consists of 76-86% w/w cellulose, 10-15% w/w hemi cellulose, 4-8% w/w lignin and 0.2-0.8% w/w mineral substances [2]. The thickness of the paper varies from 30-120mm, with natural moisture content of 6% [3]. The paper is wound onto the copper (material used for the production of the conductor) before the coils are formed, separating each turn with the next.

Before the paper is introduced to the transformer, there is in a high necessity to reduce the percentage of moisture content. The process involves drying of the paper under vacuum at 95-100°C for 10-16 days, reducing the final moisture content to less than 0.1% [3].

International Material Standards also exist to establish the requirements for the choice of the paper which will be used for the insulation of a transformer. The most common standards are IEC 60554 and ASTM D 1305 [2].

Insulation paper is a key material to the operational life-time of a transformer. It is expected to last until the end of the working life of the circuit (typically 25 years)

and the choice of the type is critical. The most preferred type of paper is the Kraft paper because of its high purity and its specific electrical resistivity. During paper production, it must be ensured that there are no metal ions present, which will otherwise affect the insulation performance of the paper. Economically, Kraft paper is a cheap source of insulation, something that needs to be considered when considering the fact that a typical power transformer requires 10-12 tonnes of this material, in the case of poor insulation properties.

1.4 Degradation of Insulating paper

The Kraft paper used in electrical transformers degrade over the time of operation, and the rate of degradation depends on the prevailing thermal, oxidative, hydrolytic, electrical and mechanical conditions within the transformer [5]. Normally, the operating temperature for a power transformer is between 80-100°C, and even at these relatively modest temperatures, the insulating paper can undergo a slow degradation, with a resultant loss in its mechanical and electrical properties. Consequently, the degradation of the insulating paper has an effect on the tensile strength of the paper by decreasing the degree of polymerization (DP) of cellulose [6]. Typically, an unaged paper has a DP value, which is the number of the monomeric units (anhydroglucose) in the cellulose chain [12], between 1000 and 1300 [7, 8]. After the reprocessing of the paper, by means of drying, the DP value decreases to 950, and ageing of the paper further decreases the DP value to 500 [8]. Over this range (950-500 DP) the tensile strength of the paper is in relatively good condition and offers constant high-quality insulation to the transformer. In the case where the DP value reduces to 150 or lower, the tensile strength of the paper has decreased to 20% of its initial value and therefore the paper has very poor strength properties [7-10].

The degradation of insulating paper can initiate a major fault in a transformer by many different mechanisms:

- ✚ The paper can break away from the transformer windings and block ducts
- ✚ Water is produced from the degradation products which can affect the resistivity of the paper and the voltage breakdown of the oil.
- ✚ The worst scenario is the production of low molecular weight carbon species from the paper which increases system conductivity and causes overheating and conductor faults [10].

1.4.1 The Paper Degradation Process

As mentioned above, degradation of paper is a result of the reduction of the degree of polymerization of cellulose. Cellulose is one of a number of natural polymers of glucose. Glucose units, and more precise D-anhydroglucopyranose, are combined together to form long chain polymers held together by covalent bonds, specifically β -1,4-glycosidic bond linkages [12]. Figure 1 represents the chemical structure of cellulose. A number of cellulose chains may be held together by extensive intermolecular hydrogen bonding which confers a degree of crystalline structure of the cellulose molecule aggregates. The formation of a single cellulose fibre provide the paper its mechanical strength due to the formation of those intramolecular and intermolecular (hydrogen bonds), and also, due to the formation of a micro crystalline structure.

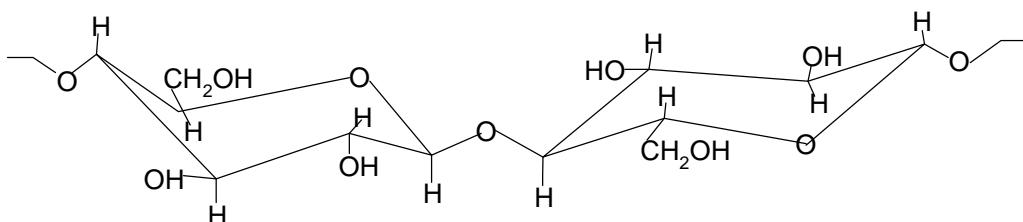


Figure 1 Cellulose; Two units of D-anhydroglucopyranose joined together by β -1,4-glycosidic bonds

The length of the cellulose molecule is measured in terms of the degree of polymerization, which as it was mentioned earlier is the average number of glucose units per cellulose molecule [12].

In general the process of cellulosic degradation involves a chain scission or depolymerization of the cellulose chain, and the release of a different number of products [4], typically:

- ✚ Hydrogen
- ✚ Hydrocarbons
- ✚ Carbon monoxide
- ✚ Carbon dioxide
- ✚ Water
- ✚ Furanic compounds [4].

Principally, the formation of specific products and hence, the degradation mechanism employed depends upon the conditions to which cellulosic degradation is subjected. Predominantly, there are three main factors which promote degradation, which will be discussed in the proceeding sections:

- ✚ Temperature
- ✚ Oxygen and oxidizing agents
- ✚ Moisture [12].

1.4.1.1 Effect of Temperature

Degradation is a chemical process and thus should obey the Arrhenius theory of reaction kinetics, which relates the log of the reaction constant to the reciprocal of the absolute temperature [13]. Values for the activation energy of degradation of cellulose in oil range, of the order of 85 KJ/mole for the oxidative degradation reaction, to 120 KJ/mole for the hydrolytic degradation reaction [7, 14-15]. It is

suggested that at about 140°C and above, the rate of degradation increases significantly, implying a change in the activation energy [15-16].

Cellulose, under higher temperature (to a maximum of 200°C) tends to be degraded via destruction of the β1, 4 glycosidic bonds to produce free glucose, moisture, carbon oxides and organics acids, see figure 2.

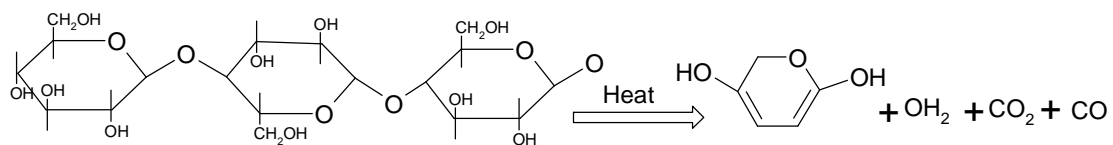


Figure 2 Thermal degradation of insulating paper

1.4.1.2 Effect of Oxygen

The second cause of paper degradation is oxygen, which can enter through the open breather system of the transformer, or the faulty seals and through the oil to affect the insulating paper. Fabre and Pichon *et al.* [17] explain that oxygen increases the rate of degradation of insulating paper which can be up to a factor of approximately 2.5. Reducing the oxygen level in oil below 30,000 ppm reduces the rate of degradation by a factor of approximately 16. Cellulose is highly susceptible to oxygen and oxidising agents. Acid attacks the hydroxyl groups of the cellulose, oxidising them to carbonyl and carboxyl groups. This process weakens the glycosidic bonds and can lead to chain scission. Moisture is also produced during this oxidative process. Figure 3 illustrates the oxidation reaction process [12, 17].

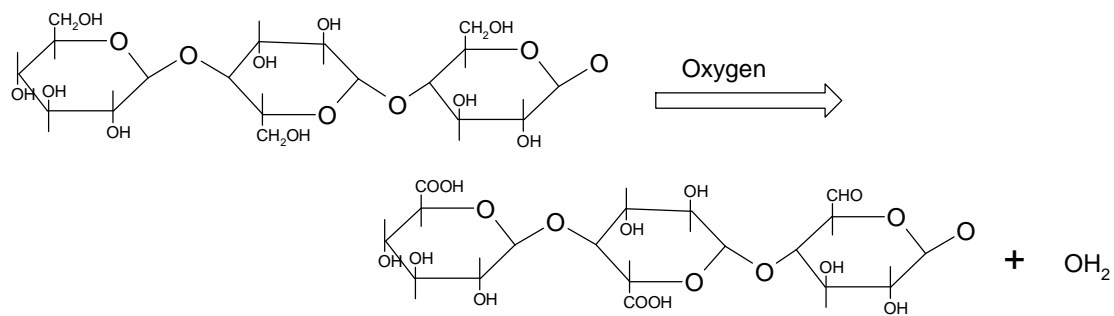


Figure 3 Oxidation of Cellulose

1.4.1.3. Effect of Moisture

The final and probably the most serious cause of accelerated paper degradation is water. Moisture, like oxygen, can enter the transformer via the main tank, through the open breather system as well as via any leaking gaskets. Also, if the paper undergoes thermal or oxidative degradation, moisture is produced, and hence hydrolytic degradation is promoted. The water in the transformer can be found mainly in three forms;

- Dissolved as a solution
- Suspended in emulsion
- As free water [18].

Water reduces the insulating properties of the paper and more importantly it reduces the tensile strength. When moisture attacks the cellulose, it can break the glycosidic bonds releasing free molecules of glucose (Fig 4). It is proposed that cellulosic paper in equilibrium with the atmosphere approximately contains 7 to 8% moisture by weight [12]. Other investigations showed that new transformers are usually specified between 0.5 and 1% of moisture content. Therefore, it is essential that the paper prior to installation at the transformer is carefully dried out to minimise the rate of degradation [18].

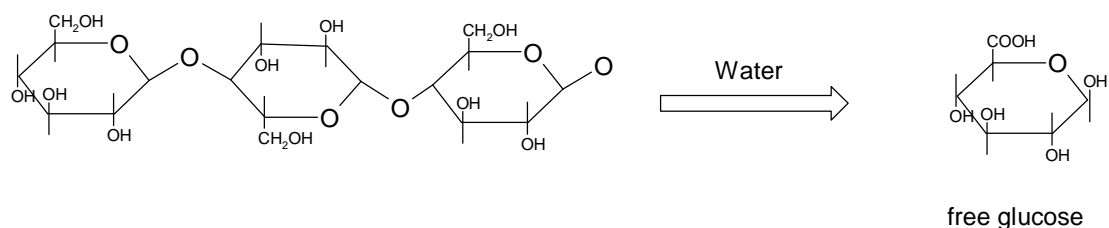


Figure 4 Hydrolytic degradation of cellulose

1.5 Furanic compounds

The cellulosic insulating paper can be degraded by the effect of the three factors described in the preceding Section. When degradation occurs one of the products that it is formed is the family of compounds known as the furans.

Furan is the parent compound of these five membered ring structures containing one oxygen atom. Some of the physical properties associated with this family of compounds include low boiling point, high flammability, a strong ether odour and miscibility with most organic solvents. Furan shows some aromatic characteristics arising from the delocalization of the four π electrons and one electron from the oxygen pairs [19]. Since they are electron rich heterocycles, these compounds can undergo polymerization; they can produce other furan derivatives by cyclodehydration, they can undergo the Michael reaction, acting as nucleophiles, and finally can undergo the Diels-Alder reaction [20-21].

There are many different types of furan derivatives, but in this project we will examine the following five, since they are the main derivatives examined from the existing method for determining the insulation state of the transformer:

- ✚ 5-hydroxymethyl-2-furfuraldehyde (5-HMF)
- ✚ 2-furfuraldehyde (2-FAL)
- ✚ 2-acetyl furan (2-ACF)
- ✚ 5-methyl-2-furfuraldehyde (5-MEF)
- ✚ Furfuryl alcohol (FOL)

Below are illustrations of the chemical structures of the furan and the five derivatives, following with a table of some of their physical properties.

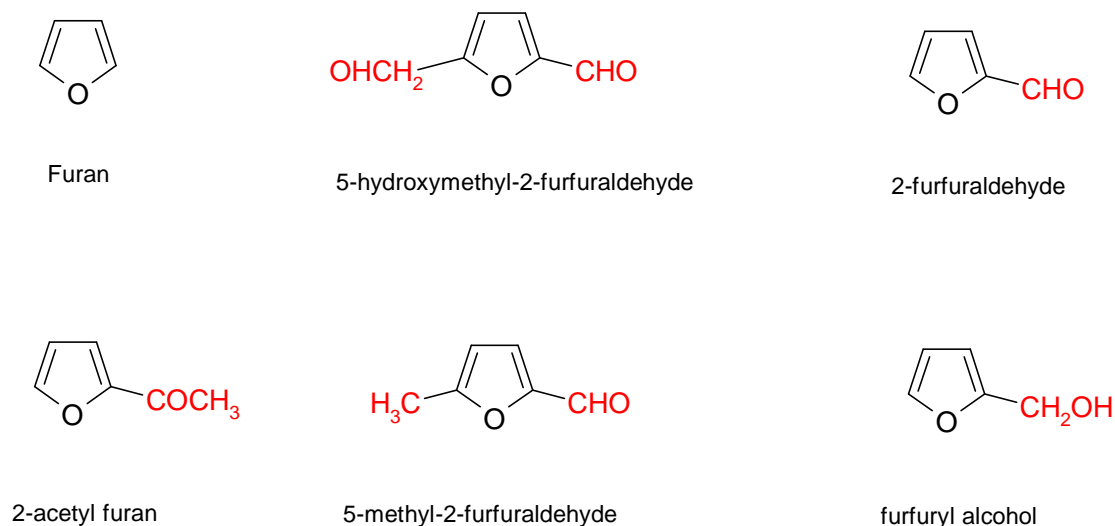


Figure 5 furan and derivatives

	CAS Registry number	Mp, °C	Bp, °C	P(20°C), g/cm ³	N _D ²⁰	Vapor Density (air=1)	Flash Point ^a , °C	Explosion Limits in air, vol %	Ignition Temperature, °C	Solubility in H ₂ O (25 °C) Wt %	Dielectric constant (20 °C)	Viscosity (25 °C) mPa.s
furfural	(98-01-1)	-36.5	161.6	1.1598	1.5261	3.3	61.7	2.1-19.3	315	8.3 ^b	41.9	1.49
Furfuryl alcohol	(98-00-0)	-29	170	1.1285	1.4868	3.4	77	1.8-16.3	391	∞		5.0
furan	(110-00-9)	-85.6	31.36	0.9178	1.4214	2.36	-33.5	2.3-14.3	282	1		6.24
Tetrahydrofurfuryl-alcohol	(97-99-4)	<80	178	1.0511	1.4520	3.52	83.9 ^c	1.5-9.7		∞	13.6	
2-Methylfuran	(534-22-5)	-88.7	64	0.913	1.4320		-27			<0.3		
2-Methyltetrahydrofuran	(96-47-9)	-136	80.2	0.854	1.4025		11.1			15.1		
Dihydropyran	(110-87-2)	-70	84	0.923	1.4380		-17.8			1.6		

Figure 6 Physical properties of furan derivatives (adapted from Ulmann's Encyclopedia 6th Ed).

It was mentioned above (see section 1.3) that insulating paper contains cellulose, lignin, mineral substances, and therefore all the three constituents under degradation process can produce furans. Production of furans can also be generated

from pentozans. Figure 7, 8, 9, shows the chemical reactions for the production of furans from cellulose, lignin and pentozans respectively.

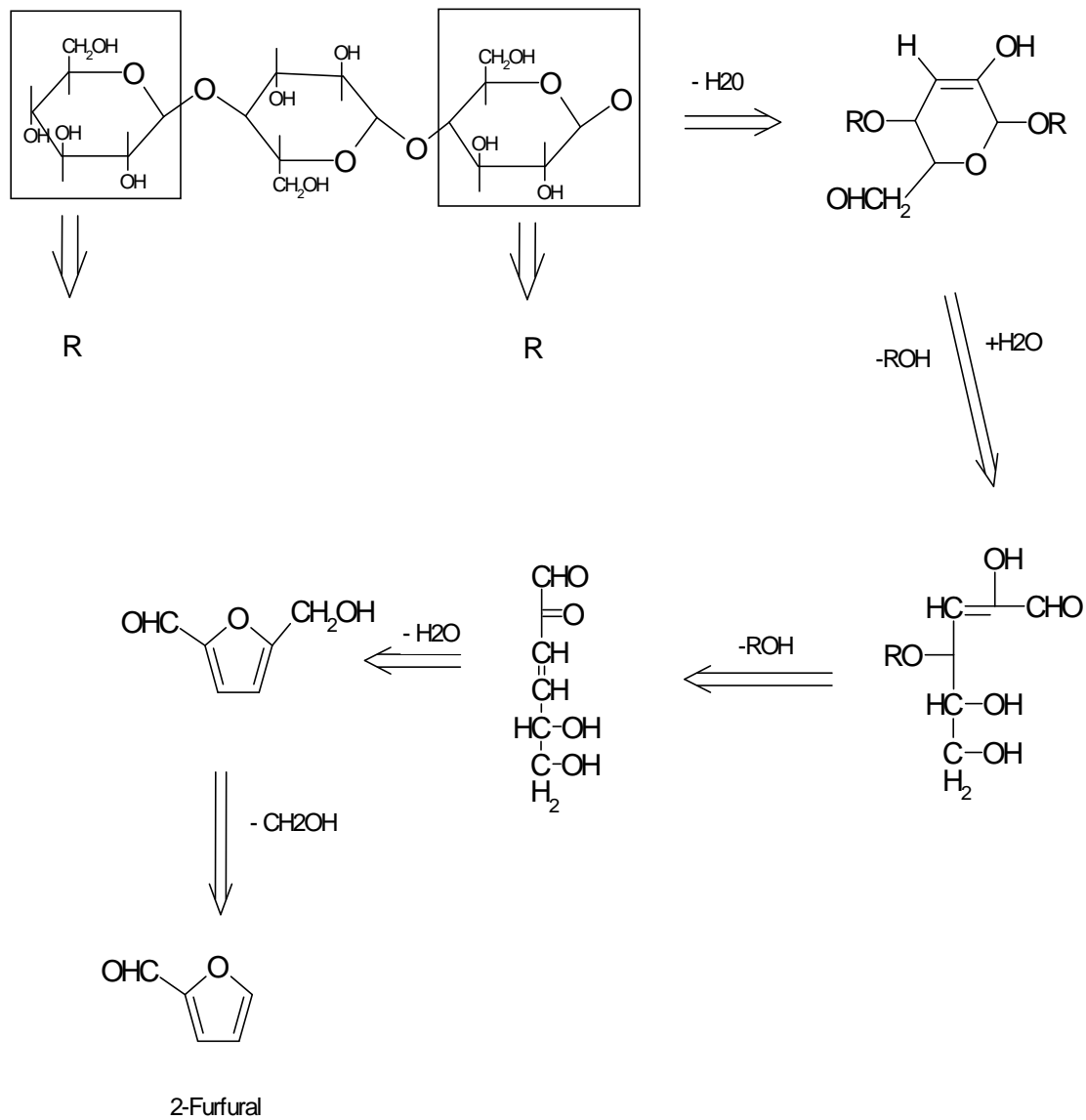


Figure 7 Production of 2-furfural from cellulose (adapted from Shafizadeh and Lai).[22]

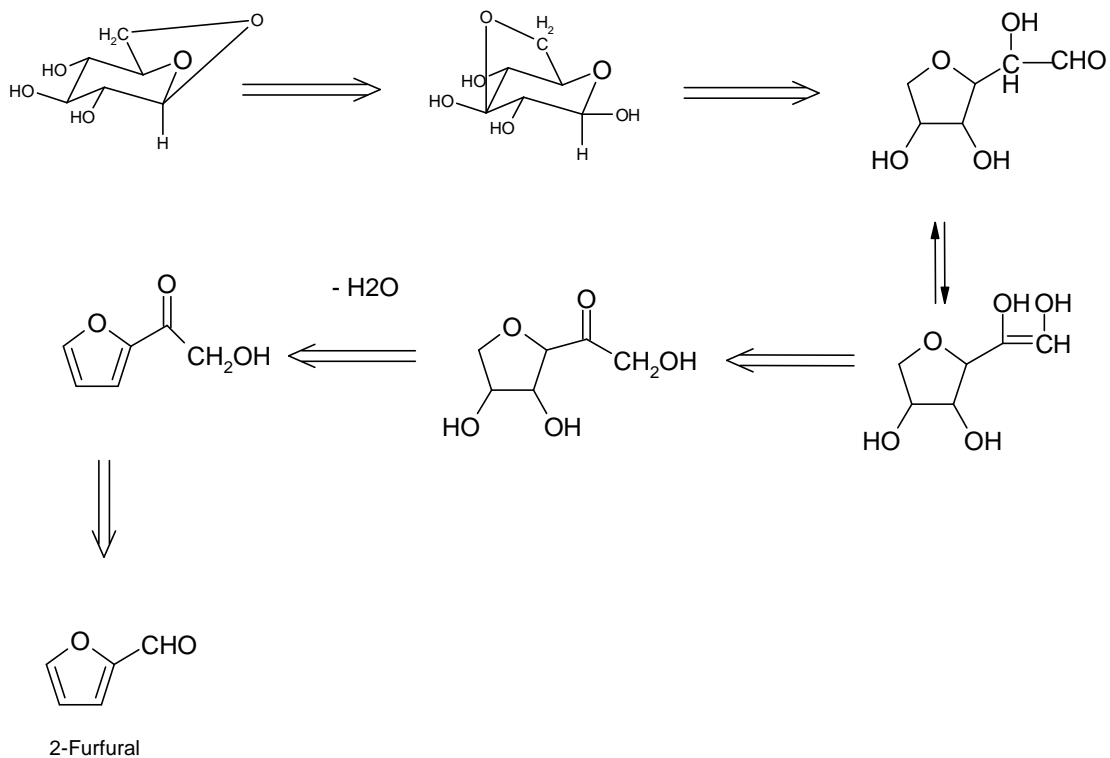


Figure 8 Production of 2-furfural from lignin (adapted from Shafizadeh and Lai).[22]

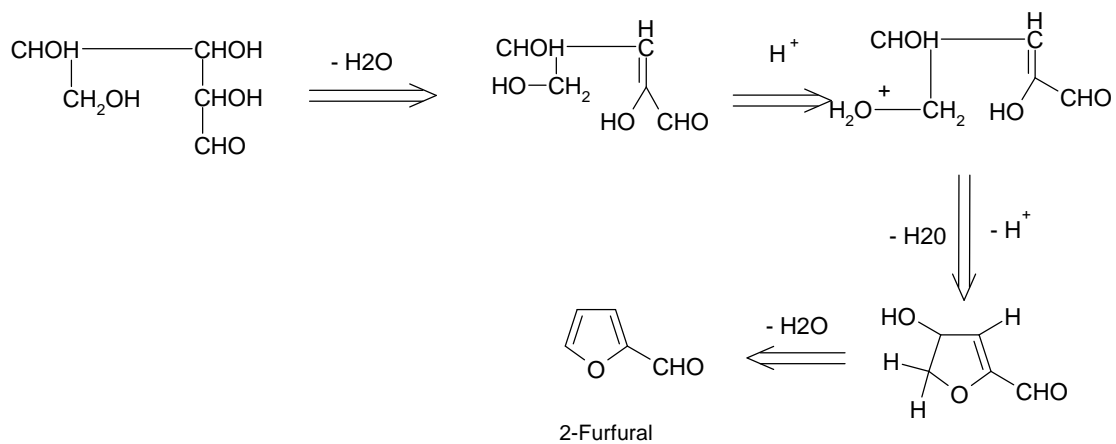


Figure 9 Production of furan from pentose (adapted from R.O.C Norman).[23]

The similarity between the three processes is the end product, which is 2-FAL. Only in the degradation of cellulose is 5-HMF produced prior to 2-FAL. In the case of the degradation of lignin it was found that after the production of 2-FAL further

degradation produces FOL but in a lower magnitude than 2-FAL [24]. When pentosans are degraded it was found that around 4 times more 2-FAL is produced when compared to cellulose degradation. The important issue regarding the degradation of pentosans is that 5-HMF is not detected. The only explanation to that difference is that 5-HMF is produced as a degradation product from hexoses, such as glucose, while 2-FAL is produced from acid hydrolysis of pentosans [24].

It is known that degradation of cellulosic insulating paper by the factors and processes described above result in the reduction of the mechanical strength of the paper by reducing the length of the cellulose molecules and therefore reducing the degree of polymerization [12]. Correspondingly it has been found that there is a relationship between DP and furfuraldehydes. Chendong [31], Scholnik [31], Pahlavanpour [31] and De Pablo [25, 31] developed a series of equations in order to express the correlation of DP with the production of 2-Fal. De Pablo [25] build a degradation model based on experimental data and field measurements from a research programme carried out for CIGRE (International Council on Large Electric Systems) and found that for every three cellulose chain scissions one furfural molecule is produced. Below are the four mathematical approaches which link the DP with the production of Furfurals:

$$\text{(Chendong)} \quad \text{DP} = (1.51 - \text{Log}_{10} 2\text{-FAL}) / 0.0035 \quad (1)$$

$$\text{(Scholnik)} \quad \text{DP} = (1.17 - \text{Log}_{10} 2\text{-FAL}) / 0.00288 \quad (2)$$

$$\text{(Pahlavanpour)} \quad \text{DP} = 800 / (0.186 * 2\text{-FAL}) + 1 \quad (3)$$

$$\text{(DePablo)} \quad \text{DP} = 7100 / 8.88 + 2\text{FAL} \quad (4)$$

These formulae correlates the amount of 2-FAL, expressed in mg/kg of the oil to the DP of the cellulosic paper in the windings of a given transformer. Rearranging equations (1) and (2) as Log2-FAL versus DP and equations (3) and (4) as 1/DP versus 2-FAL is possible to obtain linear plots [31]. It has been established that the lower limit that the DP can reach before significant transformer problems are encountered is 150 units, and by using De Pablo formula, it was found that the maximum amount of 2-FAL that can be generated is 30 mg/kg, the same value reported by CIGRE members. A problem with the formula was that it does not take account of the fact that the winding paper is not degraded to the same extent under

different conditions, notably temperature. For example, the innermost layers of the winding conductor degrade twice as fast as the outer layers. Other formulae have been developed in order to express the relation of DP versus furfural production under different conditions [27]. For instance, it can be assumed that in a normal operating transformer 20% of winding conductor insulation degrades twice as fast as the rest of it, then the maximum level of degradation should be:

$$N_{\max}=0.186*2\text{-Fal and}$$

$$DP_{\min}=800/ (0.186*2\text{-Fal) +1 [27]}$$

Assuming a variation of $\pm 50\%$ from the average, the range of degradation of remaining winding insulation becomes:

$$N=0.5*(0.67/0.8)*(2\text{-Fal}/8.88)$$

And

$$DP=800/ (0.141*2\text{-Fal}+1) [27]$$

Another relationship which has been established is between the gases produced during transformer operation and furfural production. It was found that at temperatures in excess of 140°C ; insulating paper degradation contributes to the production of hydrogen, methane, ethane and ethylene. But the most significant relationship is between the paper and the production of carbon monoxide and carbon dioxide. It was found that 50% of carbon dioxide is generated from the paper at temperatures above 140°C [28]. There are different types of relations, like the previous, even between the furans. From the five furfuraldehydes 2-Fal and 5-HMF are the most important; they can be detected more easily due to their higher rates of production. The major factor for the production of furan is temperature, but also the factor that will determine the increase of production of them and therefore the expected life time of the transformer. Dakin in 1948 showed that temperature is related with chemical changes in the mechanism of paper degradation, and follows Arrhenius equation. Later, he managed to develop an equation to predict the life-time for a transformer [31]. The equation is:

$$t = A \exp^{-E/RT} = A \exp^{-B/T} \quad [31]$$

where t is the time required for a specific property to decrease by a certain percentage at a given temperature. A and B are constants, E is the activation energy, R is the gas constant and T is the absolute temperature ($^{\circ}$ K) [31].

CHAPTER TWO

*AIM, BACKGROUND
AND THE SCOPE
OF THE PROJECT*

2.0 AIM, BACKGROUND AND THE SCOPE OF THE PROJECT

Although there is significant evidence regarding how furans are produced from the cellulosic insulating paper, the exact degradation mechanisms are not fully understood [24]. It was mentioned above (section 1.4) the three possible causes of paper degradation, but it is not known which of these three mechanisms is most likely to occur on a transformer and which end products, with the exception of 2-FAL will be produced. The intermediate steps involved are not known, and therefore which other products may be produced. Furthermore, there is no knowledge regarding the behaviour of the furans under different conditions. Furanic analysis is useful for monitoring the transformer and its operation, but specific knowledge relating to these compounds is very poor. This project will investigate these compounds and examine the furanic degradation process from a different perspective from that of previous studies, which were mainly conducted with mineral oils [12, 13,16].

It is essential that such research be conducted due to a number of problems with the current method of analysis. Furanic compounds are routinely analysed using solid phase extraction (SPE) methods, in order to separate the furans from other constituents such as carbonyl compounds, acids, followed by High Performance Liquid Chromatography (HPLC) to achieve separation of the five selected furan derivatives and also to be able to determine the concentrations of those furans present. The method that is used is the industry standard IEC 61198 method, which, despite being recognised worldwide, exhibits a number of problems:

- ✚ The first problem arises from the sampling of the oil, which is collected by the engineers for diagnostic analysis. Oil reclamation, vacuum degassing, are some influences that can affect the detection of the furans, due to reduction in furan concentrations. The equilibrium between oil and paper will be restored after a number of months of operation, where furfural, primarily, will desorb from the paper into the oil, but at a significantly lower concentration than in the untreated oil [29].

- ✚ Solid phase extraction, which is the next step of the analysis, plays a crucial role for the detection of furans. The sample is dissolved in organic solvent in order to minimize the viscosity of the oil and then passed through a silica cartridge, in order to achieve the adsorption, hence entrapment of the polar compounds such as furans. A significant issue is that the compounds are exposed to the environment during this sample preparation step, and it is known from the literature that air and moisture can affect the furans. The organic solvent might affect the furans due to different properties and most importantly the recovery of the furans from the silica might not be 100%.
- ✚ The oxidising agents that can be present in the silica preparation can affect the furans.

Several attempts have been made to establish an improved method for the detection of furanic compounds in mineral oil. Apart from HPLC, researchers have tried many different ways of analysing the samples and detecting the compounds, notably by Infrared Spectroscopy, Gas Chromatography with Mass Spectrometric detection, UV Spectroscopy [30]. Attempts to establish methods by which other compounds can be determined, to give additional information as to the condition of a transformer have been attempted.

However, before the investigation how these compounds can be detected it is essential to try and understand how the compounds behave under different conditions, such as temperature, pH and in the presence of organic matter. It is also essential to examine the possibility that the oil itself can affect the furans and lead to the production of other compounds than the furans in which with the current method they are unable to be detected. The literature indicates that temperature can affect the production and degradation of furanic compounds but in the examination of the aged mineral oil [6]. Currently, there is no literature which details the basic mechanisms by which furanic compounds react under the same conditions when they are in their neat form and not in mineral oil.

Therefore the main aims of the project are:

- ✚ To define a set of standard parameters under which furanic samples will be prepared and to decide which analytical method is most suited to the generation of reliable results with least interference problems.

- ✚ To investigate the five furan derivatives in respect to key physical properties, specifically stability and ageing, under the influence of three primary process factors: temperature, pH and solvent.

- ✚ To examine the furan degradation process and the production of other derivatives.

- ✚ To investigate the recovery and distribution of the furanic compounds with clean mineral oils and how temperature affects this process.

Therefore, this project will examine each individual furan with the aim of determining a number of factors governing compound formation and degradation, and also to determine those parameters important with respect to the development and improvement of the current industry standard method.

CHAPTER THREE

IDENTIFICATION OF FURANIC COMPOUNDS

&

CALIBRATION USING DIFFERENT

ANALYTICAL TECHNIQUES

3.0 IDENTIFICATION OF FURANIC COMPOUNDS AND CALIBRATION USING DIFFERENT ANALYTICAL TECHNIQUES

3.1 Aim

The aim of this chapter is to conduct an initial examination, in order to gain some information regarding the furan compounds in order to establish:

- ✚ The different analytical techniques that can be used for the identification of furanic compounds. There is information in the literature concerning these techniques, but only under limited conditions [12, 14, and 30].
- ✚ Which technique is most suited to proceed with the later experiments.
- ✚ Calibration information for each furan derivative, by means of determining the dynamic range of the analytical procedure. These values will determine the standard solutions to be prepared and their subsequent usage with respect to calibration of the instrument (HPLC, UV-VIS, and Infrared).

3.2.0 Materials and Methods

3.2.1 General Materials

Below is a list with the materials used throughout this study. All materials were obtained from Sigma-Aldrich:

- ✚ Furfuryl alcohol 99%, Content: 50 g, Lot No: 09675-036, Cat. No: 18,593-0, b.p. 170 C, d 1.135

- ✚ 5-Methyl Furfural 99%, Content: 25 g, Lot No: 09517-027, Cat No: 13,731-6, b.p. 187 C, d. 1.107.

- ✚ 2-Acetyl Furfural 99%, Content: 25 g, Lot No: 12865-076, Cat No: A1, 625-4, b.p. 67 C/10mm, d. 1.098.

- ✚ 5-Hydroxymethyl Furfural, Content: 5 g, Lot No: 11499-066, Cat No: H4, 080-7, b.p. 114-116 C/1mm.

- ✚ 2-Furaldehyde 99%, Content: 25g, Lot No: 60712-018, Cat No: 18,591-4, b.p. 162 C, d. 1.160.

- ✚ HPLC grade water, Content: 2.5L, Lot No: 60140, Cat No: 34877

- ✚ Tetrachloroethylene 99%, Content: 2.5L, Lot No: 0273725, Cat No: T/0600/17

3.2.2 Method for the Maximum Absorbance

Five solutions were prepared, one for each furan, by dissolving 0.2 g of the material in 100 ml of HPLC grade water. The total concentration of each solution was 0.2% w/v. Its solution was measured in a single UV-Visible spectrophotometer; model Beckman DU640 (serial number 4319046), and the device was set for initial scanning starting from 900 - 190 nm. The cell used for the analysis was quartz with 1 cm path length.

3.2.3 Calibration and Analysis Using HPLC, Infrared and Fluorescence Spectroscopy Techniques

Once the maximum wavelength of absorbance was determined, a series of solution were prepared containing 0.1 - 1000 ppm of furans in distilled water. A 1000 ppm stock solution was prepared, and was diluted to a lowest concentration of 0.1

ppm of furans. The dilutions were performed in a ratio 1:10, meaning that whenever a lower dilution was performed it was not exceeding that ratio. The double beam UV-Visible spectrophotometer measurements were performed at the specific maximum absorbance, determined experimentally and varied according to the compound analysed. Once again the cell used was a quartz cell with path length of 1 cm. table 2 and Figure 10 shows the results from the measurements and also the calibration graphs, respectively, when UV-Vis spectroscopy analysis was used for that determination.

The solutions that were prepared in Section 3.2.2 were also measured using a fluorescent spectrometer. The instrument was set to scan from 150 - 900nm, with excitation light wavelength set to the experimentally determined maximum absorbance value for each derivative. The integration time was 0.1s with an increment value of 1.0 nm. Figure 13 shows the resultant graphs obtained.

Another technique that was used to identify the furan compounds was Near Infrared (NIR) Spectroscopy. For this type of analysis another set of solutions were prepared by dissolving 0.2 g of each furan in 100 ml tetrachloroethylene to make up a solution of 20 ppm. Furan-containing solutions were placed between two plates of potassium bromide, which constituted the cell wall, and by setting the instrument for scanning from 4000 - 400 cm^{-1} . Figure 11 shows the graphs obtained from the analysis.

Finally, another set of standard solutions were produced with concentrations in the range of 0.025 ppm - 5 ppm. Solutions were prepared in water and analysed using High Performance Liquid Chromatography. The instrument was set up according to the specifications of the current IEC method for the analysis of furanic compounds. The column that was used for the separation was a C-18 silica column with 25cm length. The mobile phase of the isocratic gradient was a 15% acetonitrile in water and 70% acetonitrile in water. Two UV adsorption wavelengths were used for detection purposes, 216 nm and 278 nm, since in those two wavelengths, according to the standard method, all the five furan derivatives examined absorb light. Figure 12 shows the results.

3.3 Results

3.3.1 Initial Scanning of Absorbance of furanic compounds using UV-Vis spectroscopy

Below are the results for the five furan derivatives showing their UV absorbance maxima when scanned across the range 900 nm - 190nm.

Table 1 Initial Scanning of the five furan derivatives using UV spectroscopy. The highlighted numbers are indicating the wavelength that gives the highest absorbance.

Compound	Wavelength in nm	Absorbance
5-HMF	194.5	3.1477
	229	0.4426
	268	3.7524
	293	3.7844
	296.5	3.7797
2-ACF	191.5	2.8887
	226.5	0.4924
	261	3.9148
	286	3.7824
	359	-0.0058
FOL	197	1.2238
	205.5	3.6154
	223	3.9258
	886.5	-0.0086
	889	-0.0086
5-MEF	193	3.0445
	227.5	0.567
	273.5	3.811
	293	3.7844
	307	3.7329
2-FAL	190.5	0.8117
	229	0.6885
	268.5	3.8472
	284.5	3.7839
	886	-0.0095

3.3.2 Calibration Results & Graphs of the five furans using UV-Vis Spectroscopy.

The table below shows the results of a series of different concentrations of the five furan derivatives measured using UV-Vis spectroscopy. The measurements were performed according to the results from section 3.3.1, by reading each solution at its maximum absorption. In the table below, are shown data used to create the calibration graphs for each furan (Fig 12 a-e).

Table 2 Spectrophotometric response of the five furanic compounds in different concentrations at their maximum adsorption using UV spectroscopy.

Concentration of furanic compounds in ppm	5-HMF		2-ACF		5-MEF		2-FAL		FOL	
	Absorption	Corrected Abs	Absorption	Corrected Abs	Absorption	Corrected Abs	Absorption	Corrected Abs	Absorption	Corrected Abs
0	0.0535	0	0.261	0	0.0585	0	0.0369	0	0.0428	0
0.1	0.064	0.0105	0.2779	0.0169					0.13	0.0872
0.2	0.0758	0.0223	0.2887	0.0277	0.0631	0.0046			0.1438	0.101
0.5	0.1146	0.0611	0.3148	0.0538	0.0786	0.0201	0.0434	0.0065	0.1678	0.125
1	0.1653	0.1118	0.3556	0.0946	0.1034	0.0449	0.1558	0.1189	0.2114	0.1686
2	0.2781	0.2246	0.4808	0.2198	0.2178	0.1593	0.331	0.2941	0.29	0.2472
5	0.6245	0.571	0.9891	0.7281	0.3939	0.3354	0.6586	0.6217	0.5784	0.5356
10	1.1606	1.1071	1.2493	0.9883	0.9157	0.8572	1.6248	1.5879	0.9249	0.8821
50	3.3396	3.2861	2.0824	1.8214	3.109	3.0505	3.4367	3.3998	2.509	2.4662
100	3.4952	3.4417	2.137	1.876	3.4952	3.4367	3.4952	3.4583	2.5741	2.5313
200	3.613	3.5595	2.3404	2.0794	3.7377	3.6792	3.4367	3.3998	2.6775	2.6347
300	3.613	3.5595	2.3447	2.0837	3.7377	3.6792	3.613	3.5761	2.7268	2.684
400	3.613	3.5595	2.3447	2.0837	3.7377	3.6792	3.613	3.5761	2.9484	2.9056
500	3.613	3.5595	2.3551	2.0941	3.7377	3.6792	3.7377	3.7008	2.775	2.7322
1000	3.613	3.5595	2.407	2.146	3.9716	3.9131	3.9716	3.9347	2.9311	2.8883

Below are the calibration graphs of each individual furan showing also the degree of linearity for each occasion. The maximum point from the linearity graph will determine the initial concentration of each furan for later experiments.

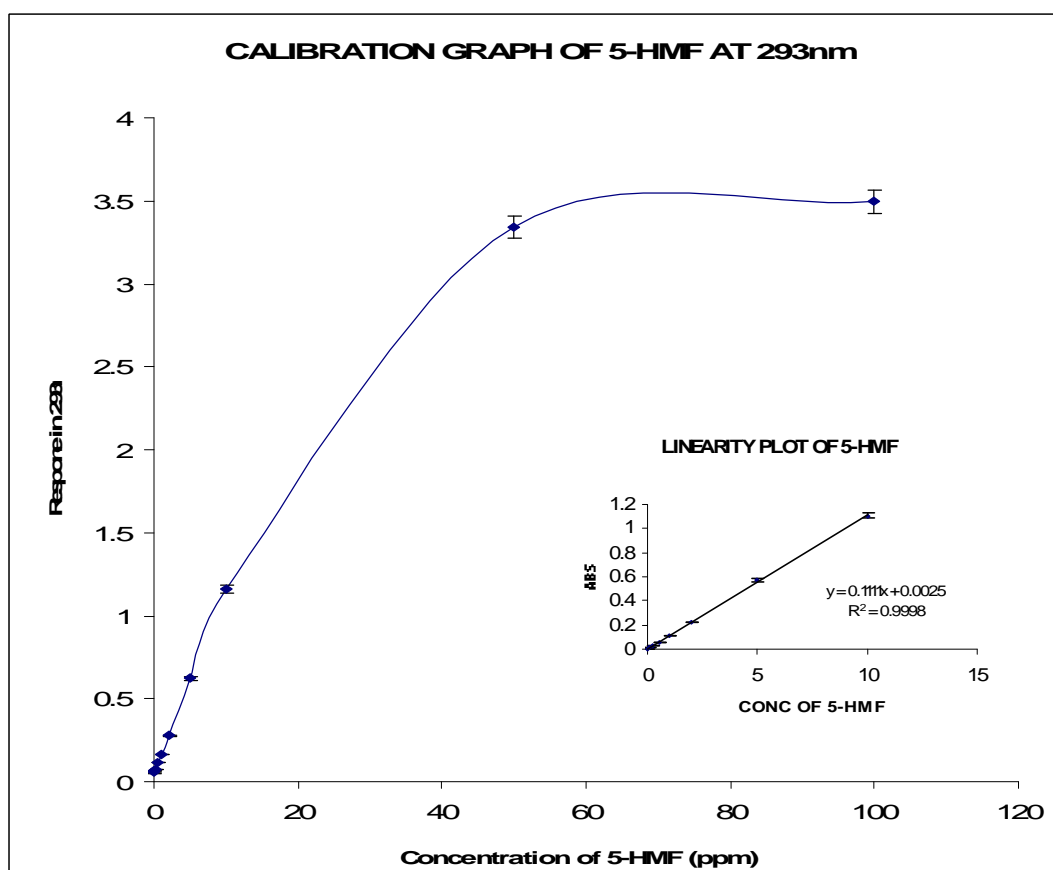


Fig 10 (a) Calibration graph of 5-HMF. The plot illustrates the concentration of each solution versus the spectrophotometric response that the compound show at 293 nm

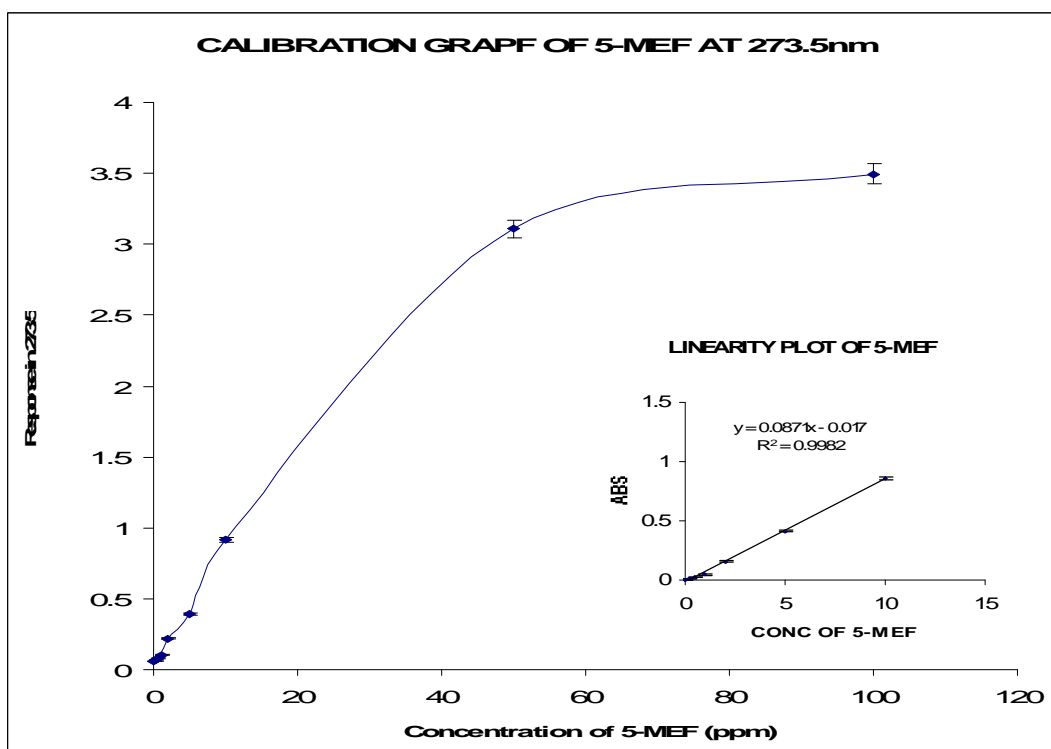


Fig 10 (b) Calibration graph of 5-MEF. The plot illustrates the concentration of each solution versus the spectrophotometric response that the compound show at 293 nm

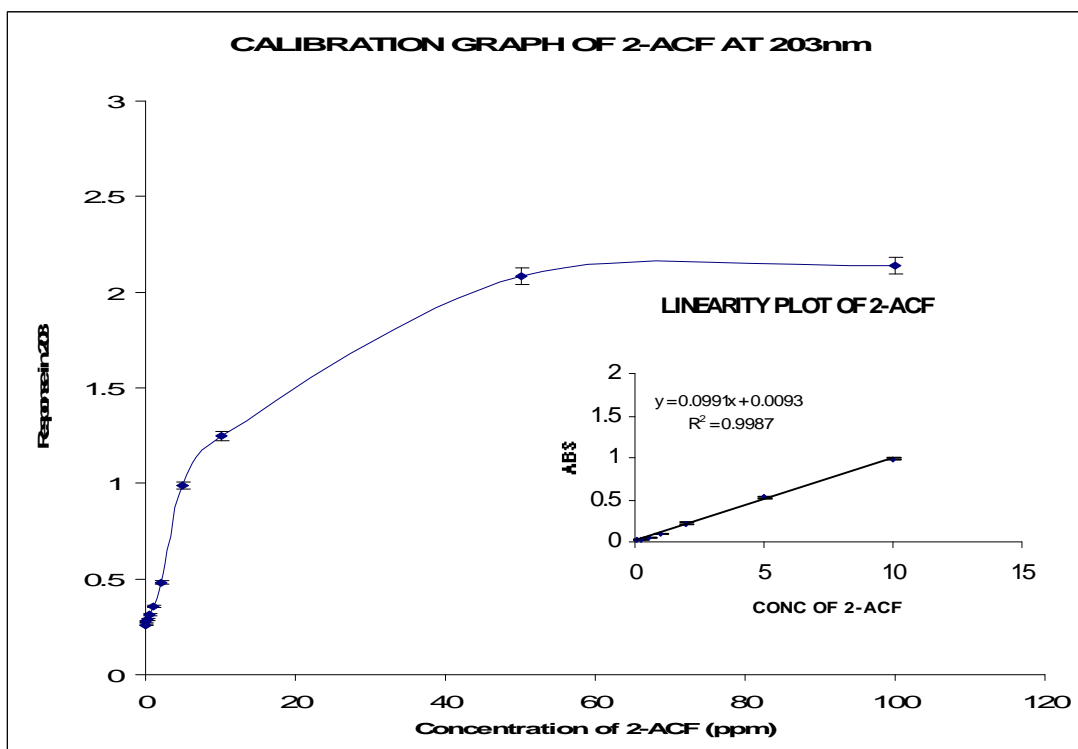


Fig 10 (c) Calibration graph of 2-ACF. The plot illustrates the concentration of each solution versus the spectrophotometric response that the compound show at 261 nm

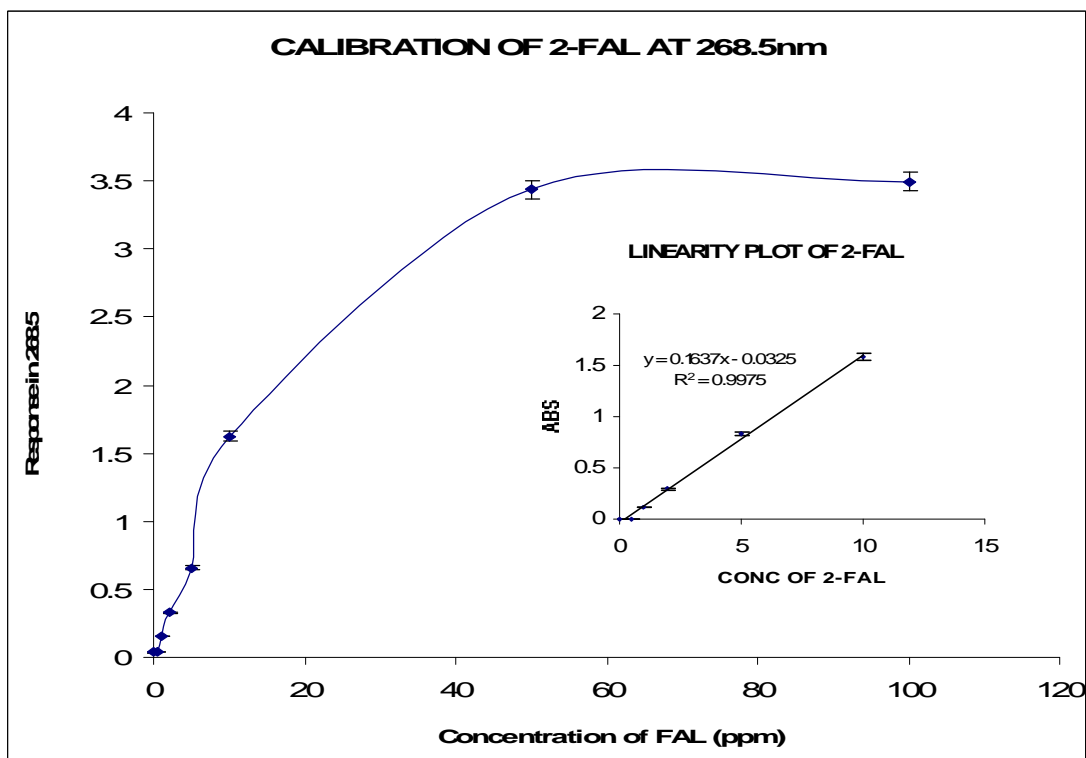


Fig 10 (d) Calibration graph of 2-FAL. The plot illustrates the concentration of each solution versus the spectrophotometric response that the compound show at 268.5 nm

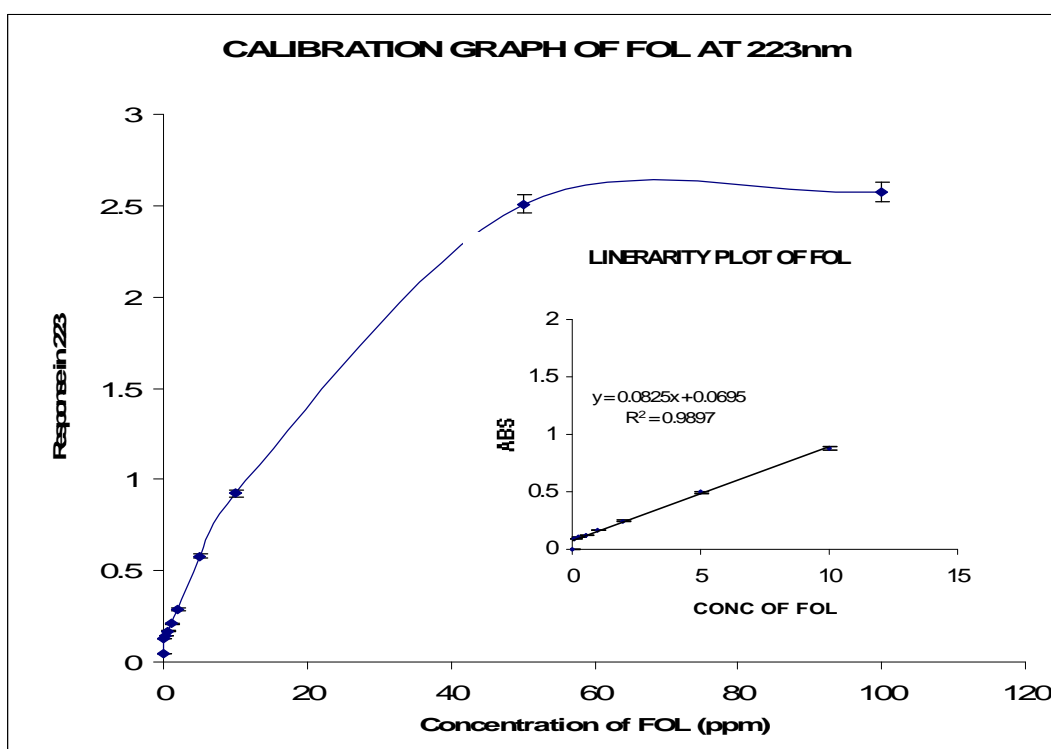


Fig 10 (e) Calibration graph of FOL. The plot illustrates the concentration of each solution versus the spectrophotometric response that the compound show at 223 nm

Figure 10 Calibration Graphs of the five furans by UV-Visible spectrophotometer. (a) 5-HMF, (b) 5-MEF, (c) 2-ACF, (d) 2-FAL and (e) FOL.

3.3.3 Spectra of the five furanic compounds using Fourier Transform Infrared Spectroscopy (FTIR).

FTIR spectroscopy is the absorption of electromagnetic radiation in the infrared region, which corresponds to 250 to 4000 cm^{-1} (2.5 to 40 μm), of the spectrum resulting in changes in the vibrational energy of molecules [32]. It was mentioned above (see section 3.2.3) the method of preparing and analysing the solutions by FTIR. The Figure (11) below shows the spectra obtained for each individual furanic compound, approximately 20 ppm w/v in tetrachloroethylene, when they were scanned from 400-4000 cm^{-1} wavenumber.

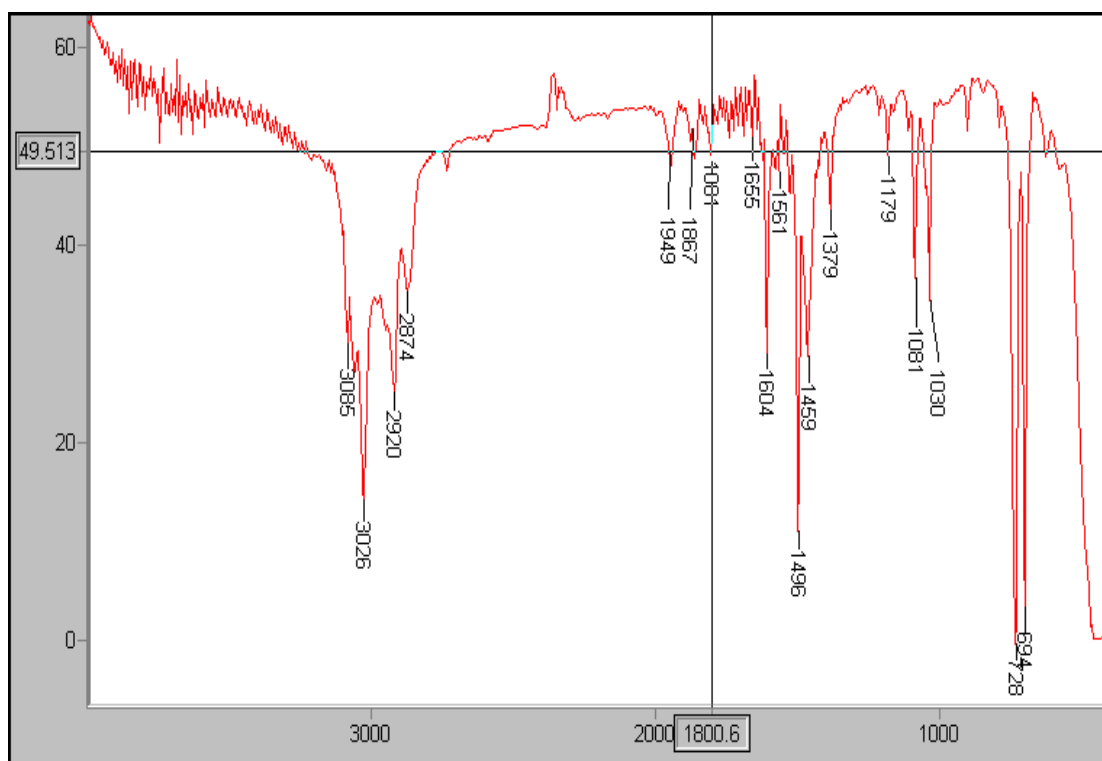


Fig 11 (a) Infrared Spectrum of 2-ACF in Tetrachloroethylene

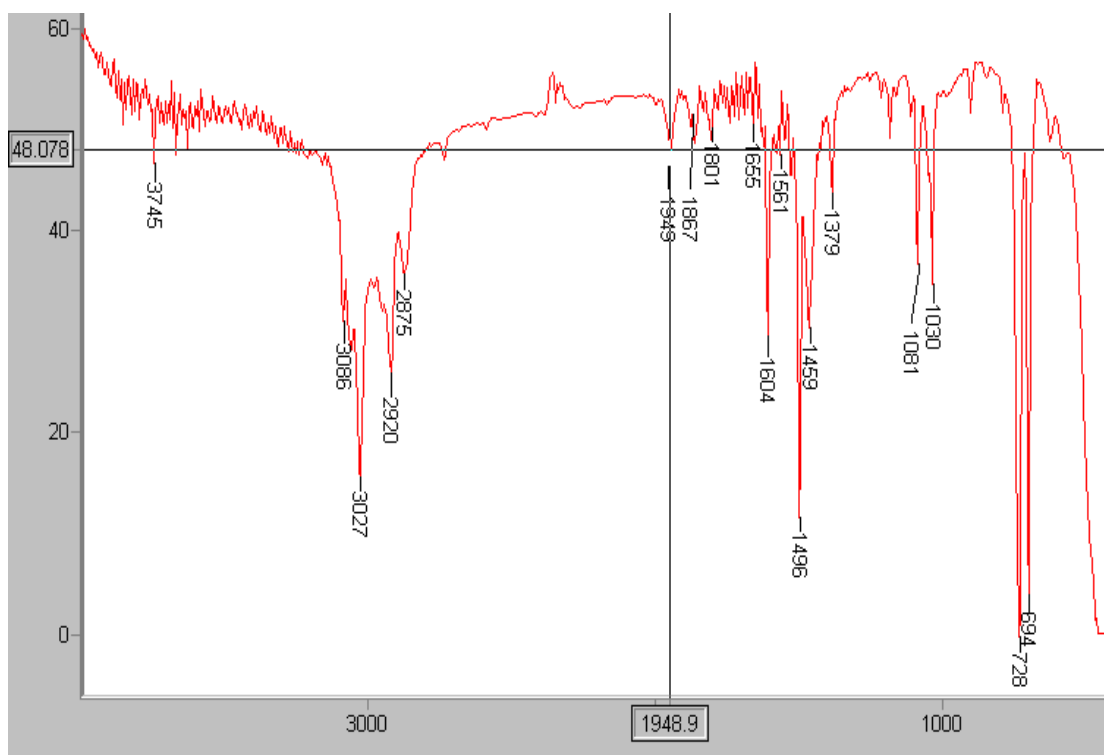


Fig 11 (b) Infrared Spectrum of 2-FAL in Tetrachloroethylene

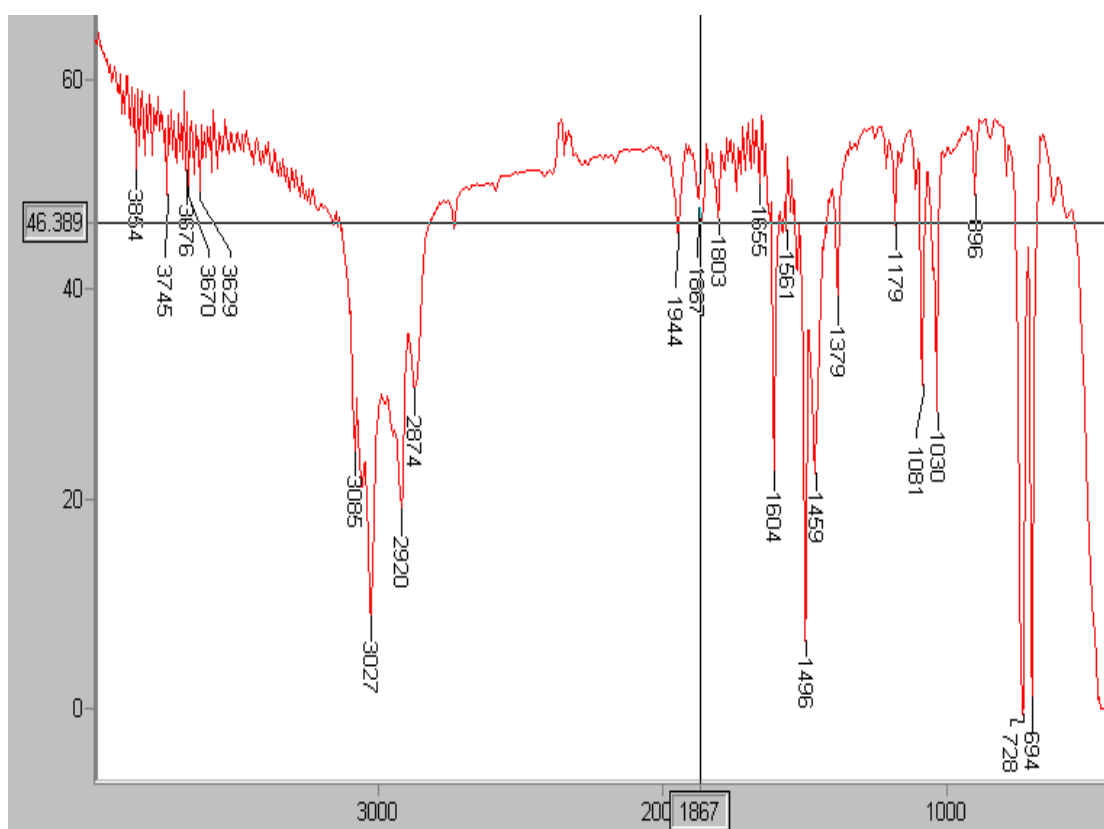


Fig 11 (c) Infrared Spectrum of FOL in Tetrachloroethylene.



Fig 11 (d) Infrared Spectrum of 5-HMF in Tetrachloroethylene

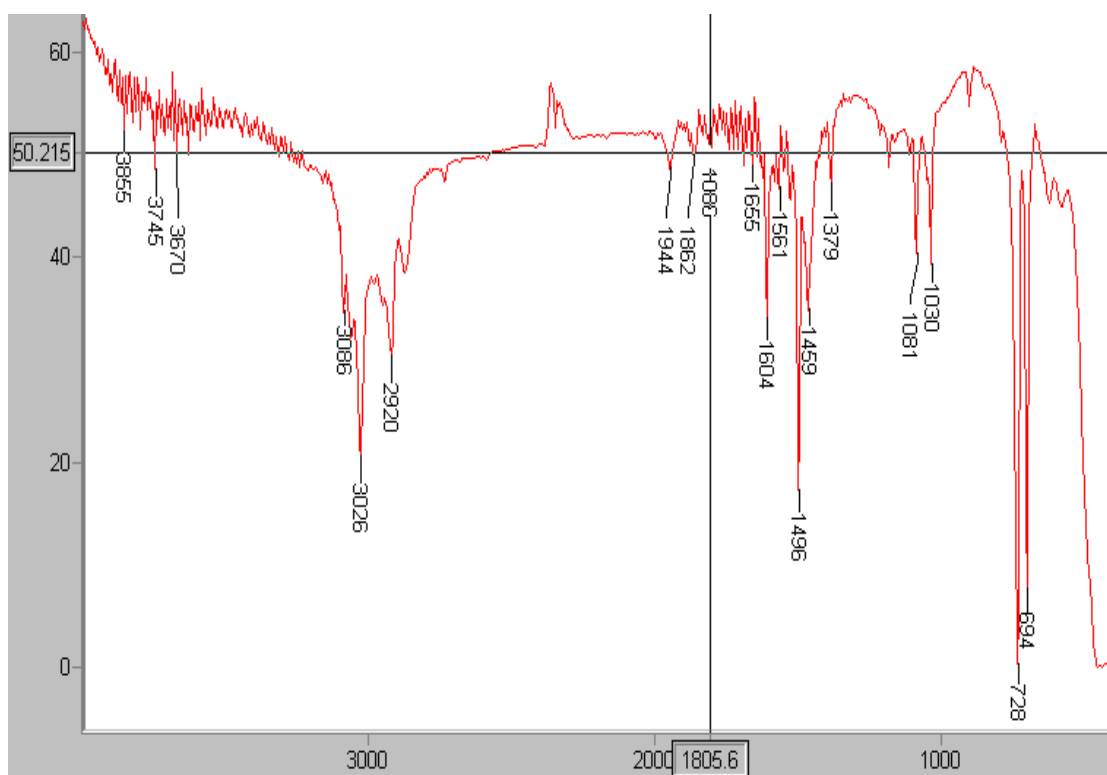


Fig 11 (e) Infrared Spectrum of 5-MEF in Tetrachloroethylene

Figure 11 Infrared Spectra of the five furans in Tetrachloroethylene solution. (a) 2-ACF, (b) 2-FAL, (c) FOL, (d) 5-HMF and (e) 5-MEF

3.3.4 High Performance Liquid Chromatography results for standard furan compounds analysed.

The table below shows the peak area obtained for each furan compound performed in a series of different concentration solutions using HPLC analysis.

Table 3 Peak area results for the five furanic compounds of different concentration solutions using HPLC. The results obtained by identifying and integrating each peak from the spectrum to determine the peak area of the appropriate furan.

CONCENTRATION (ppm)	AREA OF EACH FURAN				
	HMF	FAL	ACF	MEF	FOL
0	0	0	0	0	0
0.025	18525	9525	11539	6853	2498
0.05	36473	14373	17936	13890	4302
0.1	69492	22014	37246	27390	9618
0.5	339447	106312	198448	152600	43104
1	802902	219624	400284	320265	88343
2	1383786	541156	838544	659377	184952
5	3059593	1263765	2266884	1785384	643374

Figure 12 (a-e) shows the calibration graphs of each individual furanic derivative by using the data presented above.

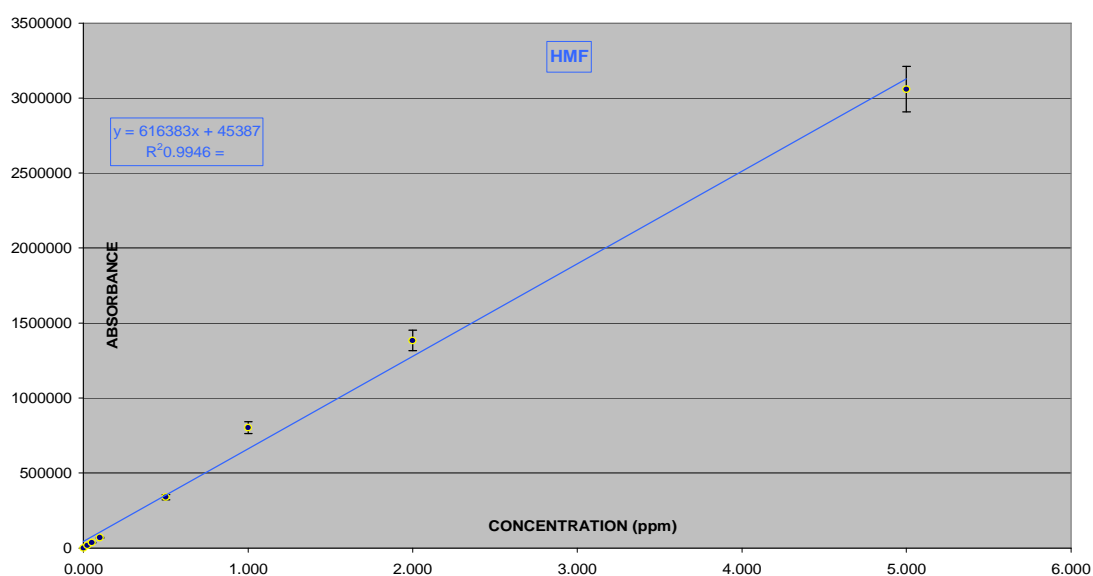


Fig 12 (a) Calibration graph of 5-HMF. The graph illustrates the concentration of each solution measured versus the absorbance.

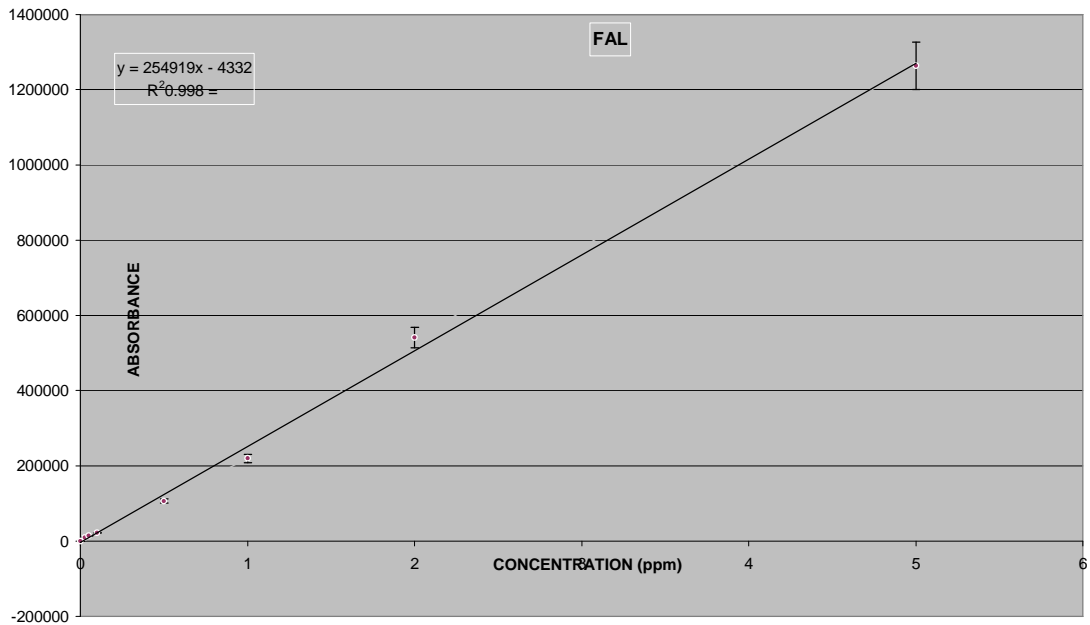


Fig 12 (b) Calibration graph of 2-FAL. The graph illustrates the concentration of each solution measured versus the absorbance.

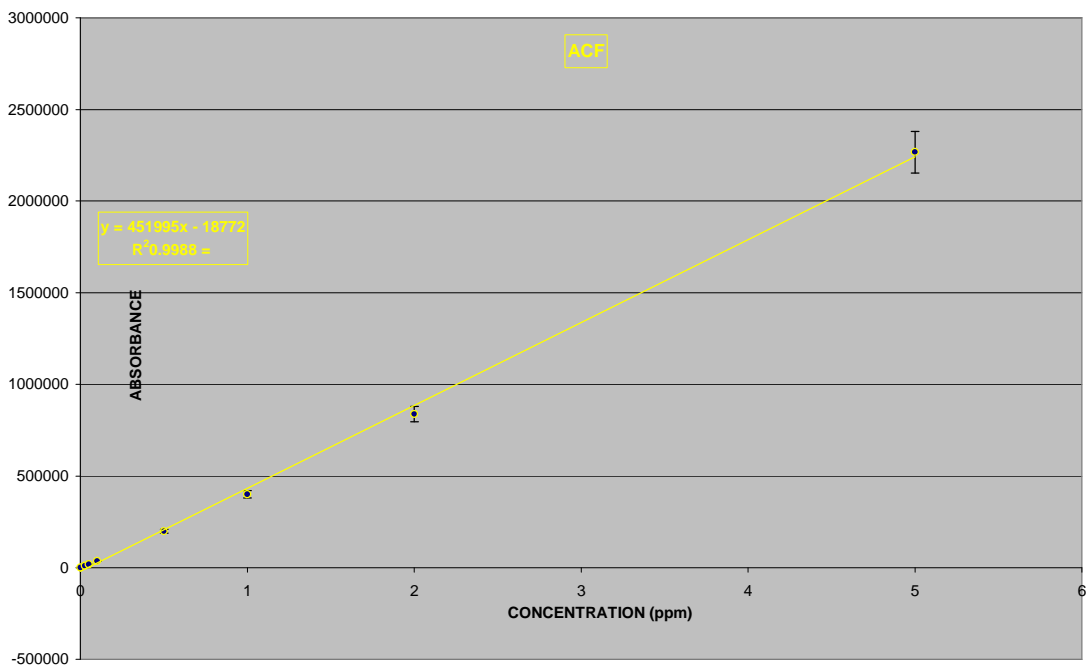


Fig 12 (c) Calibration graph of 2-ACF. The graph illustrates the concentration of each solution measured versus the absorbance.

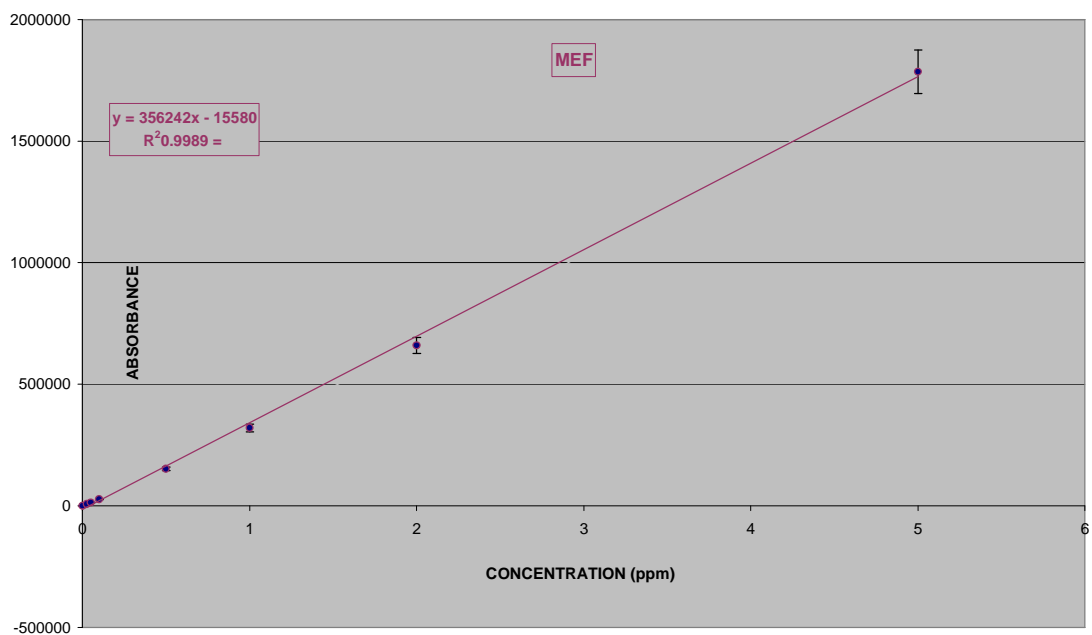


Fig 12 (d) Calibration graph of 5-MEF. The graph illustrates the concentration of each solution measured versus the absorbance.

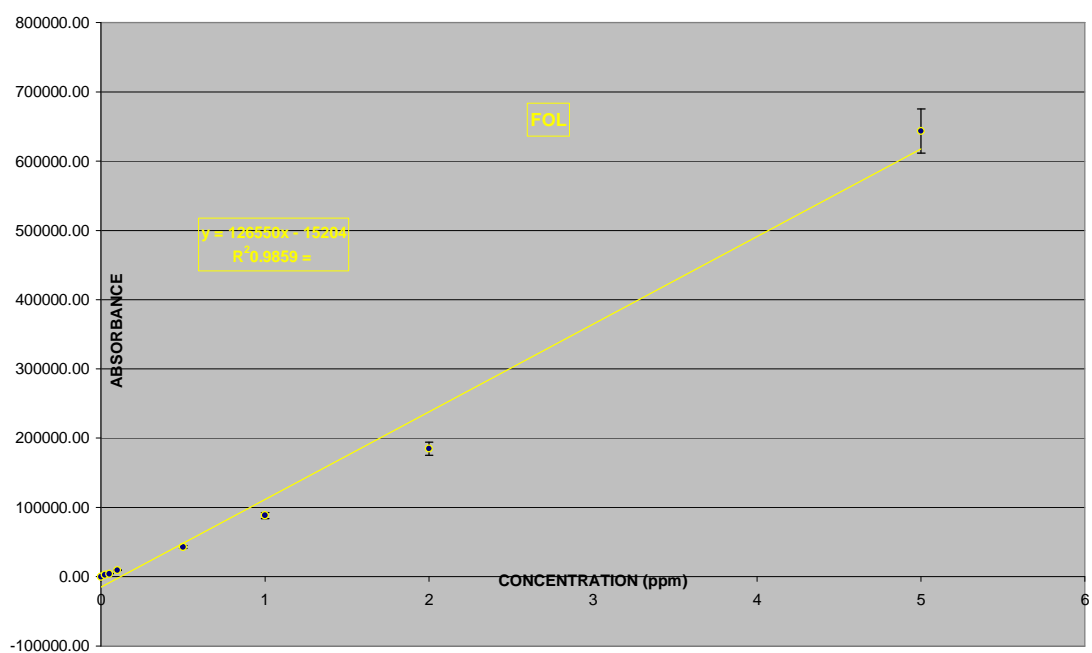


Fig 12 (e) Calibration graph of FOL. The graph illustrates the concentration of each solution measured versus the absorbance.

Figure 12 Calibration Graphs of the five furanic compounds by HPLC. (a) 5-HMF, (b) 2-FAL, (c) 2-ACF, (d) 5-MEF and (e) FOL

3.3.5 Results obtained for the five furanic compounds using Fluorescence spectroscopy analysis.

Below are the spectra obtained for the five furanic compounds when they were examined under fluorescence spectroscopy (see section 3.3.3 for the preparation method). For each compound the maximum absorbance measured in previous section (3.3.2) was used as the excitation wavelength. All the compounds were scan from 190 – 900 cm^{-1} .

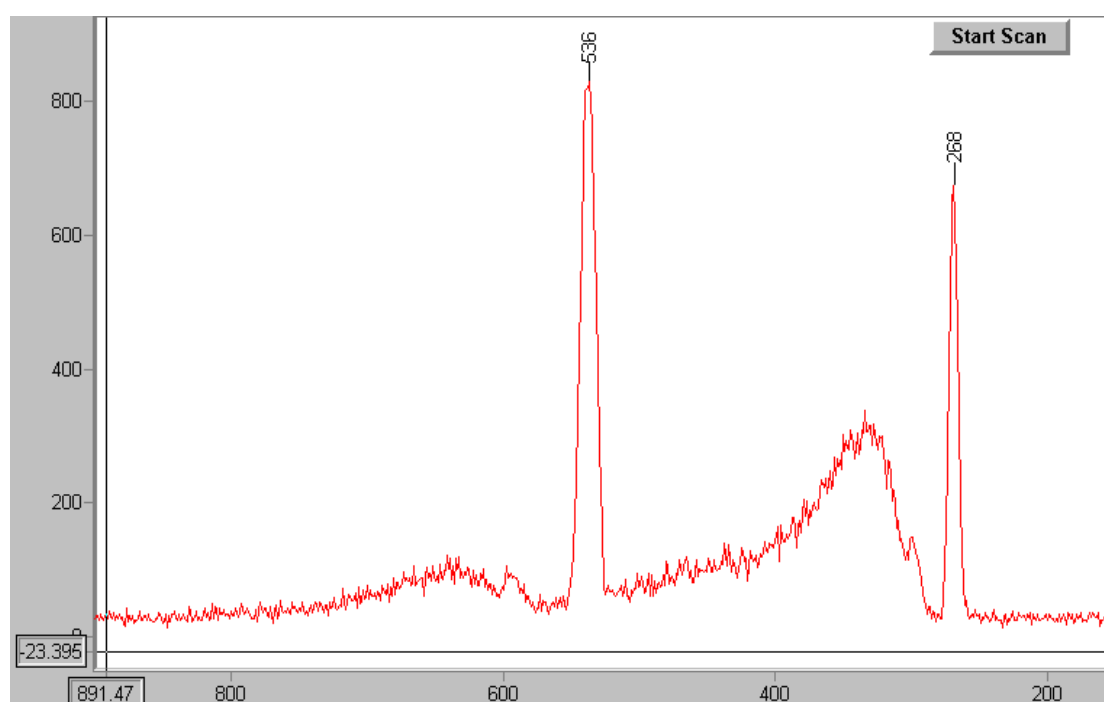


Fig 13 (a) fluorescent spectrum of 5-Hmf at 268 cm^{-1} excitation wavelength.

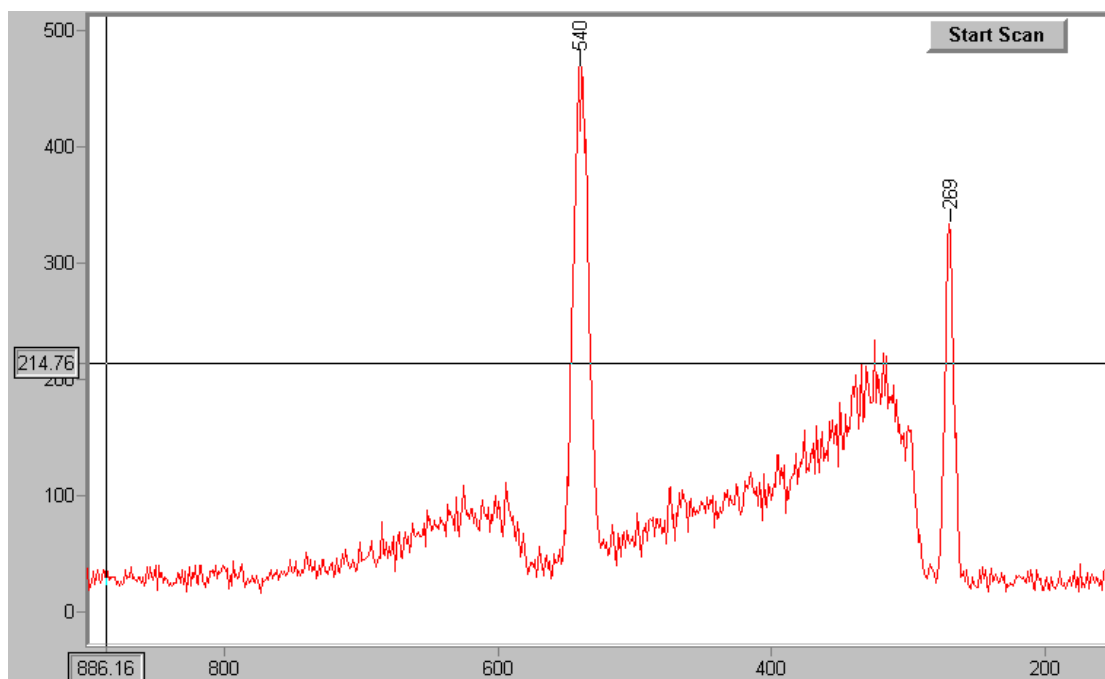


Fig 13(b) Fluorescent spectrum of 2-Fal at 268 cm^{-1} excitation wavelength.

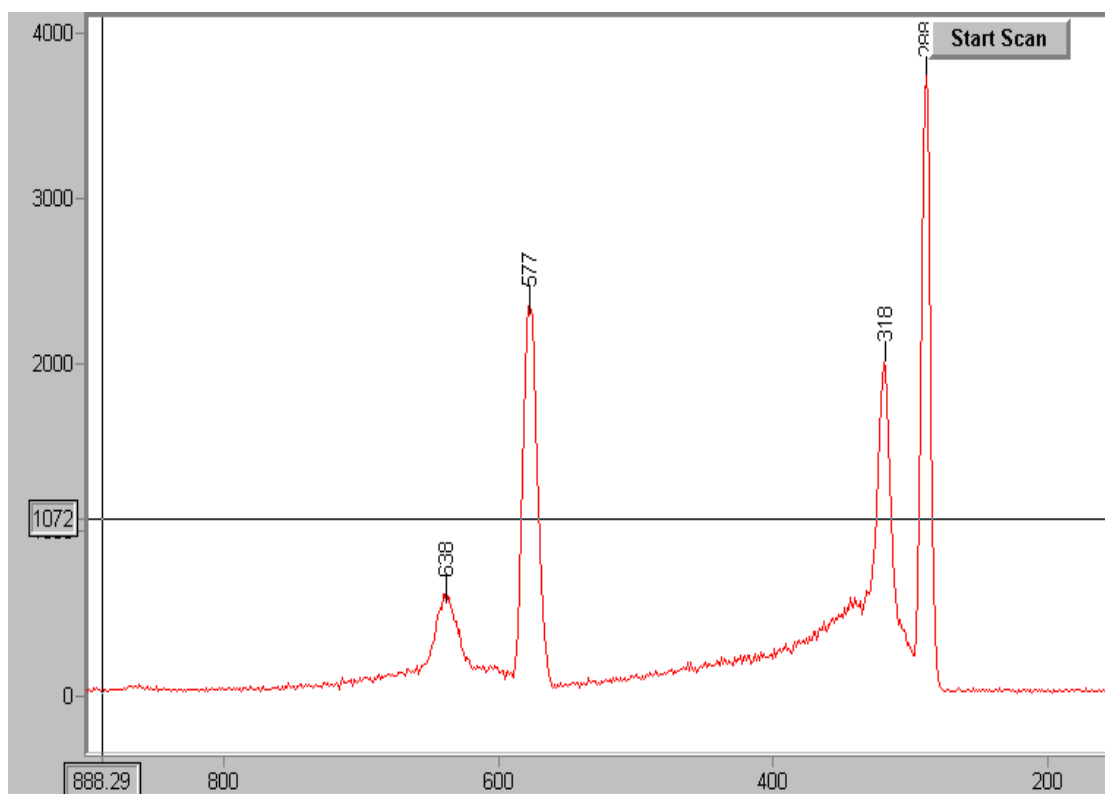


Fig 13 (c) Fluorescent spectrum of 2-Acf at 286 cm^{-1} excitation wavelength.

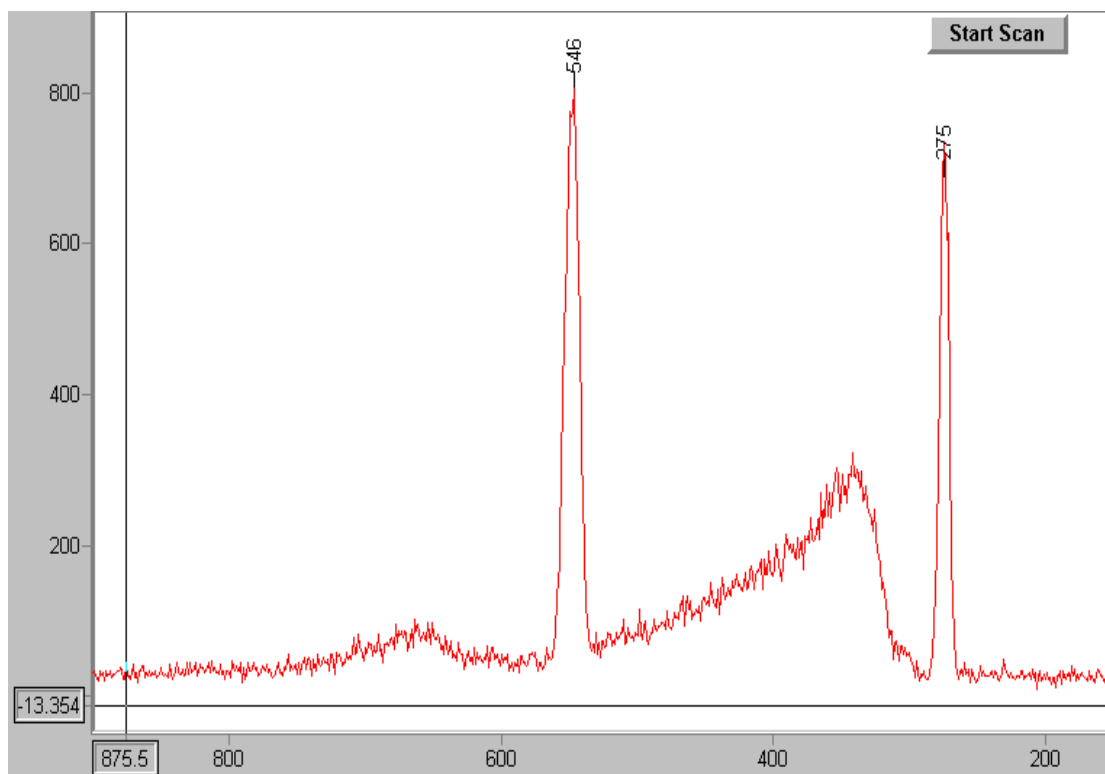


Fig 13 (d) Fluorescent spectrum of 5-Mef at 273 cm⁻¹ excitation wavelength.

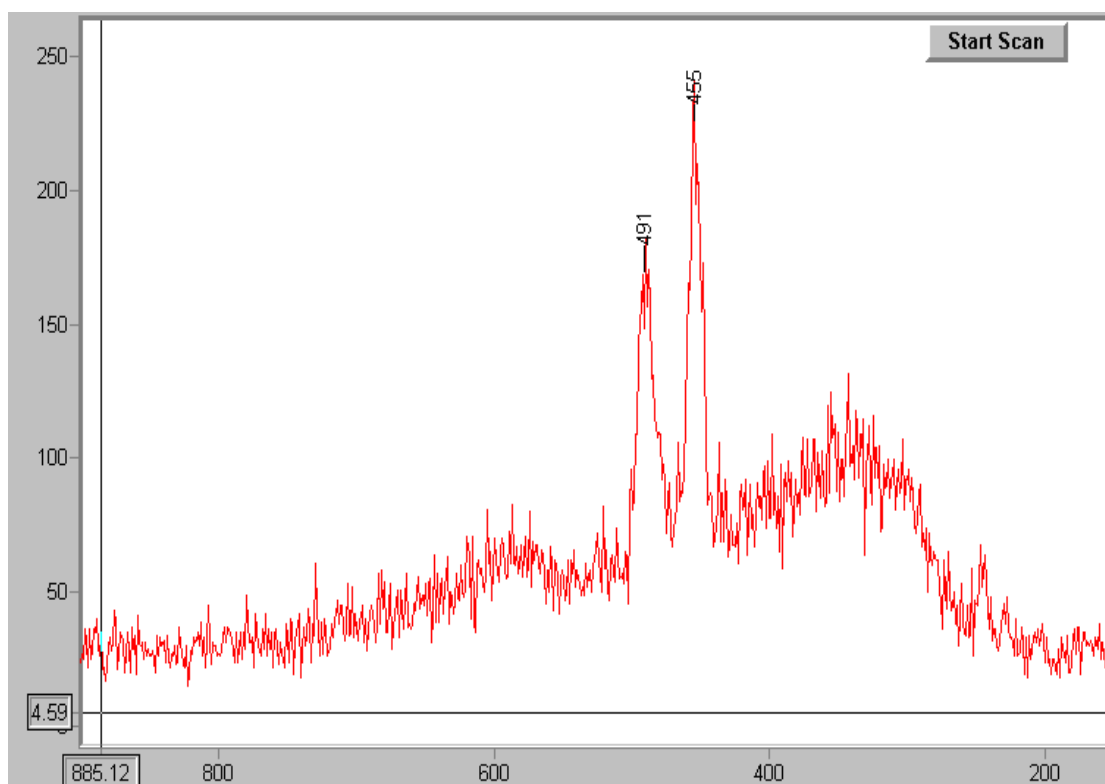


Fig 13 (e) Fluorescent spectrum of Fol at 223 cm⁻¹ excitation wavelength.

Figure 13 Fluorescent spectra of the five furanic compounds when they were scan from 190 – 900cm⁻¹, each one at a different excitation wavelength.

3.4 Discussion

As was described in Section 3.1, this chapter was aimed at elucidating a suitable approach with respect to the analytical techniques which can be used for the identification, separation or even for the calibration of the furanic compounds. The five furan derivatives were analysed using HPLC, UV-Vis spectroscopy, infrared spectroscopy and fluorescence spectroscopy. The results from Section 3.3 shows that furanic compounds can actually be identified using both spectroscopic and chromatographic techniques.

Generally, the five furans were analysed in aqueous environments mainly for two reasons. Firstly, water is a suitable solvent for the dissolution of the five furans selected without the need for a co-solvent and secondly water exhibits less interference with the methods selected. A significant issue was that water could not be used as a solvent for the analysis of the furans by infrared spectroscopy. The reason for that was the OH group from the water will interfere with the transmission peaks obtained for the furan components. For that reason dichloethylene was used, a compound that can dissolve all the furans exhibiting minimum interference effects in the IR portion of the spectrum.

It was known from the IEC method that furans can be detected by HPLC and UV-Vis spectroscopy. Literature indicates detection of furans using IR and fluorescence spectroscopy when the compounds were extracted from mineral oil, something that will be further discussed in this Section [30].

Section 3.3.1 reports the initial scanning experiments of each individual furan in order to establish the maximum UV absorbance. It can be seen from Fig. 10 that the maximum absorbance is different for each furan. The IEC method currently uses two different UV detection wavelengths 278 nm and 216 nm to detect all the furans, previously identified as the most suitable wavelength for furan detection. Because the concentrations of the solutions prepared were based purely existing literature and practical experience, a more precise indication of a maximum and minimum

detectable concentration was necessary. Such information is useful with respect to determination of the solutions required for subsequent experimentation, with particular applicability in selecting the starting concentrations for each furan with respect to stability, ageing and degradation experiments. Fig 10 shows the graphs produced when a series of different solutions were measured using UV-Vis spectroscopy and using a fixed absorbance reading, according to the maximum absorbance of each furan. It can be seen from the graphs (Fig 10) that the method response becomes increasingly saturated for all the furan derivatives for concentrations in excess of 30 ppm.

Blue *et.al.* [30] have used infrared spectroscopy to detect degradation of insulating paper. It was found that there is a linear correspondence between the furanic concentrations with infrared absorption. Also, it was found that the five specific furan derivatives absorb below 1700 cm^{-1} , which agrees with the results obtained in Section 3.3.3. Although, Blue *et al.* used different solvents and different sample treatment protocols, the results are nevertheless comparable. Interpretation of the spectra from Section 3.3.3 shows all the main constituents of the furan derivatives, such as C-H bond adsorption at 2960 cm^{-1} , alkenes at 3020 cm^{-1} and aromatics at 3026 cm^{-1} . All these components also absorb also at lower regions such as 1400 cm^{-1} to 1600 cm^{-1} . It may be noted that all the spectra exhibit some similarities, primarily because all the furfuraldehydes examined are derivatives of the parent compound furan.

Fluorescence spectroscopy was used also for the detection of furanic compounds. From Figure 16, which illustrates the spectra obtained, it can be seen that furanic compounds exhibit fluorescence at around 500 nm. For each furan derivative, the excitation wavelength used was selected according to the maximum absorption values from the previous experiment obtained in section 3.3.1. According to literature, Blue *et.al* used fluorescence spectroscopy to detect FFA in mineral oil and showed that at a range of $540 - 615\text{ cm}^{-1}$ wavelength a furan compounds excite light. Once again, Blue and co-workers used different conditions and different concentrations of FFA from those examined in this project, but with similar end-results being obtained.

3.5 Conclusion

The work presented in this chapter has provided an initial approach with respect to the selection and development of suitable analytical methods for the determination of the selected furan derivatives. The five-furan derivatives were 5-HMF, 2-FAL, 2-ACF, 5-MEF and FOL in which they were examined in their pure form. Generally, this chapter investigated some of the properties of the furans, their ability to react with other materials and an attempt has been made to correlate the results of this project against existing literature.

In summary, this aspect of the study has examined the choice of solvent for experiment, indicated useful optical properties for each individual furan, and furthermore, provided information regarding potential methods for the analysis of the derivatives via different analytical techniques.

It was shown that;

- ✚ Water was a suitable solvent for the majority of studies potentially exhibiting less interference effects when compared to the use of organic solvents. This observation is of interest from the perspective that later experiments may be performed in aqueous environments.
- ✚ Each of the five furan derivatives has a different absorption value, but all exhibit a maximum detection limit at around 30 ppm analyte.
- ✚ All the furanic compounds can be analysed by HPLC, UV-Vis, Infrared and fluorescence spectroscopy provided that the appropriate conditions for detection are applied. Some of the techniques are more sensitive than others, but due to the conditions that will be applied to furan containing solutions, it was decided that UV-Vis and HPLC techniques are the most appropriate for subsequent experiments.

✚ Generally the results obtained from this chapter correlate with the literature. It should be noticed that the conditions used for the investigation in this project were completely different from the condition of the literature, but the correlation was successful.

CHAPTER FOUR
AGEING, STABILITY &
DEGRADATION PRODUCTS

4.0 AGEING, STABILITY & DEGRADATION PRODUCTS

4.1 Aim

In this chapter, furanic compounds will undergo a series of different experiments using two different analytical techniques to observe and to record the changes happening to the compounds, during the ageing process. The furans will be monitored frequently, for a period of time (approximately 2 months), to study the behaviour of them under the influence of three parameters;

- ✚ Temperature
- ✚ pH
- ✚ Alternative solvents.

(For further explanations of the choice of the conditions see section 4.4)

The results for these experiments will allow calculation of the rates of ageing of each furan, their stability under the three imposed conditions, and the furanic derivatives produced as a result of the degradation of each initial furan.

4.2 Materials and Methods

4.2.1 Materials

The furan derivatives which were used in this chapter were the same materials used in section 3.2.1. In addition to those, the following materials, provided from Sigma-Aldrich, were used;

- ✚ Sodium Carbonate Anhydrous, Content: 2.5 Kg, Cat No: s/2840/62, Lot No: 0119422.
- ✚ Sodium Hydroxide, Content: 500g, Cat No: 102524X, Lot No: B247450-306.
- ✚ Potassium di-Hydrogen Phosphate 99.5%, Content: 250g, Cat No: 60221, Lot No: 1154873.

- ✚ Sodium bicarbonate 99%, Content: 250g, Cat No: 88208, Lot No: 1137344.
- ✚ Di-Sodium Hydrogen Phosphate Dihydrate 99%, Content: 250g, Cat No: 71633, Lot No: 1157421.
- ✚ Acetic Acid glacial, Content 2.5Lt, Cat No: A/0400/PB17, Lot No: 9911889-109
- ✚ Methanol HPLC gradient grade, Content: 2.5Lt, Cat No: M/4058/17, Lot No: 0397335.
- ✚ Acetonitrile HPLC gradient grade, Content 2.5Lt, Cat No: 34851, Lot No 53220.

4.2.2 Method

The ageing of furanic compounds against time was performed in three different solvents, at four different temperatures and at three different pH values (see table below).

Table 4 Illustration of the different conditions that the furanic compounds will be investigated for the purpose of ageing, stability and degradation analysis.

SOLVENTS	TEMPERATURE	PH
FURANS IN AQUEOUS SOLUTION	0°, 40°, 60°, 80°	4, 7, 11
FURANS IN ACETONITRILE	0°, 40°, 60°	
FURANS IN METHANOL	0°, 40°, 60°	

Initially the furans were dissolved in water with a controlled pH i.e. the buffer solution. Three different buffers were prepared for this experiment with pH 4.6, 6.8 and 10.

The buffer solution with pH 4.6 was produced by dissolving 10 g of Sodium Hydroxide in 2.5 L of water. Slowly addition of 30 g of Acetic Acid was introduced

in order to decrease the pH and to stabilise at 4.6. For the buffer solution with pH 6.8 11.125 g of di-Sodium Hydrogen Phosphate were dissolved in water, 2.5Lt, and 8.5 g of Potassium di-Hydrogen Phosphate was added to bring and to adjust the pH at 6.8. Finally, for the last buffer, 5.25g of Sodium Carbonate was dissolved in water, 2.5 Lt, and 6.625g of Sodium bicarbonate was used and dissolved to the solution in order to fix the pH at 10. For all the pH measurements the instrument which was used was a microprocessor pH meter from HANNA instruments, model pH 213, and purchased from Sigma-Aldrich. Those buffer solutions were used as the solvent material for the production of standard solutions, but also for the production of the samples which will undergo the investigation.

For the construction of the standard solutions the same process was performed as in section 3.2.3, and the concentrations of the standards were as follow; 5, 10, 20, 30, 40, and 50 ppm of furanic compounds. For the production of the samples each furan was treated separately from each other by producing each sample at concentration of 30 ppm at the three different pH values. The reason of producing each furan at 30 ppm was the fact that; this was the point from the calibration at section 3.2.3 where the linearity of the graph was tend towards a zero order response profile. For each furan four identical solutions were produced in order that each one of them to be stored at the four different temperatures (0, 40, 60 and 80°C). Therefore 12 samples for each furan were produced. The standard solutions were kept at 0°C in order to minimize the degradation effect, and were used for the initial calibration graph. The equation by the graph will be used for calculating the amount of concentration which each furan is aged, but also is a way to observe and to monitor the condition of the instrument.

Initially 5 ml of each sample from all the different conditions were taken out from the place of storage and analysed using UV-Vis spectroscopy to obtain their absorbance values at the specific wavelength according to the maximum limit of detection for each individual species (see section 3.3.1).

Ageing of furanic compounds were also investigated in the presence of two other solvents; acetonitrile and methanol. The only difference to the previous experiment was that the sample consists of all the furan derivatives at 30 ppm each,

and the pH of the final solution was not controlled. Once again, a new set of standard solutions was produced but this time in an organic solvent. In other words, a stock solution of 1000 ppm of all the furans was produced by dissolving 0.5 g of each furan in 500 ml of either Acetonitrile or Methanol. Dilutions were followed to produce the standard solutions (concentrations of 1, 5, 10, 20, 30, 40 and 50 ppm) and the samples at 30 ppm. Each sample was prepared in triplicate and stored at temperatures of 0, 40 and 60°C. Another difference with the aqueous ageing investigation was that the samples in organic matter were not stored at 80°C, due to either close or above the boiling point of the solvent. A 2 ml volume of sample was analysed using HPLC in order to separate the furan species, and by using the peak area obtained from the chromatograph, the furan concentration at that point in the aging process was calculated. For the HPLC instrument the same conditions applied as in Section 3.2.3.

4.3 Results & Discussion

The experiments performed in this section illustrate how the ageing of furanic compounds is well correlated with the stability that each individual furan shows against specific parameters such as pH, temperature and under the influence of different solvents.

Three different solvents were used; water, Acetonitrile and Methanol and the choice of those specific solvents arise from the fact that those materials are used from the existing method of either as solvent extractors of furans (the water) or as mobile phase during the separation and the detection of those compounds using HPLC. The choice of the pH was a general observation of the behaviour of furan in acidic (pH 4.6), neutral (pH 6.8) and basic (pH 10) environment. More precisely, the main reason was to establish if the mineral insulating oil is under those conditions how it can affect the stability and the detection of furans. Finally, the different temperatures were chosen simply by the different temperatures that a transformer can operate (normally between 50 to 70°C) or according to the physical properties of the physical properties of the solvent used for the investigation.

Initially the furanic compounds were examined individually in aqueous environment under the different pH and temperatures described.

4.3.1 Ageing results in aqueous environment

Below are the results of the ageing experiment, when the furans, diluted in water, were introduced into a specific and controlled environment, analysed over a period of time using either UV-Vis spectroscopy or HPLC. Further below are the graphs from the calibration of the standards but also the graphs from the results obtained for each furan for the purposes of calculating the losses.

Table 5 Results from the calibration of the five furanic compounds under HPLC analysis

CONC OF FURANIC COMPOUNDS	CALIBRATION OF 5-HMF			CALIBRATION OF 2-FAL			CALIBRATION OF 2-ACF			CALIBRATION OF 5-MEF			CALIBRATION OF FOL		
	ABS	ABS OF H2O	CORRECTED ABS	ABS	ABS OF H2O	CORRECTED ABS	ABS	ABS OF H2O	CORRECTED ABS	ABS	ABS OF H2O	CORRECTED ABS	ABS	ABS OF H2O	CORRECTED ABS
0			0			0			0			0			0
5	0.638	0.0684	0.5696	0.769	0.1243	0.6447	0.473	0.046	0.4272	0.5002	0.0991	0.4011	0.494	0.16	0.334
10	1.288	0.0684	1.2196	1.408	0.1243	1.2837	0.923	0.046	0.8772	0.9184	0.0991	0.8193	0.828	0.16	0.668
20	2.162	0.0684	2.0936	2.533	0.1243	2.4087	1.768	0.046	1.7222	1.7066	0.0991	1.6075	1.422	0.16	1.262
30	2.972	0.0684	2.9036	3.261	0.1243	3.1367	2.518	0.046	2.4722	2.4509	0.0991	2.3518	1.787	0.16	1.627
40	3.312	0.0684	3.2436	3.354	0.1243	3.2297	2.966	0.046	2.9202	3.0531	0.0991	2.954	2.179	0.16	2.019
50	3.326	0.0684	3.2576	3.495	0.1243	3.3707	3.205	0.046	3.1592	3.286	0.0991	3.1869	2.261	0.16	2.101

STANDARD GRAPH OF 5-HMF

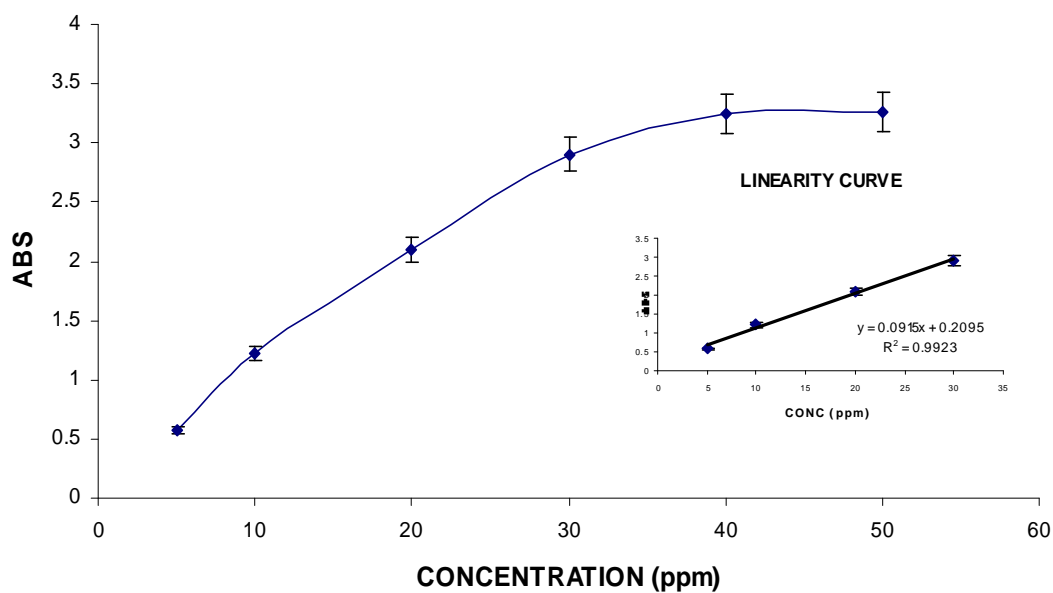


Fig 14 (a) Standard graph of 5-HMF of different concentration solutions in aqueous solution measured by HPLC.

STANDARD GRAPH OF 2-FAL

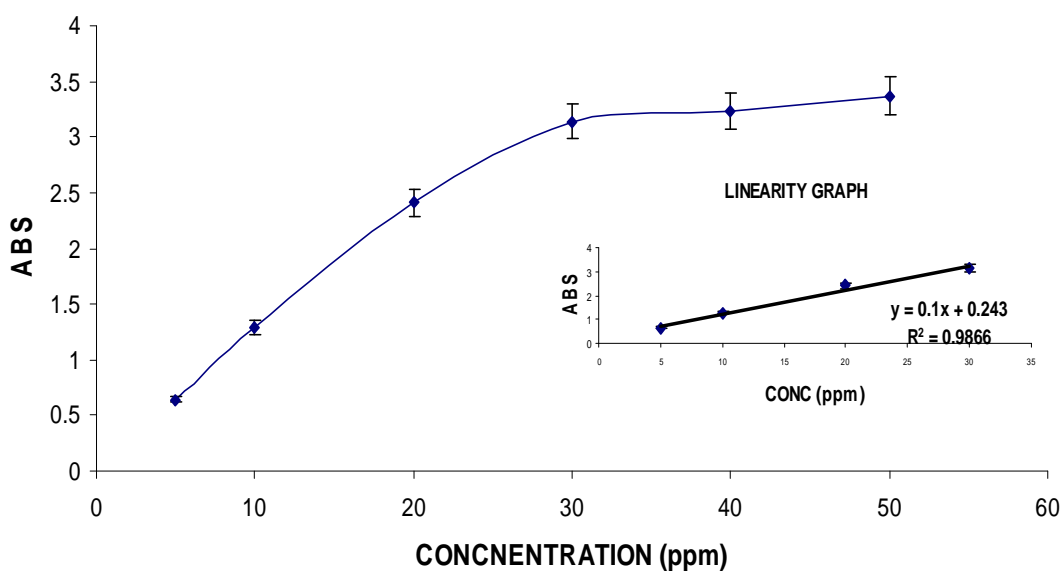


Fig 14 (b) Standard graph of 2-FAL of different concentration solutions in aqueous solution measured by HPLC.

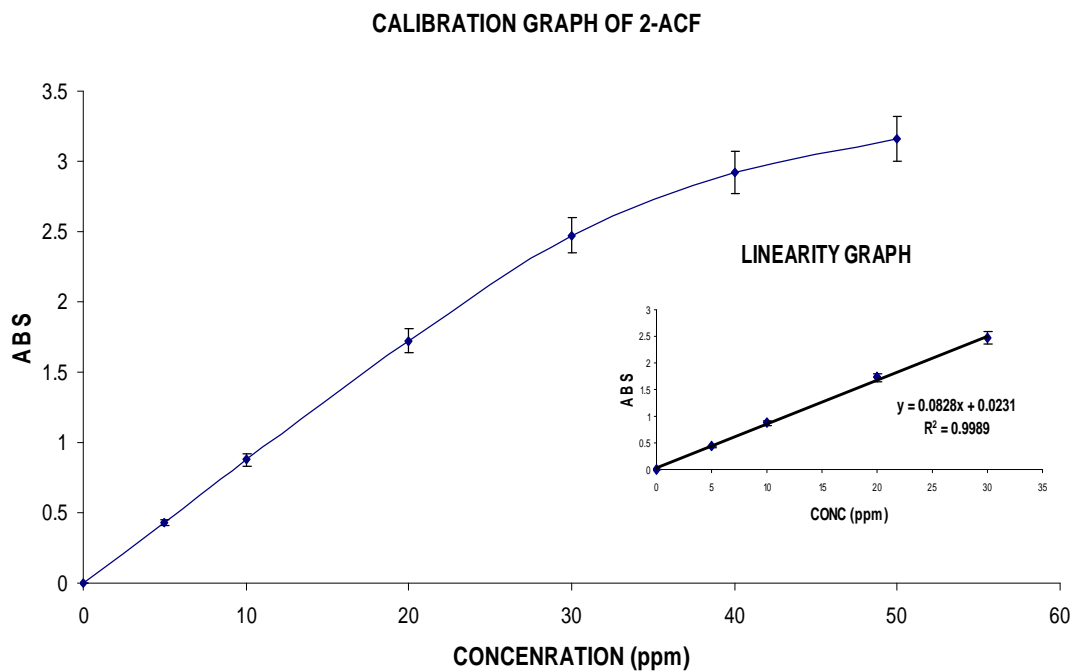


Fig 14 (c) Standard graph of 2-ACF of different concentration solutions in aqueous solution measured by HPLC.

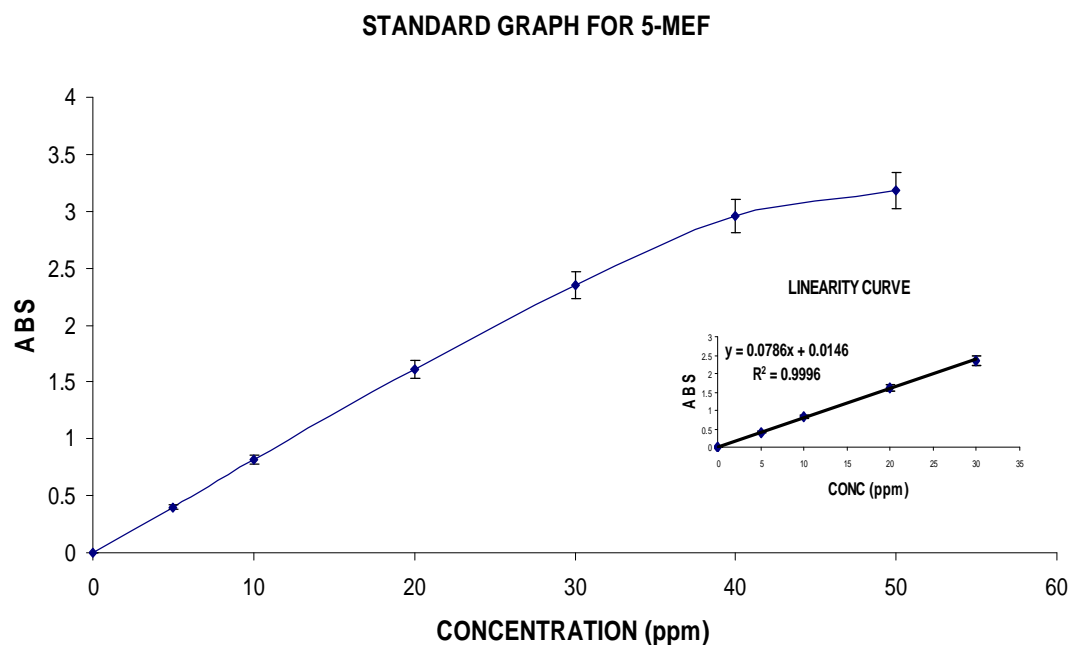


Fig 14 (d) Standard graph of 5-MEF of different concentration solutions in aqueous solution measured by HPLC.

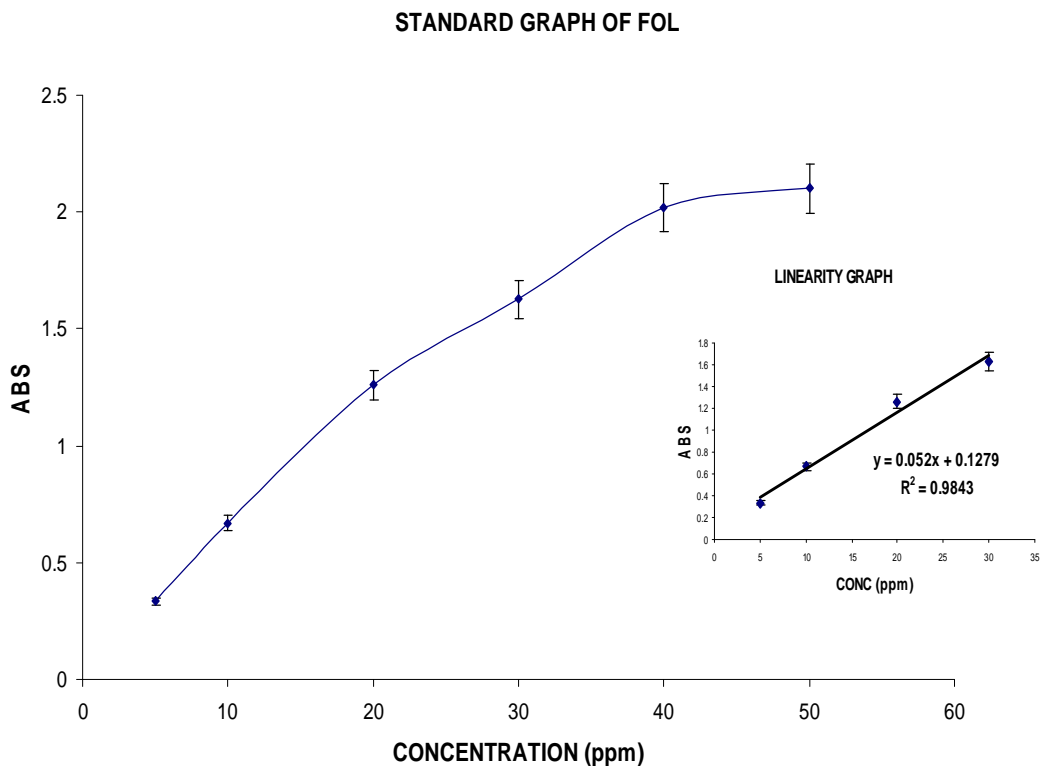


Fig 14 (e) Standard graph of FOL of different concentration solutions in aqueous solution measured by HPLC.

Figure 14 Calibration graphs of the five furanic compounds in water using UV-Vis spectroscopy; (a) 5-HMF, (b) 2-FAL, (c) 2-ACF, (d) 5-MEF and (e) FOL.

The previous graphs show the calibration graphs for the five furanic compounds. Below is a graphical representation of the ageing experiment for 5-HMF under the different conditions applied and analysed for a period of 63 days. For a detailed presentation of all the results obtained throughout that experiment see appendix B.

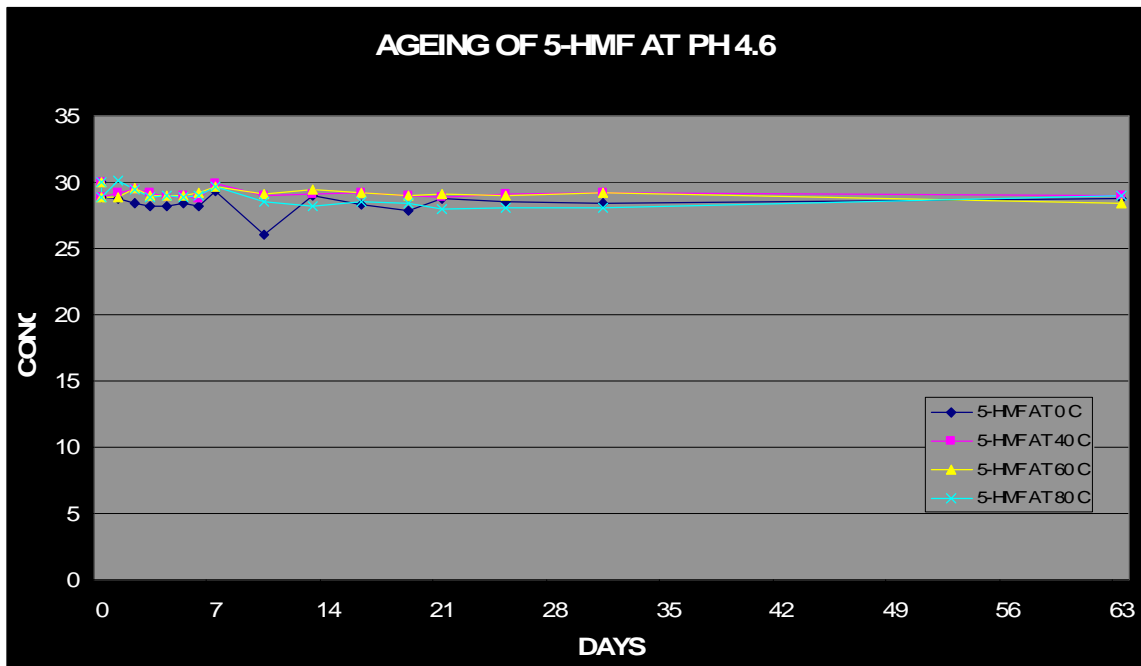


Fig15 (a) Ageing illustration of 5-HMF under different temperatures at a specific pH.

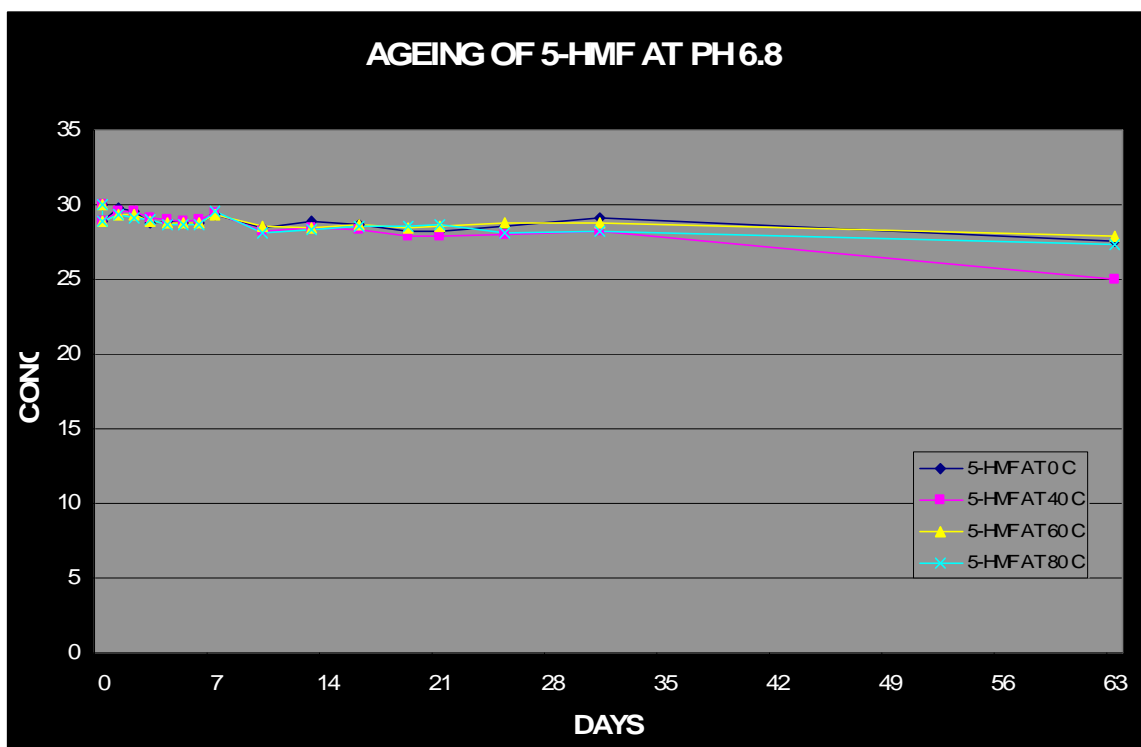


Fig 15 (b) Ageing illustration of 5-HMF under different temperatures at a specific pH

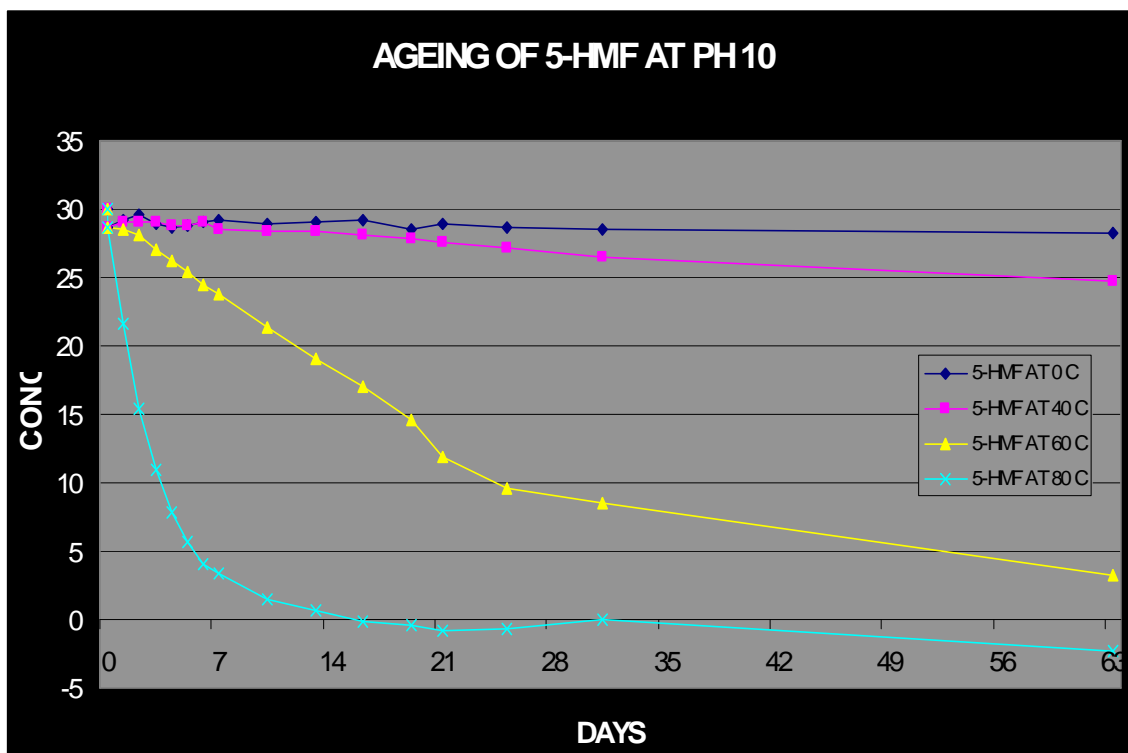


Fig 15 (c) Ageing illustration of 5-HMF under different temperatures at a specific pH

Figure 15 Ageing of 5-HMF at different pH under different temperatures.

Figure 15 illustrates the ageing examination of 5-HMF over 63 days and it can be observed that at pH values of 4.6 and 6.8 that the compounds are stable at all temperatures. Only in the case of pH 10 and at temperatures 60°C and 80°C the compound shows signs of degradation. At 80°C the degradation is immediate and much steeper than the ageing at 60°C, which has a much smoother decrease. It is important to mention that the literature recommends that 5-HMF is the least stable compound since its degradation, when the compound oxidised, produces other furan derivatives, but according to the graphs provided in this investigation shows that 5-HMF is fairly stable under those conditions(at least for pH 4.6 and 6.8).

Below is a graphical representation of the ageing experiment for 2-FAL under the different conditions applied and analysed for a period of 63 days.

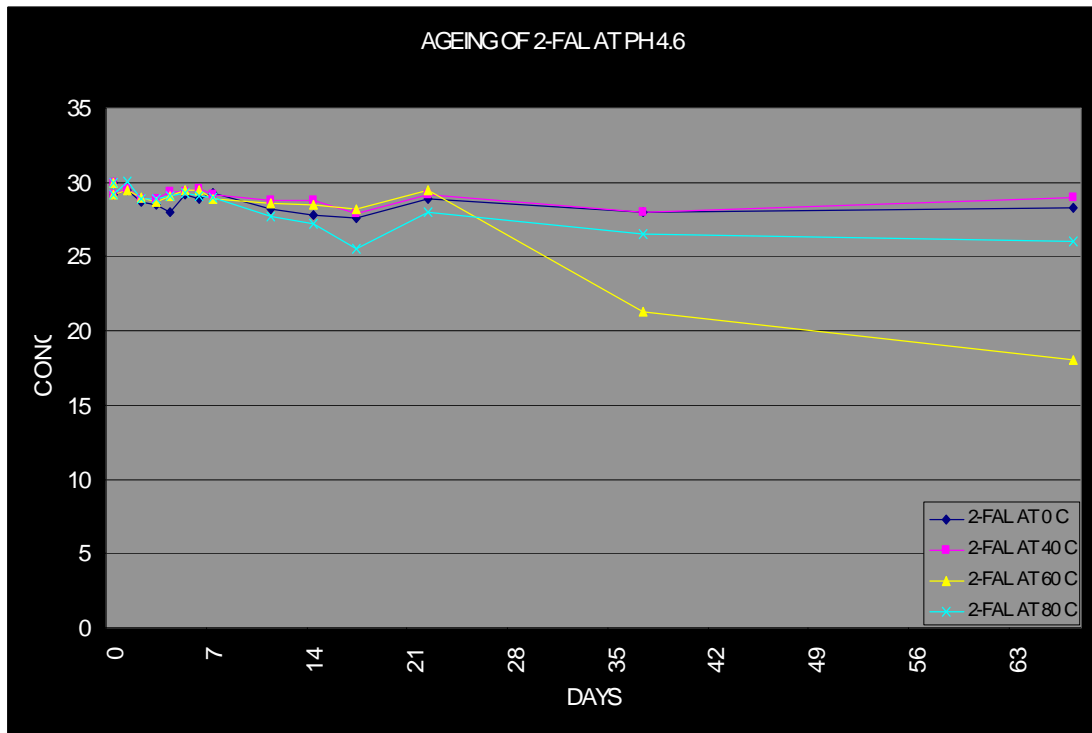


Fig 16 (a) Ageing illustration of 2-FAL under different temperatures at a specific pH

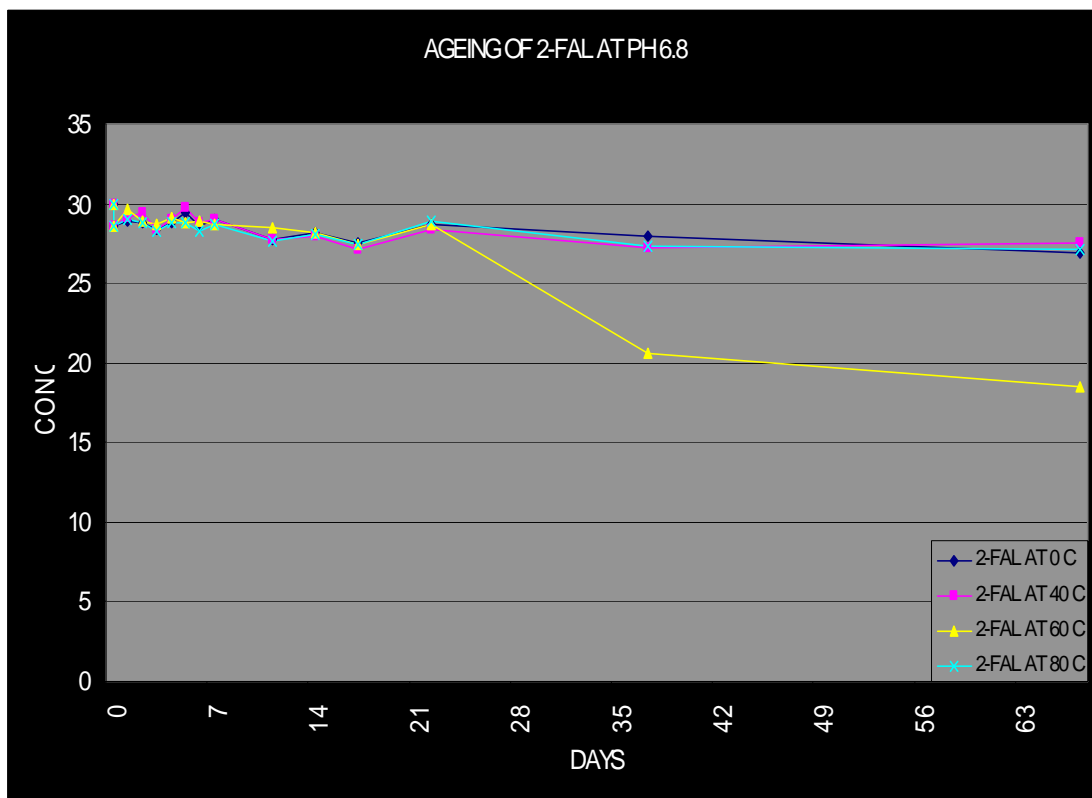


Fig 16 (b) Ageing illustration of 2-FAL under different temperatures at a specific pH

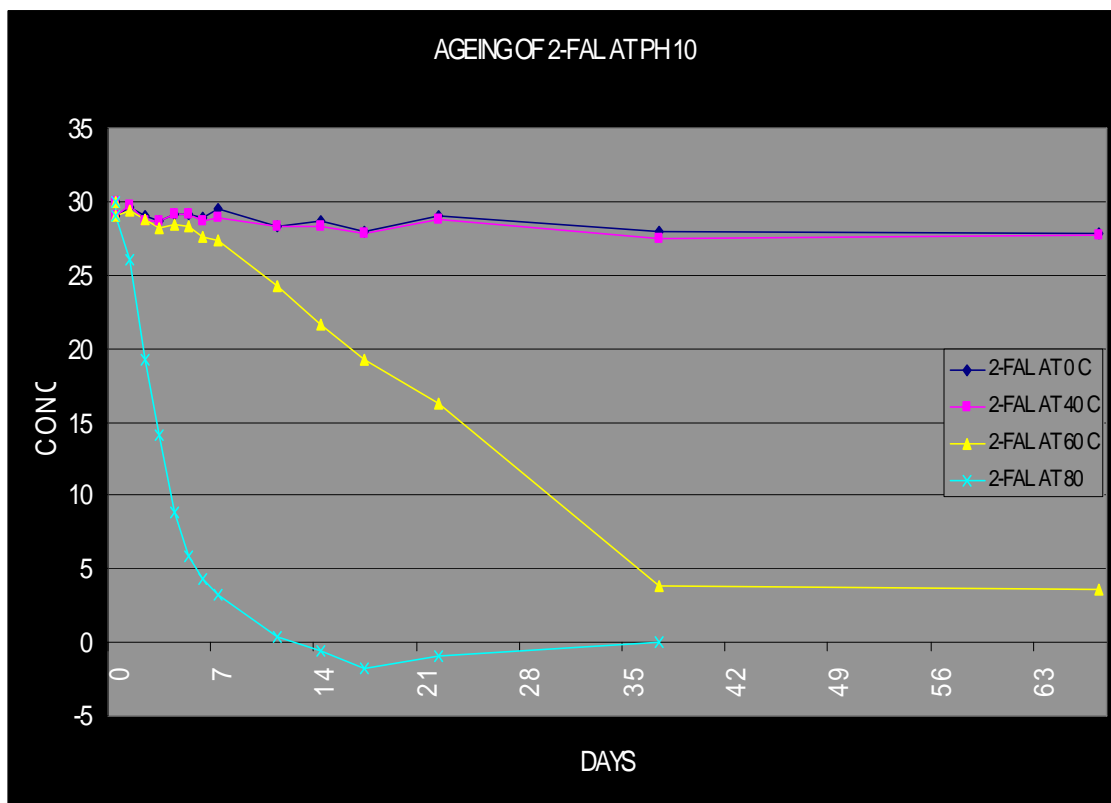


Fig 16 (c) Ageing illustration of 2-FAL under different temperatures at a specific pH

Figure 16 Ageing of 2-FAL at different pH under different temperatures

2-FAL in Figure 16 shows a different behaviour than the other furan derivatives. At pH 4.6 and only at 60°C shows ageing after 21 days. The same profile follows at pH 6.8, but at pH 10 the degradation is much more obvious, especially at 60 and 80°C. After 10 days 2-FAL under that condition was not observed.

Below is a graphical representation of the ageing experiment for 2-ACF under the different conditions applied and analysed for a period of 63 days.

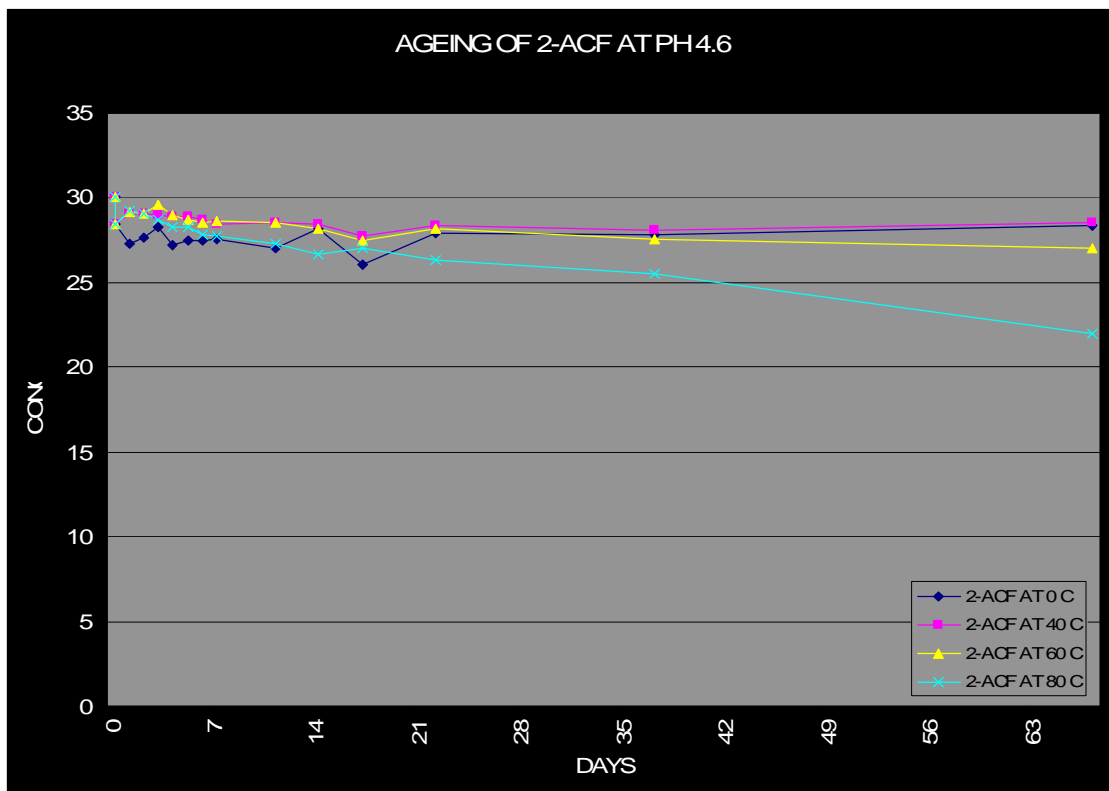


Fig 17 (a) Ageing illustration of 2-ACF under different temperatures at a specific pH

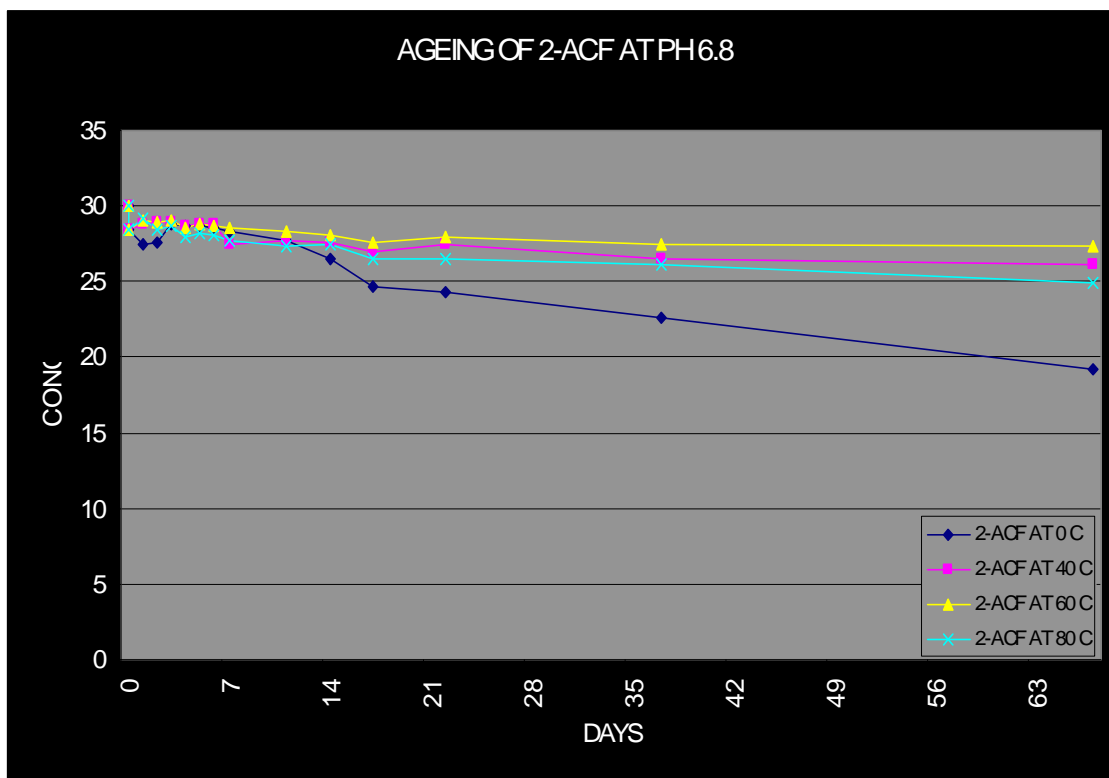


Fig 17 (b) Ageing illustration of 2-ACF under different temperatures at a specific pH

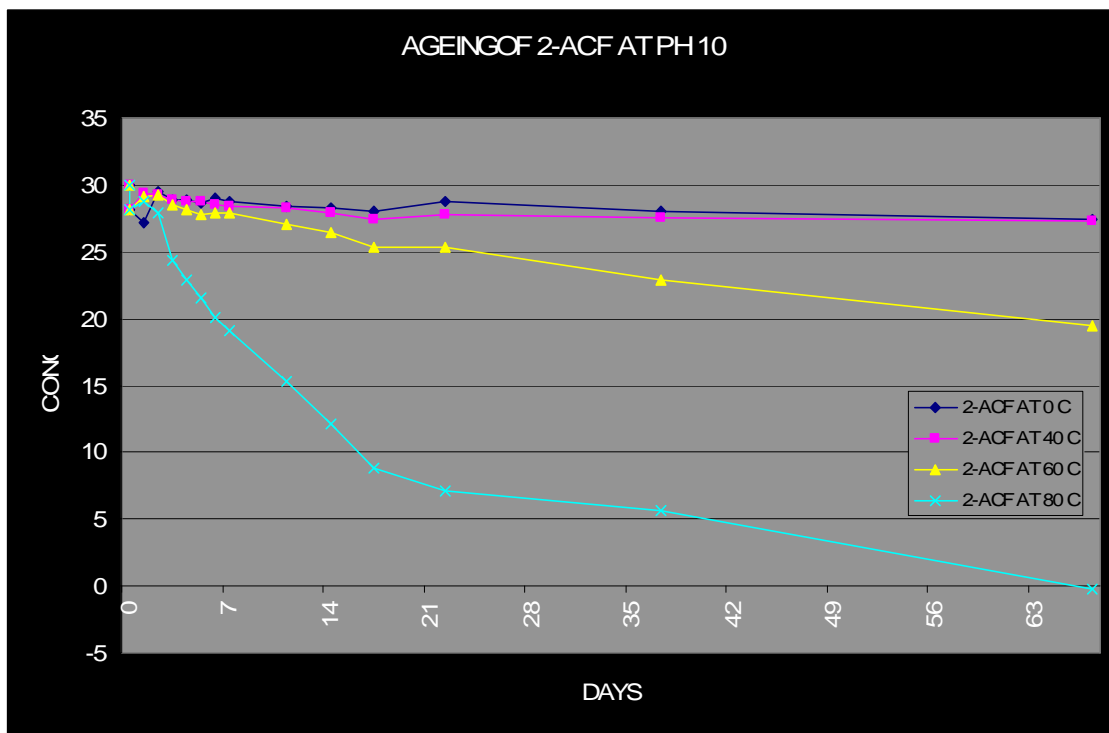


Fig 17 (c) Ageing illustration of 2-ACF under different temperatures at a specific pH
Figure 17 Ageing of 2-ACF at different pH under different temperatures.

2-ACF (Fig 17) behaves differently at the three pH values studied. Initially, there is a small degradation at pH 4.6 and at 80°C, but that profile changes at pH 6.8 when the solution stored at 0°C shows the only sign of degradation. In the case of pH 10, once again 2-ACF follows the same pattern as 5-HMF and 2-FAL, with the only difference that this compound needs 63 days to aged and not be detectable.

Below is a graphical representation of the ageing experiment for 5-MEF under the different conditions applied and analysed for a period of 63 days.

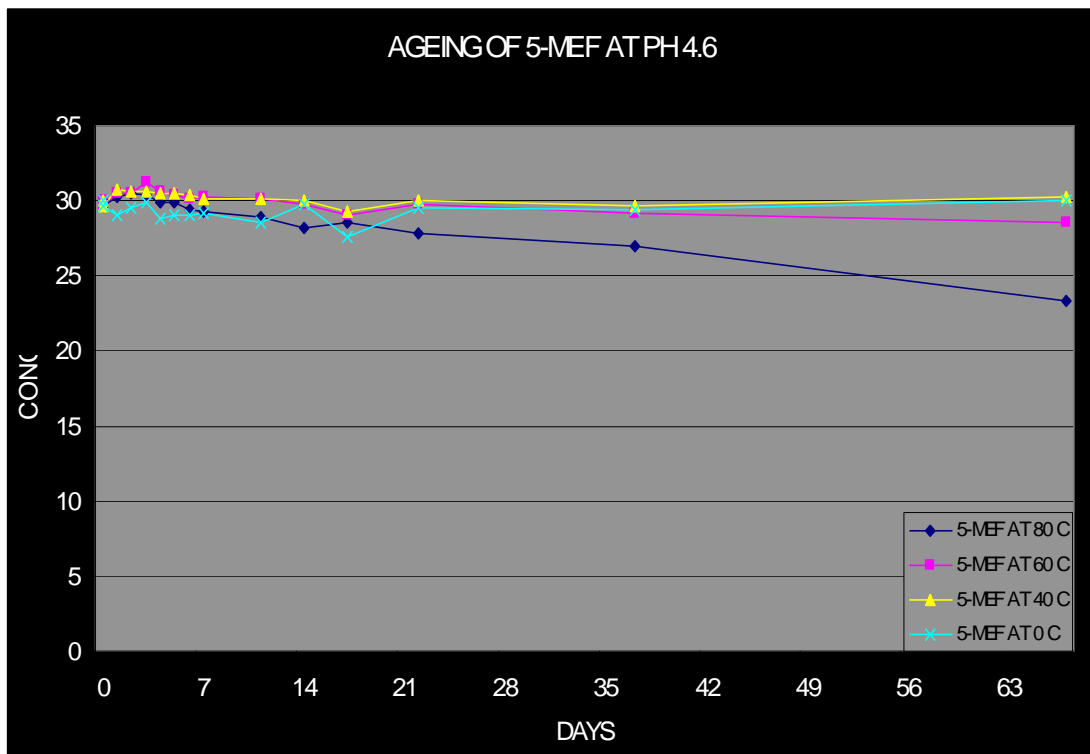


Fig 18 (a) Ageing illustration of 5-MEF under different temperatures at a specific pH

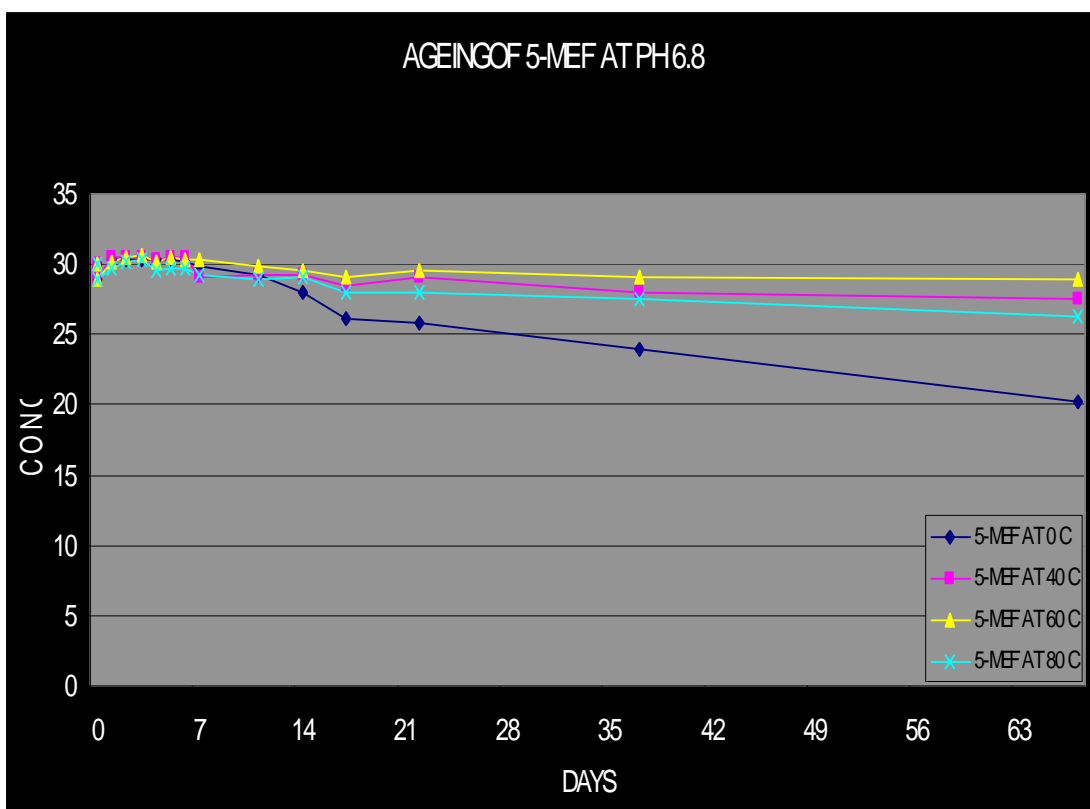


Fig 18 (b) Ageing illustration of 5-MEF under different temperatures at a specific pH

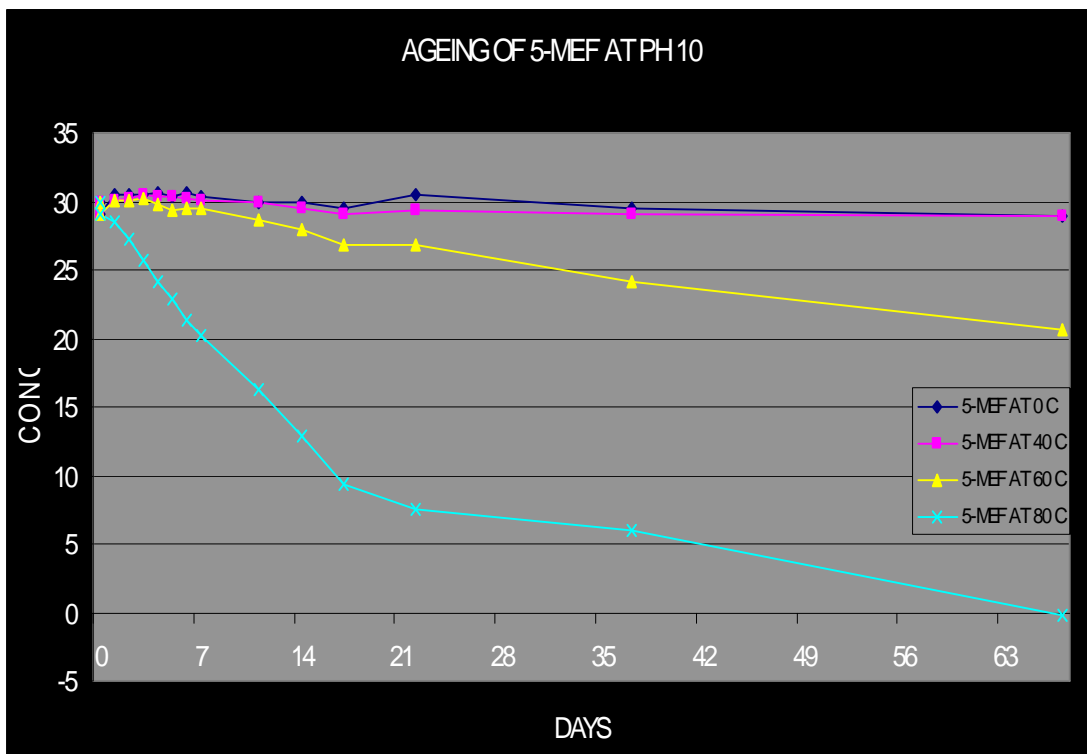


Fig 18 (c) Ageing illustration of 5-MEF under different temperatures at a specific pH
Figure 18 Ageing of 5-MEF at different pH under different temperatures.

When 5-MEF (Fig 18) was examined, the results showed that this furan follows the same path of degradation as the furan 2-ACF, but only in the cases with pH 6.8 and pH 10. When the furan was studied at pH 4.6 and at 0°C, only then, there were significant signs of degradation of about 6 ppm over the period of 63 days.

Below is a graphical representation of the ageing experiment for FOL under the different conditions applied and analysed for a period of 63 days.

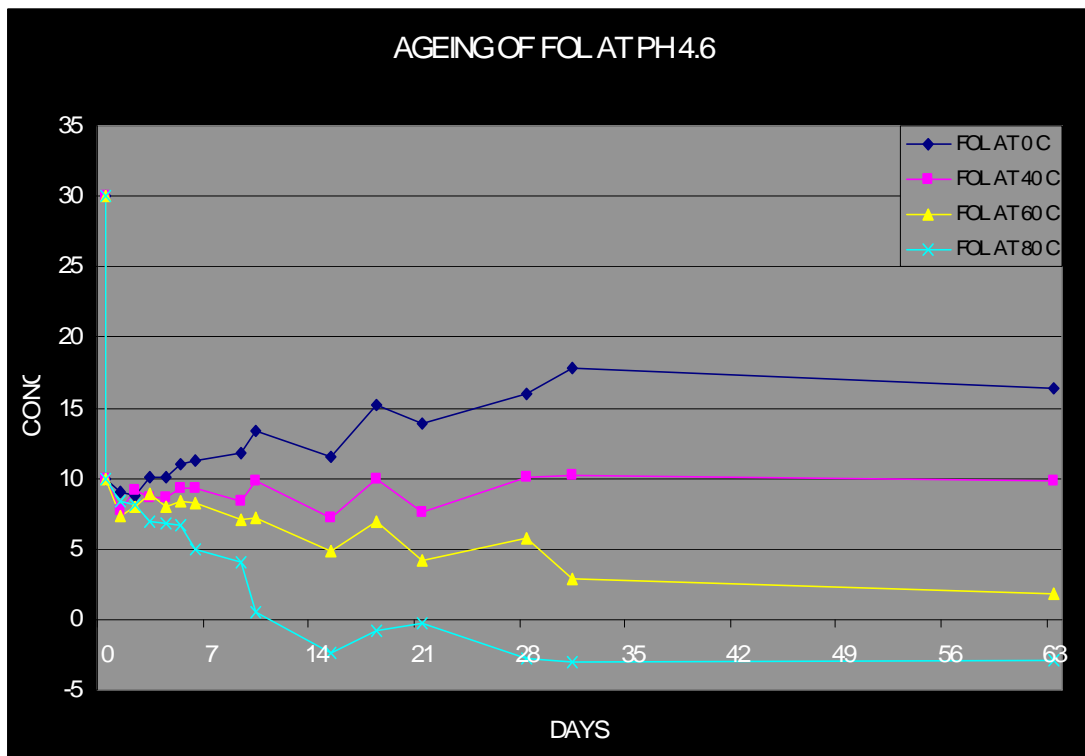


Fig 19 (a) Ageing illustration of FOL under different temperatures at a specific pH

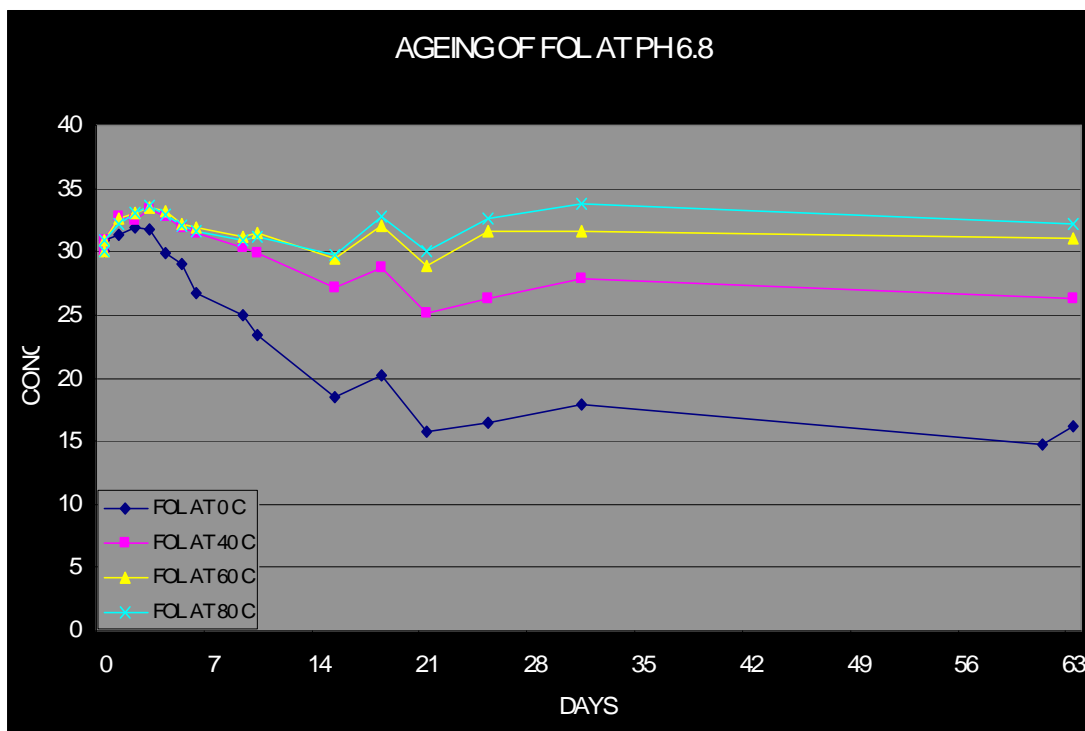


Fig 19 (b) Ageing illustration of FOL under different temperatures at a specific pH

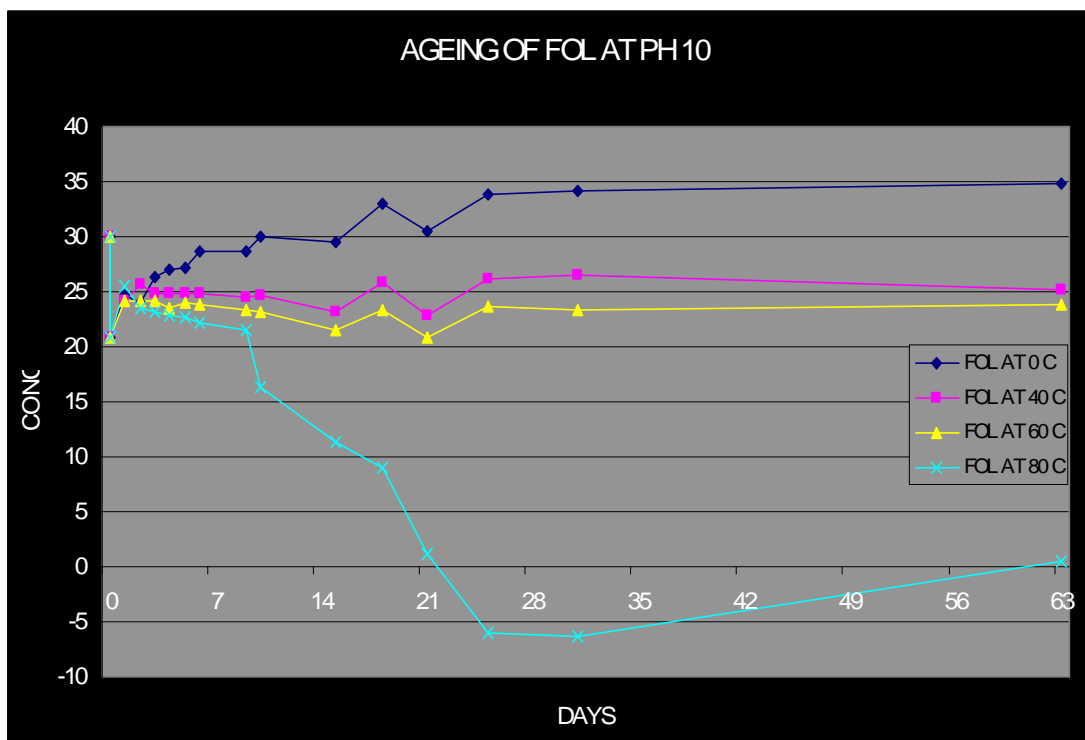


Fig 19 (c) Ageing illustration of FOL under different temperatures at a specific pH

Figure 19 Ageing of FOL at different pH under different temperatures.

Figure 19 shows the examination of FOL for 63 days at the three different pH and four different temperatures examined. It was noticed that FOL at pH 4.6 and at all temperatures there was an instant loss of the compound, approximately by 20 ppm. The instant loss was noticed as soon as the furanic compound was dissolved in that particular buffer. At 0°C there was a small increase of concentration over the period of analysis, at 40°C the compound remain stable, at 60°C a gradual decrease and finally, at 80°C FOL was not detected after a period of 12 days. The initial and instant decrease of the compound at pH 4.6 was a rapid reaction of the compound with the buffer. It was noticed that if the pH of the solution was altered and changed from 4.6 to 6.8 after the initial measurement, the second reading will be the same as for the initial reading of the solution prepared at buffer with pH 6.8. That means that FOL under acidic environment shows sign of tautomerism between Keto-enol formations.

In other words FOL changes formation which is not able to be detected at that specific wavelength. There is a possibility that at 0°C the solution is trying to revert back to its original keto structure and that is why that only a small increase of concentration was observed. When FOL examined at pH 6.8 that instant loss of

concentration was detected, but at 0°C there were signs of ageing. By looking at the two graphs (Fig 19 a, b) it can be noticed that after 63 days of analysis the concentration of FOL at 0°C is the same in both cases. Finally, in the case of FOL with buffer at pH 10 that spontaneous decrease of concentration also occurred, but with less effect, and the ageing of the compound follows the same pattern as with the other furan derivatives.

In that section it was showed the investigation of each individual furanic compound in aqueous environment under different conditions. The graphical representation shows how those conditions affect the concentration of the furanic compounds over a period of 63 days.

4.3.2 Ageing results of the furanic compounds in acetonitrile and methanol

The ageing process of the furan derivatives where also examined in an organic environment. In that case the only difference to the previous study was the solvent without altering the pH of the solutions. The study took place under three different temperatures due to limitations of the solvents to high temperatures.

In this section are the results from the ageing experiment when the furanic derivatives were dissolved in acetonitrile and methanol and analysed by HPLC. Below are the results from the calibration with the graphs, which was used to retrieve the values of the ageing of the furanic compounds. The results and the illustration of the graphs are further below.

Table 6 Results of a series of different solutions used for the calibration of the furan derivatives by HPLC.

CALIBRATION OF FURANS DISSOLVED IN ACETONITRILE USING HPLC						
CONCENTRATION	PEAK AREA					

	5-HMF	2-FAL	2-ACF	5-MEF	FOL	
0	0	0	0	0	0	
1	30.1099	50.6088	40.6921	32.4741	25.4428	
5	168.435	232.8	189.7	157	125.677	
10	354.362	471.895	385.739	319.475	256.071	
20	798.52	1030.52	845.1	699.82	560.5	
30	1250	1598	1315	1189	1115	
40	1907.74	2412.79	1997.72	1665.16	1364.4	
50	2423.02	3120.92	2562.5	2137.32	1743.45	

CALIBRATION OF FURANS DISSOLVED IN METHANOL USING HPLC						
CONCENTRATION	PEAK AREA					
	5-HMF	2-FAL	2-ACF	5-MEF	FOL	
0	0	0	0	0	0	
1	45.5923	58.6989	47.337	38.4255	31.3075	
5	229.553	289.369	232.928	195.299	157.356	
10	420.886	529.909	428.212	364.212	290.262	
20	910.426	1156.95	933.325	792.036	637.494	
30	1193.6	1494.09	1212.51	1027.14	827.166	
40	1493	1799.89	1463.7	1237.73	997.137	
50	1956.82	2455.1	1997.71	1691.44	1361.86	

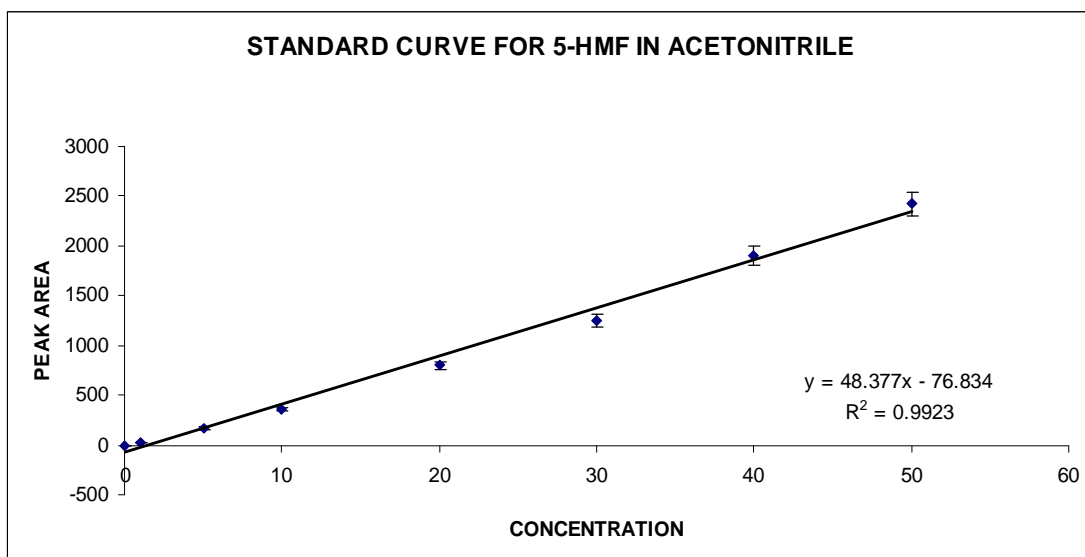


Fig 20 (a) Standard graph of 5-HMF of different concentration solutions in acetonitrile measured by HPLC

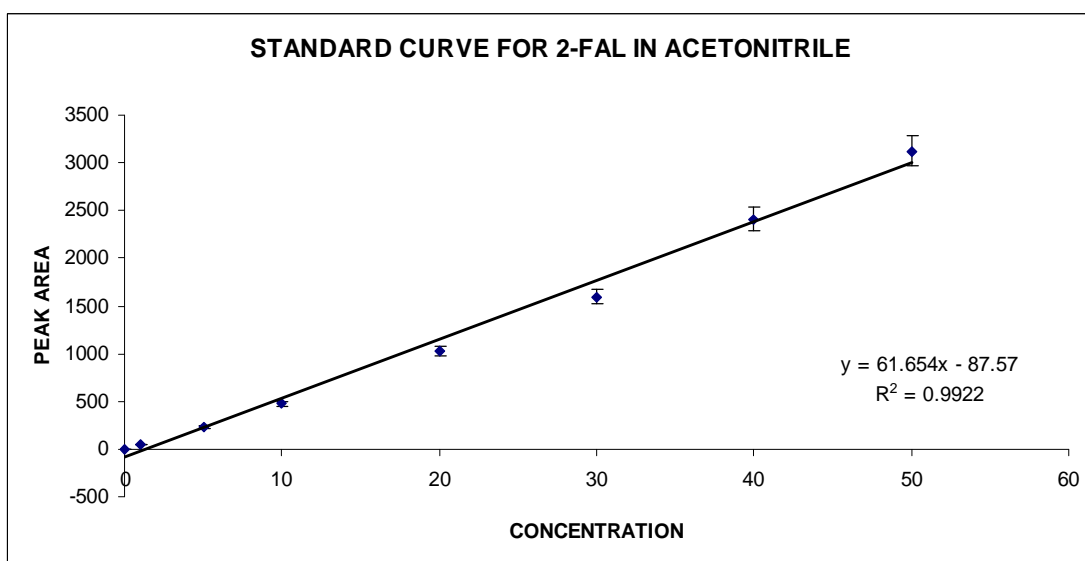


Fig 20 (b) Standard graph of 2-FAL of different concentration solutions in acetonitrile measured by HPLC

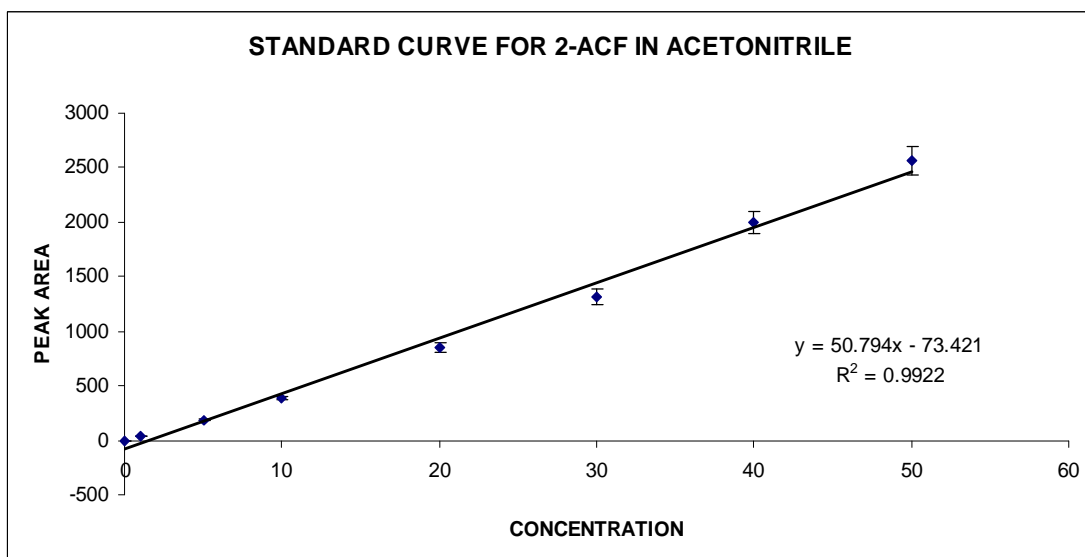


Fig 20 (c) Standard graph of 2-ACF of different concentration solutions in acetonitrile measured by HPLC

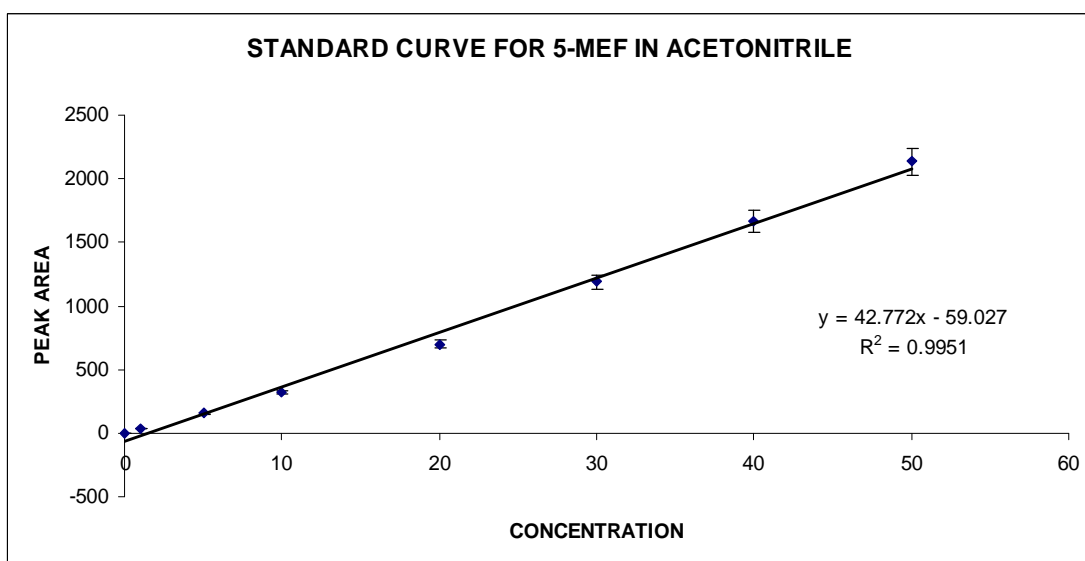


Fig 20 (d) Standard graph of 5-MEF of different concentration solutions in acetonitrile measured by HPLC

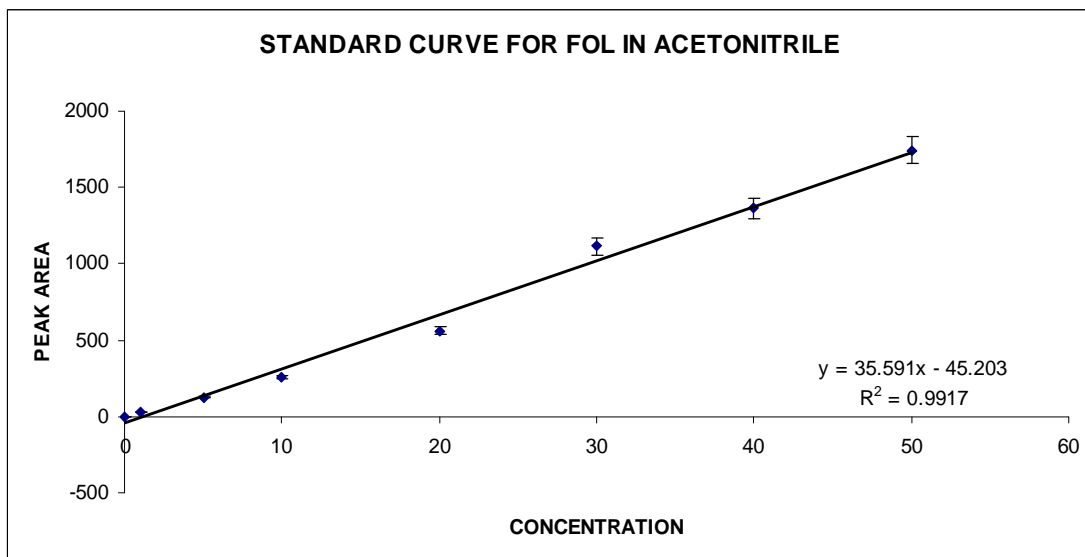


Fig 20 (e) Standard graph of FOL of different concentration solutions in acetonitrile measured by HPLC

Figure 20 Calibration graphs in Acetonitrile of (a) 5-HMF, (b) 2-FAL, (c) 2-ACF, (d) 5-MEF and (e) FOL.

Below are the calibrations graphs of the five furanic compounds from a series of different concentrations in methanol solution.

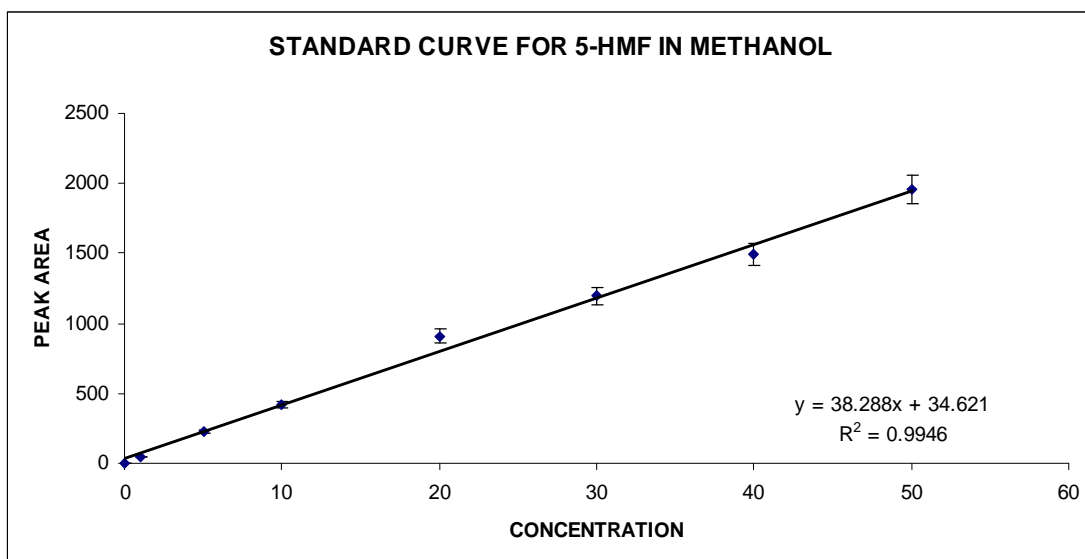


Fig 21 (a) Standard graph of 5-HMF of different concentration solutions in methanol measured by HPLC

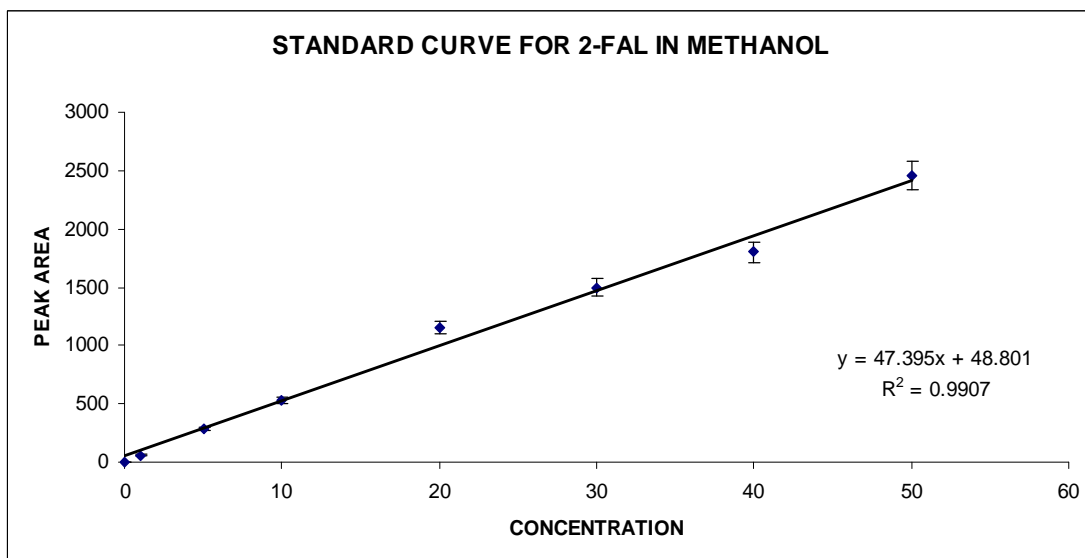


Fig 21 (b) Standard graph of 2-FAL of different concentration solutions in methanol measured by HPLC

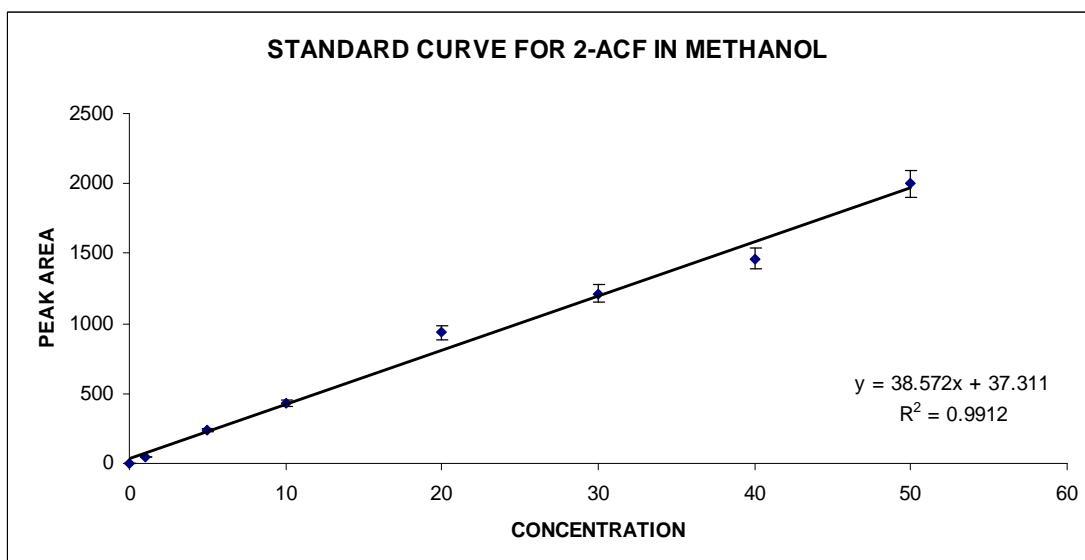


Fig 21 (c) Standard graph of 2-ACF of different concentration solutions in methanol measured by HPLC

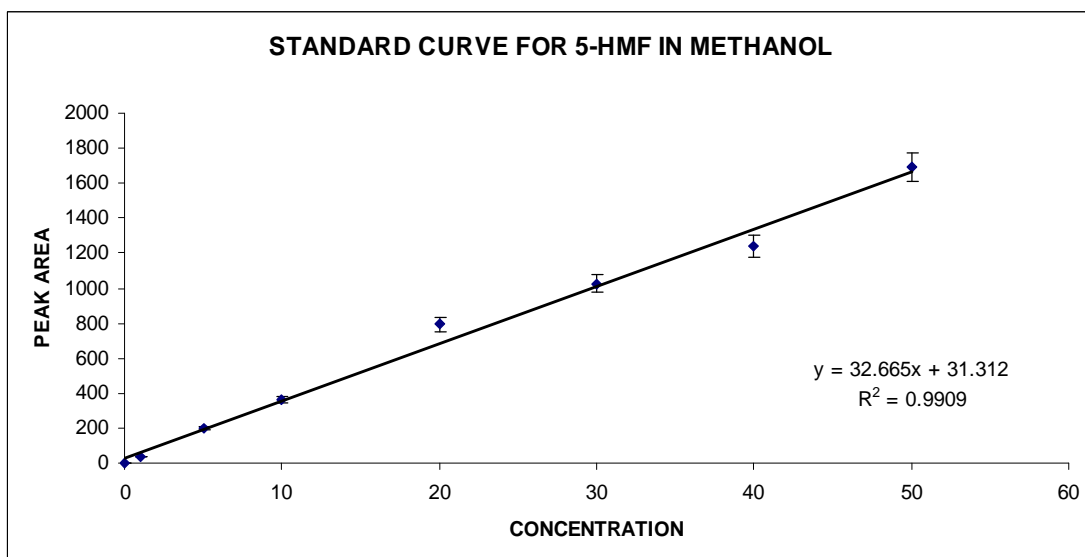


Fig 21 (d) Standard graph of 5-MEF of different concentration solutions in methanol measured by HPLC

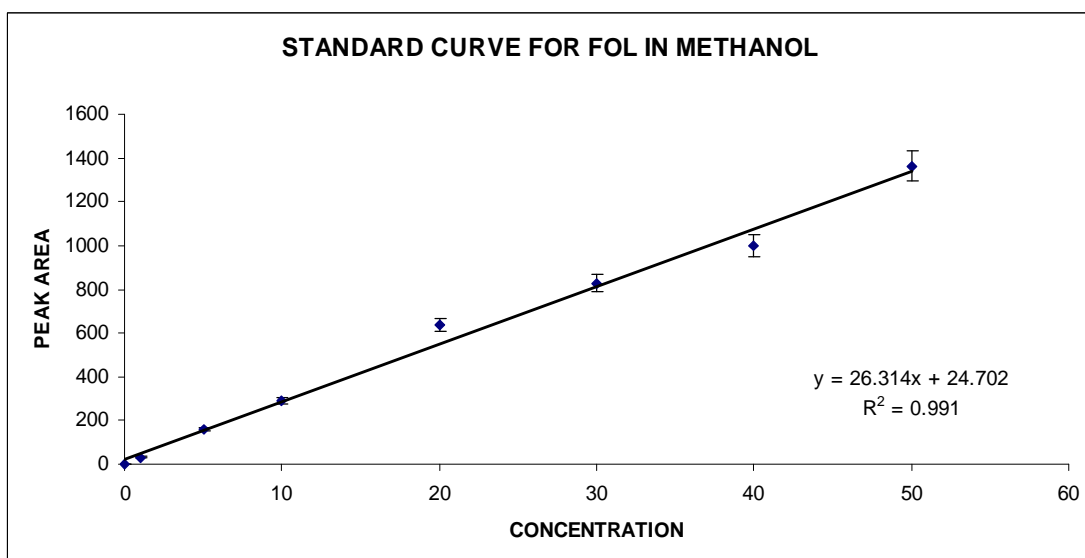


Fig 21 (e) Standard graph of FOL of different concentration solutions in methanol measured by HPLC

Figure 21 Calibration graphs in Methanol of (a) 5-HMF, (b) 2-FAL, (c) 2-ACF, (d) 5-MEF and (e) FOL.

The table below shows the ageing results of 5-HMF in acetonitrile and methanol solution measured for a period of 31 days of monitoring by HPLC.

Table 7 Results for the ageing of 5-HMF in Acetonitrile and Methanol.

5-HMF IN ACETONITRILE STORED AT 0 C			5-HMF IN ACETONITRILE STORED AT 40 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION (ppm)	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION (ppm)
1.00	1167.00	25.71	1.00	1203.00	26.46
3.00	929.10	20.79	3.00	1252.60	27.48
4.00	1154.00	25.44	4.00	1186.00	26.10
5.00	1173.00	25.84	5.00	1248.00	27.39
6.00	1402.00	30.57	6.00	1482.00	32.22
7.00	1178.00	25.94	7.00	1394.00	30.40
12.00	993.60	22.13	12.00	947.80	21.18
24.00	554.40	13.05	24.00	593.40	13.85
31.00	521.30	12.36	31.00	574.20	13.46
5-HMF IN ACETONITRILE STORED AT 60 C			5-HMF IN METHANOL STORED AT 0 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION (ppm)	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION (ppm)
1.00	1252.00	27.47	1.00	1537.92	39.26
3.00	1489.00	32.37	3.00	1536.00	39.21
4.00	1186.00	26.10	4.00	1343.40	34.18
5.00	1234.00	27.10	5.00	1385.00	35.27
6.00	1206.00	26.52	6.00	1359.30	34.60
7.00	1161.00	25.59	7.00	1378.00	35.09
12.00	1191.00	26.21	12.00	1337.00	34.02
24.00	482.80	11.57	24.00	1489.00	37.99
31.00	496.30	11.85	31.00	1354.08	34.46
5-HMF IN METHANOL STORED AT 40 C			5-HMF IN METHANOL STORED AT 60 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1236.00	31.38	1.00	1228.00	31.17
3.00	1308.00	33.26	3.00	1385.00	35.27
4.00	1402.30	35.72	4.00	1376.30	35.04
5.00	1336.70	34.01	5.00	1030.30	26.00
6.00	986.64	24.86	6.00	1029.75	25.99
7.00	1171.20	29.68	7.00	1254.20	31.85
12.00	1310.00	33.31	12.00	1277.70	32.47
24.00	1216.50	30.87	24.00	983.90	24.79
31.00	1129.00	28.58	31.00	1033	26.08

Below is a graphical representation of the results from the ageing experiment for 5-HMF in acetonitrile and methanol solutions and analysed for a period of 31 days.

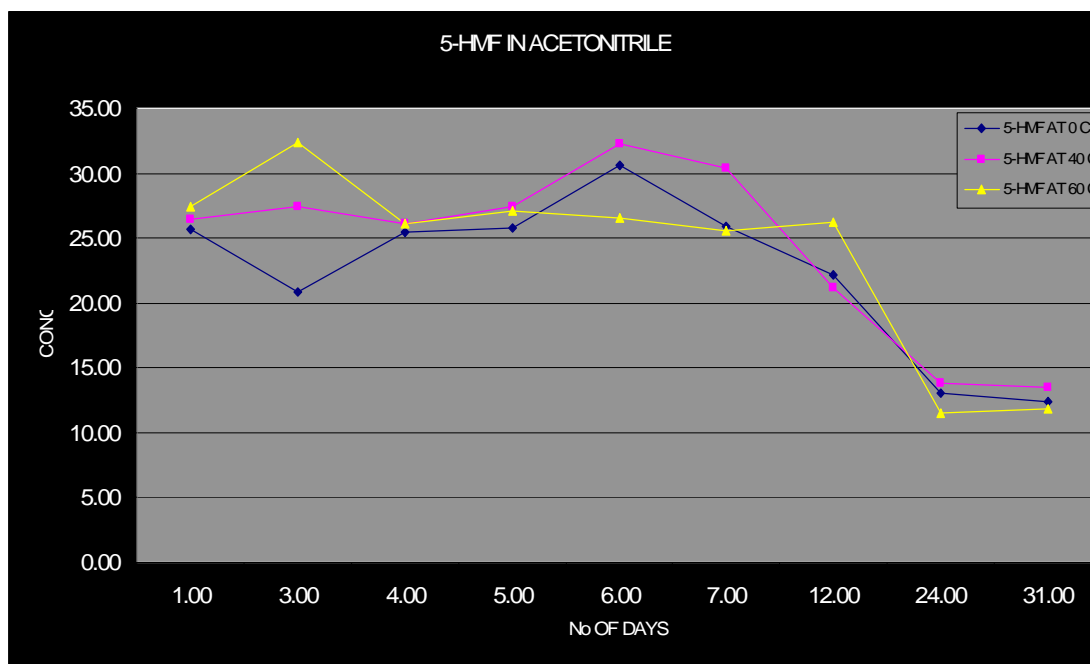


Fig 22 (a) Ageing illustration of 5-HMF in Acetonitrile solution under different temperatures.

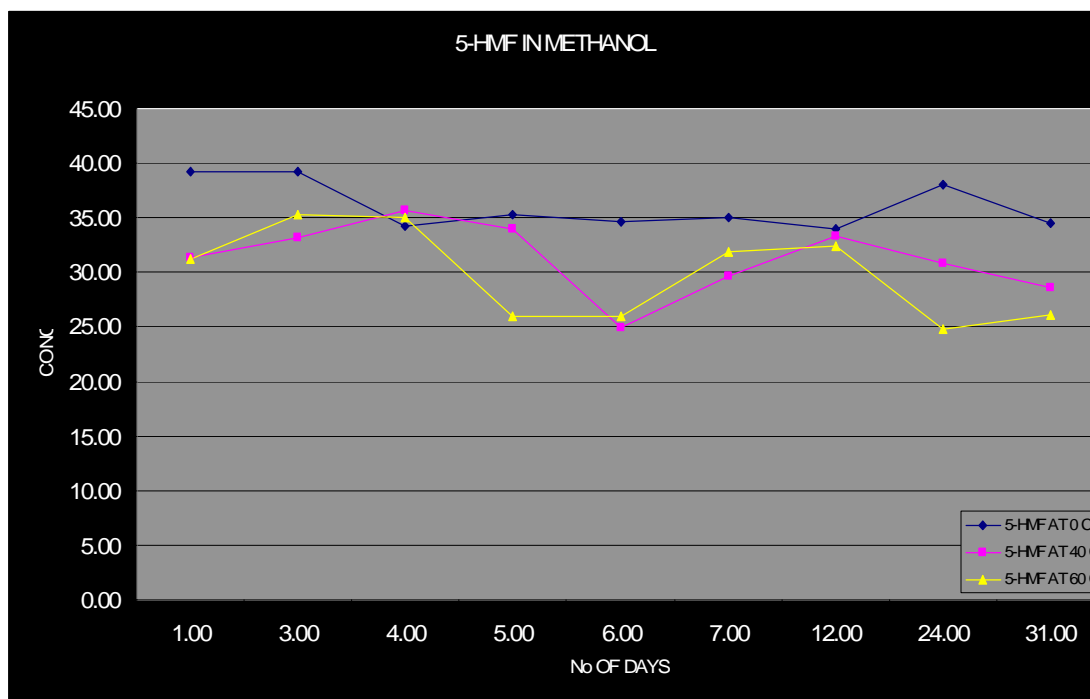


Fig 22 (b) Ageing illustration of 5-HMF in Methanol solution under different temperatures.

Figure 22 Ageing progress of 5-HMF in (a) Acetonitrile and (b) Methanol over time.

Figure 22-26 shows the ageing results and the graphs obtained from that study. Mainly, all the furan derivatives follow the same profile in all temperatures and at both solvents. The only difference is with 5-HMF when treated in acetonitrile where signs of degradation appears in all temperatures after the 12th day.

Overall, the furanic compounds in methanol are less stable compared to acetonitrile, and the results obtained between 40°C and 60°C it can be seen that the ageing at 40°C is a day in delay from the ageing at 60°C. At 0°C the furan derivatives in methanol shows great stability to their initial measurement, whereas in the case of the acetonitrile the most stable results observed at 60°C.

An assumption that can be made in the solutions in acetonitrile is that the degradation of 5-HMF results in the production of the other furan derivatives, and hence is a possible explanation as to the increase of 2-FAL, 2-ACF, 5-MEF and FOL, especially at 40°C. At 0°C temperature, it can be seen that all the furanic compounds at the 12th day they start to degradate but due to the loss of 5-HMF and maybe to the production of other furans, the concentrations of the other furans increase and then stabilize.

The final observation that was made was the increase of the concentration of the solutions made in methanol. Initially all the samples were prepared to have a starting concentration of 30 ppm, but the initial measurements shows an increase to that value and only after the 5th day the concentration decreases to the proposed value. This would suggest that there is a reaction between the furans with the methanol.

The table below shows the ageing results of 2-FAL in acetonitrile and methanol solution measured for a period of 31 days of monitoring by HPLC.

Table 8 Results for the ageing of 2-FAL in Acetonitrile and Methanol.

2-FAL IN ACETONITRILE STORED AT 0 C			2-FAL IN ACETONITRILE STORED AT 40 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1466.00	25.20	1.00	1501.00	25.77
3.00	1179.80	20.56	3.00	1541.00	26.41
4.00	1465.00	25.18	4.00	1233.00	21.42
5.00	1488.00	25.56	5.00	1515.00	25.99
6.00	1785.00	30.37	6.00	1848.00	31.39
7.00	1495.00	25.67	7.00	1739.90	29.64
12.00	1208.00	21.01	12.00	1881.00	31.93
24.00	1521.40	26.10	24.00	1623.40	27.75
31.00	1485.00	25.51	31.00	1494.00	25.65
2-FAL IN ACETONITRILE STORED AT 60 C			2-FAL IN METHANOL STORED AT 0 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1587.00	27.16	1.00	1886.00	38.76
3.00	1809.00	30.76	3.00	1836.20	37.71
4.00	1520.00	26.07	4.00	1513.00	30.89
5.00	1534.00	26.30	5.00	1518.00	31.00
6.00	1498.00	25.72	6.00	1474.40	30.08
7.00	1441.80	24.81	7.00	1616.40	33.08
12.00	1475.00	25.34	12.00	1579.00	32.29
24.00	1491.00	25.60	24.00	1609.00	32.92
31.00	1464.00	25.17	31.00	1647.07	33.72
2-FAL IN METHANOL STORED AT 40 C			2-FAL IN METHANOL STORED AT 60 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1482.25	30.24	1.00	1470.00	29.99
3.00	1836.20	37.71	3.00	1504.70	30.72
4.00	1577.00	32.24	4.00	1454.00	29.65
5.00	1426.00	29.06	5.00	1117.00	22.54
6.00	986.60	19.79	6.00	1211.30	24.53
7.00	1385.00	28.19	7.00	1476.50	30.12
12.00	1519.60	31.03	12.00	1548.80	31.65
24.00	1482.00	30.24	24.00	1195.00	24.18
31.00	1294.70	26.29	31.00	1163.20	23.51

Below is a graphical representation of the results from the ageing experiment for 2-FAL in acetonitrile and methanol solutions and analysed for a period of 31 days.

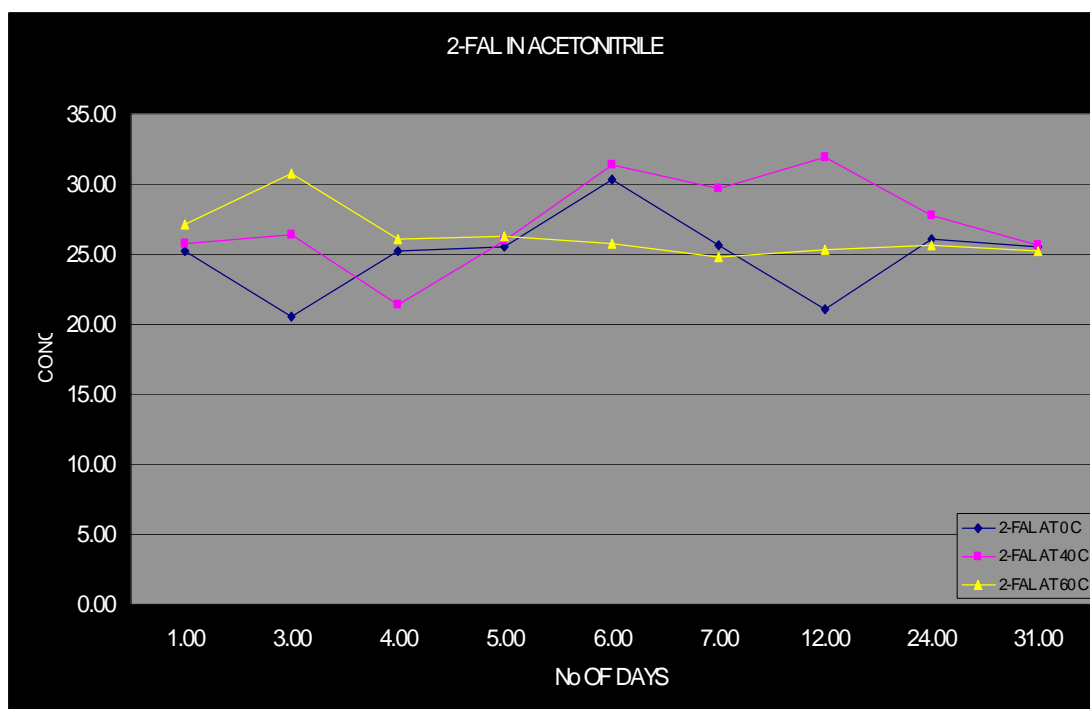


Fig 23 (a) Ageing illustration of 2-FAL in Acetonitrile solution under different temperatures.

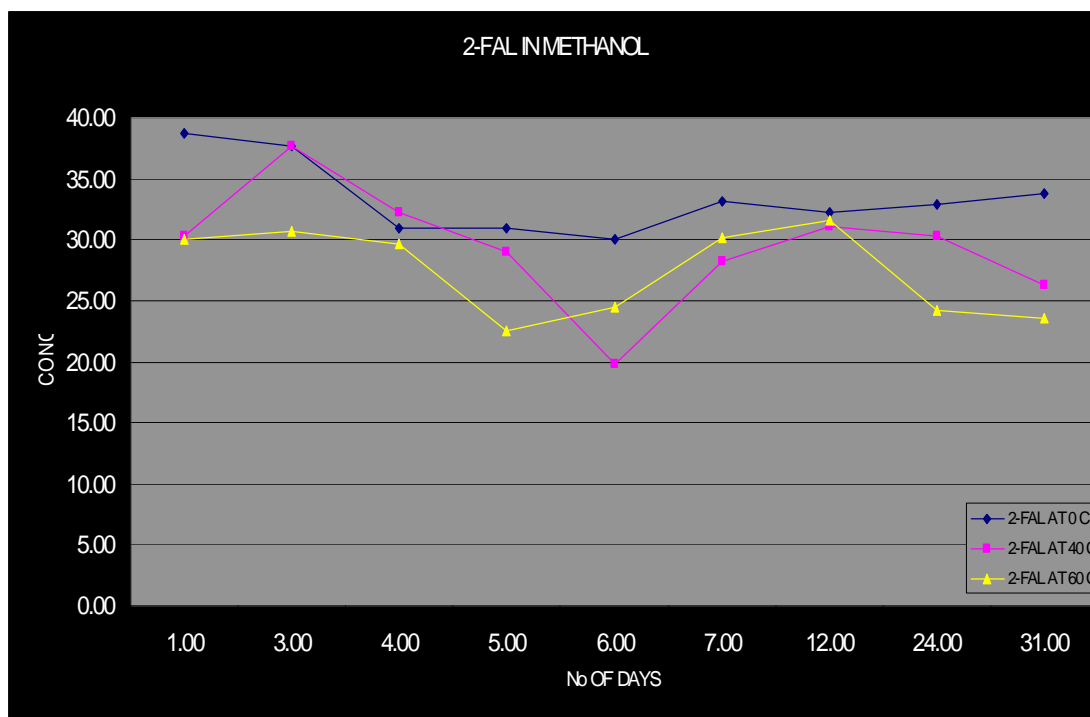


Fig 23 (b) Ageing illustration of 2-FAL in Methanol solution under different temperatures.

Figure 23 Ageing progress of 2-FAL in (a) Acetonitrile and (b) Methanol over time

The table below shows the ageing results of 2-ACF in acetonitrile and methanol solution measured for a period of 31 days of monitoring by HPLC.

Table 9 Results for the ageing of 2-ACF in Acetonitrile and Methanol.

2-ACF IN ACETONITRILE STORED AT 0 C			2-ACF IN ACETONITRILE STORED AT 40 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1210.66	25.28	1.00	1243.00	25.92
3.00	968.40	20.51	3.00	1280.00	26.65
4.00	1204.00	25.15	4.00	1233.00	25.72
5.00	1259.00	26.23	5.00	1266.00	26.37
6.00	1475.00	30.48	6.00	1544.00	31.84
7.00	1289.00	26.82	7.00	1445.50	29.90
12.00	1014.00	21.41	12.00	1580.00	32.55
24.00	1255.10	26.16	24.00	1344.00	27.91
31.00	1221.00	25.48	31.00	1237.90	25.82
2-ACF IN ACETONITRILE STORED AT 60 C			2-ACF IN METHANOL STORED AT 0 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1307.00	27.18	1.00	1547.81	39.16
3.00	1497.30	30.92	3.00	1525.80	38.59
4.00	1253.30	26.12	4.00	1289.40	32.46
5.00	1273.00	26.51	5.00	1282.00	32.27
6.00	1245.90	25.97	6.00	1298.90	32.71
7.00	1194.20	24.96	7.00	1358.30	34.25
12.00	1226.80	25.60	12.00	1331.00	33.54
24.00	1245.60	25.97	24.00	1506.00	38.08
31.00	1493.60	30.85	31.00	1416.56	35.76
2-ACF IN METHANOL STORED AT 40 C			2-ACF IN METHANOL STORED AT 60 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1224.86	30.79	1.00	1221.67	30.71
3.00	1241.30	31.21	3.00	1303.00	32.81
4.00	1344.20	33.88	4.00	1280.40	32.23
5.00	1228.90	30.89	5.00	966.30	24.08
6.00	938.80	23.37	6.00	1031.30	25.77
7.00	1177.00	29.55	7.00	1245.60	31.33
12.00	1292.00	32.53	12.00	1307.40	32.93
24.00	1235.70	31.07	24.00	1030.20	25.74
31.00	1050.00	26.25	31.00	961.10	23.95

Below is a graphical representation of the results from the ageing experiment for 2-ACF in acetonitrile and methanol solutions and analysed for a period of 31 days.

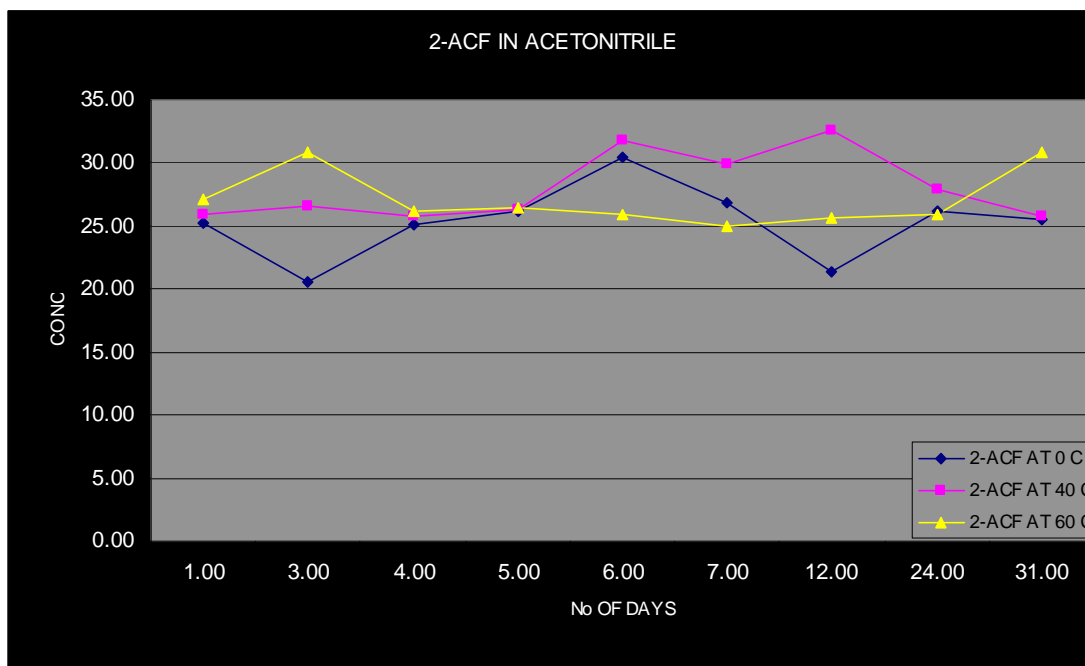


Fig 24 (a) Ageing illustration of 2-ACF in Acetonitrile solution under different temperatures

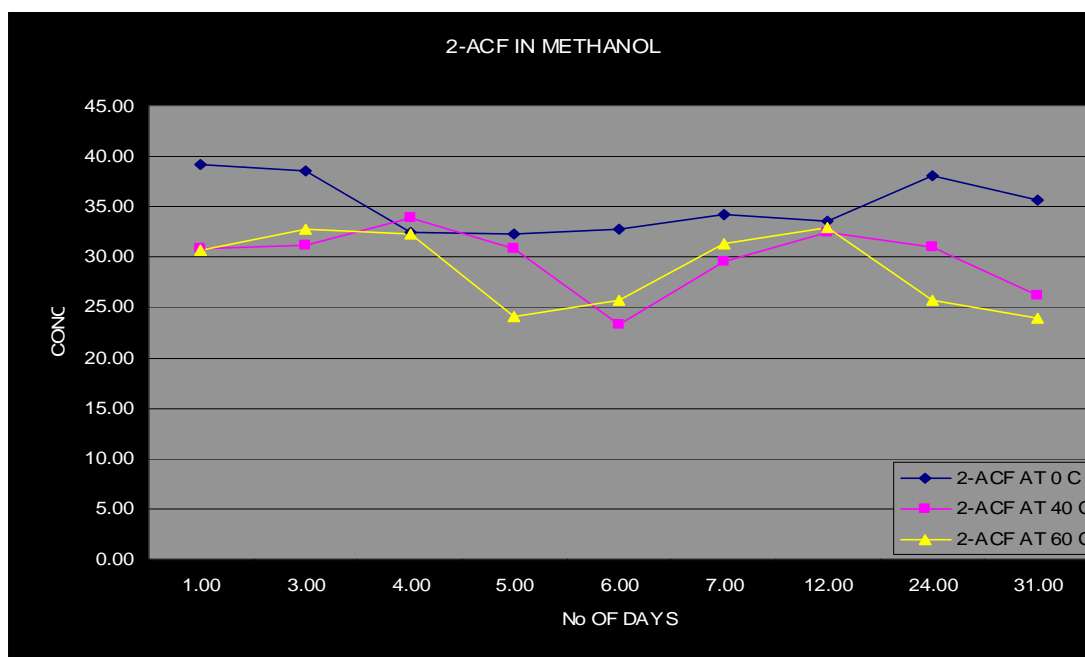


Fig 24 (b) Ageing illustration of 2-ACF in Methanol solution under different temperatures

Figure 24 Ageing progress of 2-ACF in (a) Acetonitrile and (b) Methanol over time

The table below shows the ageing results of 5-MEF in acetonitrile and methanol solution measured for a period of 31 days of monitoring by HPLC.

Table 10 Results for the ageing of 5-MEF in Acetonitrile and Methanol.

5-MEF IN ACETONITRILE STORED AT 0 C			5-MEF IN ACETONITRILE STORED AT 40 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1009.68	24.99	1.00	1034.79	25.57
3.00	808.30	20.28	3.00	1072.10	26.45
4.00	1001.00	24.78	4.00	1020.00	25.23
5.00	1098.00	27.05	5.00	1055.00	26.05
6.00	1241.60	30.41	6.00	1331.00	32.50
7.00	1023.40	25.31	7.00	1203.60	29.52
12.00	838.40	20.98	12.00	1312.00	32.05
24.00	1042.60	25.76	24.00	1111.90	27.38
31.00	1022.40	25.28	31.00	1034.80	25.57
5-MEF IN ACETONITRILE STORED AT 60 C			5-MEF IN METHANOL STORED AT 0 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1088.04	26.82	1.00	1311.69	39.20
3.00	1251.50	30.64	3.00	1296.50	38.73
4.00	1045.50	25.82	4.00	1100.20	32.72
5.00	1024.00	25.32	5.00	1098.00	32.66
6.00	1055.00	26.05	6.00	1211.40	36.13
7.00	993.90	24.62	7.00	1154.10	34.37
12.00	1020.00	25.23	12.00	1138.00	33.88
24.00	1033.00	25.53	24.00	1271.30	37.96
31.00	1322.40	32.30	31.00	1169.57	34.85
5-MEF IN METHANOL STORED AT 40 C			5-MEF IN METHANOL STORED AT 60 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	1038.55	30.84	1.00	1031.25	30.61
3.00	1060.20	31.50	3.00	1116.10	33.21
4.00	1143.60	34.05	4.00	1098.40	32.67
5.00	1052.40	31.26	5.00	833.70	24.56
6.00	811.00	23.87	6.00	906.40	26.79
7.00	1051.70	31.24	7.00	1053.40	31.29
12.00	1092.70	32.49	12.00	1106.70	32.92
24.00	1035.30	30.74	24.00	920.90	27.23
31.00	889.00	26.26	31.00	803.10	23.63

Below is a graphical representation of the results from the ageing experiment for 5-MEF in acetonitrile and methanol solutions and analysed for a period of 31 days.

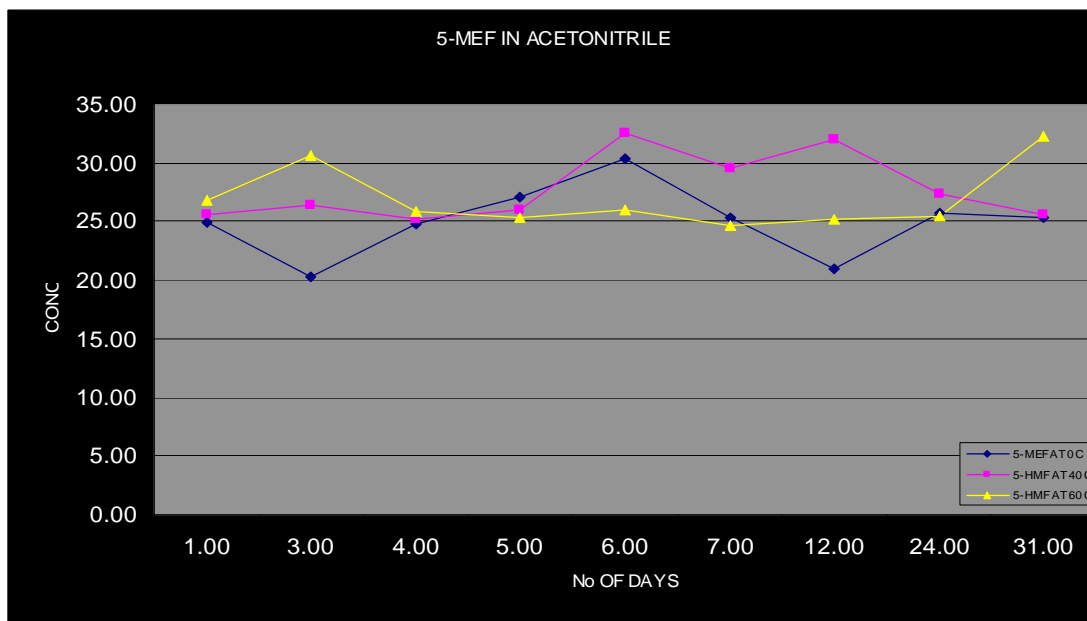


Fig 25 (a) Ageing illustration of 5-MEF in Acetonitrile solution under different temperatures

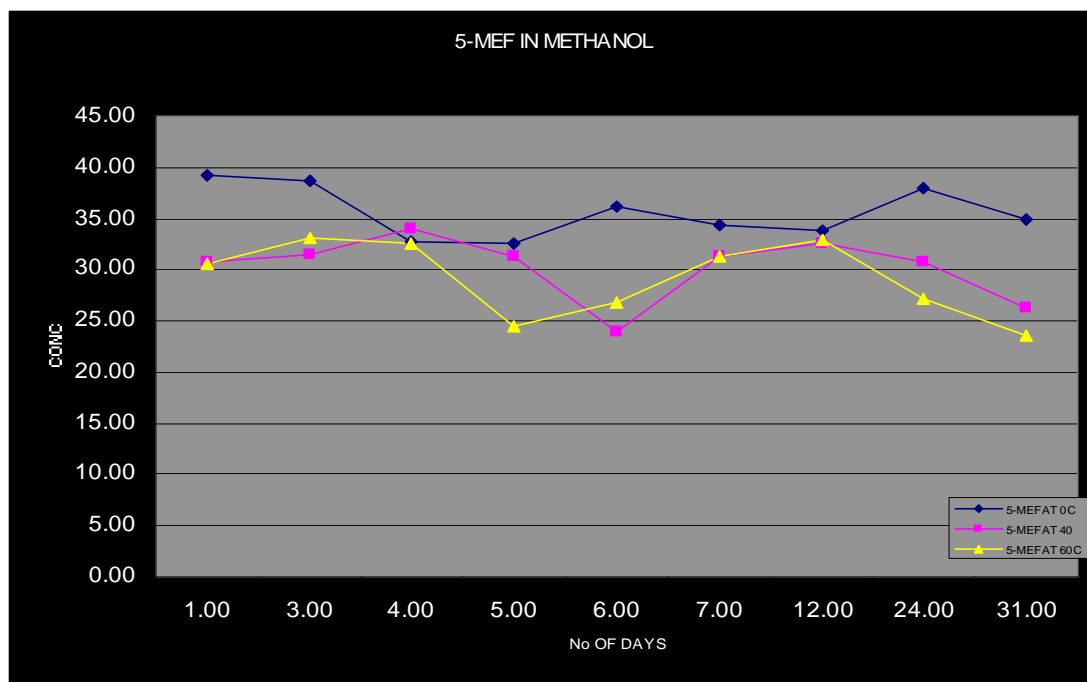


Fig 25 (b) Ageing illustration of 5-MEF in Methanol solution under different temperatures

Figure 25 Ageing progress of 5-MEF in (a) Acetonitrile and (b) Methanol over time.

The table below shows the ageing results of FOL in acetonitrile and methanol solution measured for a period of 31 days of monitoring by HPLC.

Table 11 Results for the ageing of FOL in Acetonitrile and Methanol.

FOL IN ACETONITRILE STORED AT 0 C			FOL IN ACETONITRILE STORED AT 40 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	830.36	24.60	1.00	846.05	25.04
3.00	697.60	20.87	3.00	927.80	27.34
4.00	813.54	24.13	4.00	829.51	24.58
5.00	861.30	25.47	5.00	899.20	26.53
6.00	1045.80	30.65	6.00	1093.40	31.99
7.00	863.40	25.53	7.00	1016.30	29.83
12.00	737.90	22.00	12.00	1142.20	33.36
24.00	883.60	26.10	24.00	955.90	28.13
31.00	857.80	25.37	31.00	879.00	25.97
FOL IN ACETONITRILE STORED AT 60 C			FOL IN METHANOL STORED AT 0 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	878.82	25.96	1.00	1067.55	39.63
3.00	1056.20	30.95	3.00	1103.00	40.98
4.00	857.10	25.35	4.00	975.70	36.14
5.00	864.06	25.55	5.00	934.70	34.58
6.00	892.00	26.33	6.00	938.00	34.71
7.00	853.60	25.25	7.00	985.20	36.50
12.00	869.20	25.69	12.00	972.60	36.02
24.00	889.10	26.25	24.00	1075.00	39.91
31.00	1028.50	30.17	31.00	1040.00	38.58
FOL IN METHANOL STORED AT 40 C			FOL IN METHANOL STORED AT 60 C		
No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION	No OF DAYS OF MEASUREMENT	PEAK AREA	CONCENTRATION
1.00	851.75	31.43	1.00	858.07	31.67
3.00	946.00	35.01	3.00	1005.00	37.25
4.00	1015.10	37.64	4.00	980.10	36.31
5.00	926.90	34.29	5.00	743.20	27.30
6.00	679.97	24.90	6.00	787.90	29.00
7.00	805.20	29.66	7.00	865.00	31.93
12.00	945.00	34.97	12.00	970.50	35.94
24.00	885.10	32.70	24.00	726.00	26.65
31.00	752.30	27.65	31.00	695.00	25.47

Below is a graphical representation of the results from the ageing experiment for FOL in acetonitrile and methanol solutions and analysed for a period of 31 days.

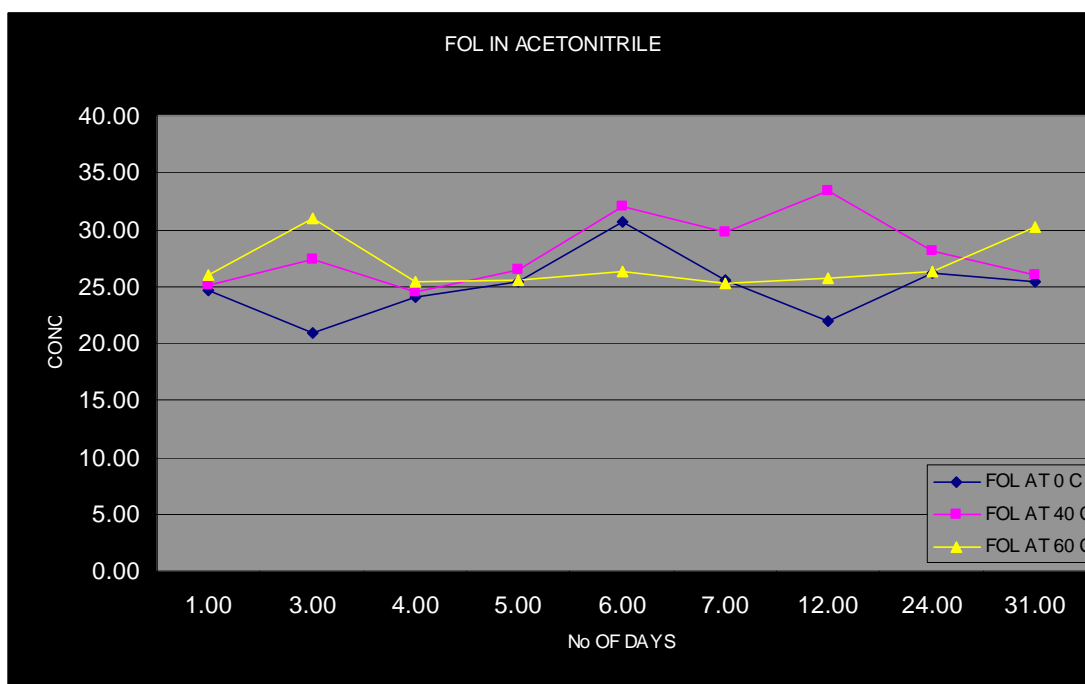


Fig 26 (a) Ageing illustration of FOL in Acetonitrile solution under different temperatures

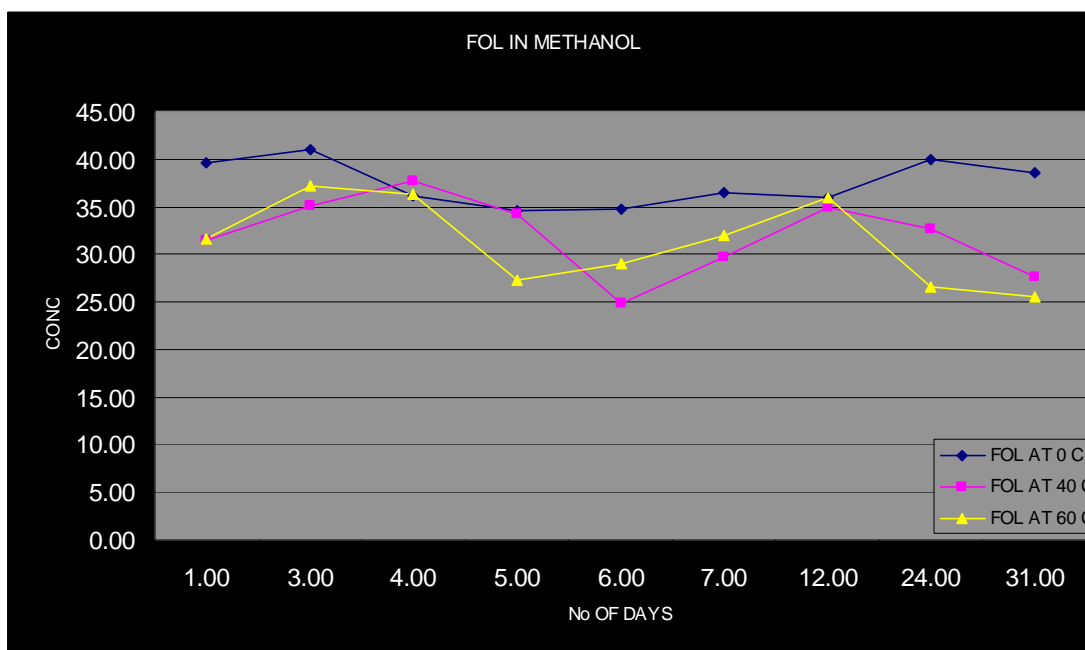


Fig 26 (b) Ageing illustration of FOL in Acetonitrile solution under different temperatures

Figure 26 Ageing progress of FOL in (a) Acetonitrile and (b) Methanol over time.

4.3 Results from the precipitation matter and the solutions at all pH at 60°C and 80°C.

An interesting observation for the solutions stored at 80°C with pH 10 was the formation of precipitation matter. That effect took place after the 7th day when the solutions became cloudy and the precipitation process started. Although the pH of the solutions was not changed significantly (from 10 to 11.2) that process indicates that a reaction takes place between the furans and the buffer favouring the reaction towards the formation of what may well be solid carbonate-based matter, since the original compounds used for the buffer solution were sodium carbonate and sodium bicarbonate. Therefore, the solution was filtered in order to collect the precipitate matter for analysis by HPLC for the purpose of examining the possibility that other furanic compounds were trapped during the precipitation process. Also, the remaining solution was examined, alongside the other solutions at the other two pHs tested, and finally all the solutions stored at 60°C. The purpose of the experiment was to investigate the possibility of formation of furan derivatives with a starting material of a single furan. Table 12 shows the results obtained from that investigation and show that;

- ✚ During the formation of the precipitation matter at the solution with pH 10 stored at 80°C the furan compound was trapped, possibly due to a reaction with the buffer since from each individual furan, as a starting material, formation of the other furans were detected, except of the formation of FOL. However, FOL as the starting compound and after a period of time can result in the production of the other four furanic compounds.
- ✚ It is possible from a single furan to produce other furan derivatives under specific conditions.
- ✚ Although, for that experiment HPLC analysis was used the results agree with the results produced when the solutions were analysed with UV-Vis spectroscopy.

Below are the results for the analysis of the precipitation matter that was formed at all the solutions with pH10 stored at 80°C. Also analysis of the solutions were performed for those particular samples, and for the samples stored at 60°C in order to investigate any similarities or differences to that effect. For the calibration graphs used to determine each value see appendix 2B.

Table 12 Results from the precipitation matter formed and also from the solutions filtered for each furan derivative in all pH at 60 C and 80 C using HPLC

FURAN	STATE OF FURAN	TEMPERAT STORED	PH	PEAK AREA OF DETECTABLE FURANS/CONCENTRATION (ppm)									
				5-HMF		2-FAL		2-ACF		5-MEF		FOL	
				AREA	CONC	AREA	CONC	AREA	CONC	AREA	CONC	AREA	CONC
5-HMF	SOLUTION	60	4.6	2819	34.42								
			6.8	3143	38.28								
			10	23.9	1.19	9.2	0.96	26.7	0.41	58.2	1.50		
	SOLUTION	80	4.6	4179	50.60								
			6.8	1917.1	23.70								
			10	16.9	1.11	38.7	1.37	92.5	1.23				
PRECIPITA		10	15.7	1.09	18.4	1.09	53.3	0.74	76.2	1.77			
2-FAL	SOLUTION	60	4.6			2568	36.90						
			6.8			2547	36.61						
			10			95.3	2.17	43.4	0.62				
	SOLUTION	80	4.6			1513.8	22.09						
			6.8			1635	23.80						
			10	3.4	0.95	13.2	1.01			51.2	1.39		
PRECIPITA		10	20.1	1.15	18.3	1.08	40.8	0.59	45.8	1.31			
2-ACF	SOLUTION	60	4.6					2713	33.84				
			6.8					2374	29.62				
			10	6.4	0.98	15	1.04	2129	26.57				
	SOLUTION	80	4.6					1433.7	17.92				
			6.8	354.6	5.12	76.1	1.90	706.9	8.87				
			10	59.3	1.61	51	1.54			87.2	1.93		
PRECIPITA		10	19.6	1.14	13.4	1.02	14.7	0.26	10.7	0.78			

Table 13 Results from the precipitation matter formed and also from the solutions filtered for each furan derivative in all pH at 60 C and 80 C using HPLC

FURAN	STATE OF FURAN	TEMPERATURE STORED	PH	PEAK AREA OF DETECTABLE FURANS/CONCENTRATION (ppm)									
				5-HMF		2-FAL		2-ACF		5-MEF		FOL	
				AREA	CONC	AREA	CONC	AREA	CONC	AREA	CONC	AREA	CONC
5-MEF	SOLUTION	60	4.6			7.9	0.94			1611.8	24.78		
			6.8			4.4	0.89			1670	25.66		
			10			4.2	0.89	2.7	0.11	596.7	9.57		
	SOLUTION	80	4.6			11.9	0.99			1071.2	16.68		
	SOLUTION		6.8	5.1	0.97	5.8	0.91			1407	21.71		
	SOLUTION		10	33.9	1.31								
	PRECIPITATION		10	1.1	0.92	16.6	1.06	36.3	0.53				
FOL	SOLUTION	60	4.6	5.5	0.97	42.2	1.42	11	0.22			158	2.38
			6.8	1.3	0.92	20	1.11	24.1	0.38			2048	32.40
			10	1.4	0.92	4.1	0.89	9.8	0.20			1729	27.33
	SOLUTION	80	4.6	3.1	0.94	26.2	1.20	7.5	0.17				
	SOLUTION		6.8	21.5	1.167909	21.2	1.130498					1295.9	20.45
	SOLUTION		10									1687	26.67
	PRECIPITATION		10	2.4	0.94	2.4	0.86	3.6	0.12				

4.4 Conclusion

In this chapter, furanic compounds were examined in different environments under different conditions in order to observe parameters such as ageing, degradation and production of furans and stability. The study showed that;

- ✚ The ageing of furans depends upon the local environment.
- ✚ Each furan shows different ageing sensitivity towards the conditions used.
- ✚ In aqueous environment with controlled pH, the furans are less stable compared to furans in an organic environment.
- ✚ Between the two organic environments examined the furans shows greater stability in the acetonitrile rather than the methanol.
- ✚ FOL degrades instantly in acidic environment due to tautomerism. The other furanic compounds do not have that ability of changing formation.
- ✚ Degradation of a single furan results to the production of the other furan derivatives.
- ✚ General order of degradation from more to less, according to the results, in aqueous environment of the furans is
2-FAL>5-HMF>FOL>2-ACF>5-MEF
- ✚ Degradation of 5-HMF, 2-FAL, 2-ACF and 5-MEF does not result in the formation of FOL but vice versa is possible.

CHAPTER FIVE
SUMMARY OF CONCLUSIONS &
FUTURE WORK

5.0 SUMMARY OF CONCLUSIONS AND FUTURE WORK

The research work presented at this thesis investigates a series of different properties that furanic compounds show. The specific furanic compounds analysed are the products of the degradation process of the insulating cellulosic paper. It is believed, according to the standard method IEC 6119, that 5-HMF, 2-FAL, 2-ACF, 5-MEF and FOL are the main products of the degradation of the paper and investigation of those compounds provide information relating to the state of the insulating paper.

This work presented the various techniques that are possible to use for the analysis and detection of the furanic compounds, indicating also, by presenting standard graphs, the amounts of furans which will be examined. It was established that UV-Vis and HPLC were the two techniques which will be used for the completion of the analysis of the furans.

The furanic compounds were examined under specific and controlled environment, such as buffer solution at specific pH and temperature (chapter 4), to determine the ageing, stability and degradation factors for the compounds. The results showed that each furan behave differently from each other, depending to the environment. In general, furans are less stable; degradate much faster in the aqueous state than in an organic phase (Acetonitrile and Methanol). The pH of the environment that the furans are located specify the rate of degradation, and in some cases can act as a reagent by altering and changing the formation of the compound, like in the case of FOL in acidic conditions where the compound showed signs of tautomerism between the Keto-enol formation. Also, it is possible from one furan derivative and after a period of degradation to produce other furan derivatives.

Obviously, the research work is an initial step of understanding the behaviour of furanic compounds under different conditions.

Further work is needed to establish;

- ✚ A kinetic model of the degradation of the furans. Basically the same experiment of the ageing and stability must be repeated and from all the results to try apply some kinetic parameters in order to explain the rate of degradation.
- ✚ Examination of ageing and stability of furans under different organic environments, such as cyclohexane, dichloromethane, tetrahydrofuran, in order to have a more general knowledge of the behaviour of furanic compounds in organic matter.
- ✚ Investigation of the maximum possible recovery of the furans that favours the migration towards the oil.
- ✚ Use of other extraction methods and matters, apart from silica cartridge that the standard method recommends, to achieve maximum extraction of furans and more stable, repeatable results.

The observations of the results from such investigation will provide valuable information to improve the existing method for a better detection of the furanic compounds and hence better knowledge of the insulating state of the transformer.

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APPENDIX A

CHAPTER A
RECOVERY & DISTRIBUTION OF
FURANIC COMPOUNDS

A. RECOVERY & DISTRIBUTION OF FURANIC COMPOUNDS

A.1 Aim

It is well known that furanic compounds are hydrophilic molecules, favouring their presence towards aqueous environment, and therefore an examination of the distribution of those compounds when they come in contact with other phases, e.g mineral oil, was a necessity. Also, the recovery of the compounds from a matrix such as oil will allow a determination of the amount that is recoverable as well as the loss. It is essential to understand that in a transformer there is an exchange of furans between the water residing in the insulating paper with the water residing in the insulating oil. Hence, such an investigation will indicate the amount of furans that prefer to stay in the water of the oil according to the distribution properties of the compounds.

A.2 Materials and method

A.2.1 Materials

The materials used for that experiment were;

- ✚ Water for gradient elution; Content: 2.5L, Lot No: 60140, Cat No: 34877, provided from Sigma-Aldrich
- ✚ Mineral insulating oil, provided from NYNAS Naphthenics Ltd.

A.2.2 Method

Initial solutions were prepared containing all the furanic compounds, each at concentrations from 0.1 ppm to 50 ppm. Those solutions were used as standard

solutions as well as the samples which will be investigated. The process of constructing those solutions is the same as in the case of section 3.2.3.

It was essential that the mineral insulating oil used, was saturated with water, so that no further water would be absorbed when the sample was introduced into the oil, which would later have lead to inaccuracies. Hence, 5 L of the oil was mixed with 200ml of water, in order for the oil to become saturated; visible observation of the free water in the oil used as the indicator of such saturation. 100ml of that oil was mixed with 10 ml of the sample, each time with different concentration of the sample, and stored for 30 minutes in an oven with 80°C temperature. In total 8 samples were stored, at varying furan concentrations. After 30 minutes that mixture was transferred in a separating funnel to retrieve the aqueous phase. The remaining oil was washed with another 10 ml of pure water and stored for another 30 minutes in the oven. Once again, the aqueous phase was separated from the oil. The samples after the collection were examined using HPLC in order to retrieve the data and to observe the changes that occurred from the initial samples, i.e standards. In a further experiment the same process was repeated with the only difference that this time the experiment took place at 60°C temperature. Also, the moisture content of the oil was recorded, before and after the experiment, in order to study, how the temperature affects the oil and how the different amounts of furanic compounds introduced into the oil can alter the moisture of it.

A.3 Results

Below are the results obtained from the samples with different concentrations at two different temperatures after two extractions when the samples where mixed with clean mineral oil. The technique used for that investigation was HPLC analysis. Extraction 1 is the amount of furan left in the water. Extraction 2 is the amount of furan recovered from the oil.

First, recovery of 5-HMF.

Table 14 Recovery results for 5-HMF after two extractions indicating the total concentration recovered with the percentage that corresponded to the extraction.

TEMPERATURE °C	CONCENTRATION (ppm)	EXTRACTION	5-HMF		TOTAL CONC (ppm)	% RECOVERY
			PEAK AREA	CONC (ppm)		
60	0.1	1	0.01	0.36	0.91	360.38
		2	14.70	0.55		553.45
	0.5	1	27.70	0.72	1.16	144.85
		2	5.40	0.43		86.25
	1	1	12.90	0.53	0.96	52.98
		2	5.33	0.43		43.03
	5	1	316.43	4.52	5.25	90.35
		2	28.50	0.73		14.70
	10	1	567.10	7.81	9.39	78.11
		2	92.50	1.58		15.76
	20	1	1456.00	19.49	21.41	97.45
		2	118.90	1.92		9.61
	30	1	2398.80	31.88	35.96	106.26
		2	283.40	4.08		13.61
	40	1	3429.80	45.42	47.98	113.56
		2	167.40	2.56		6.40
80	0.1	1	21.83	0.65	1.49	647.13
		2	36.60	0.84		841.18
	0.5	1	45.78	0.96	1.58	192.36
		2	19.27	0.61		122.70
	1	1	70.20	1.28	1.77	128.26
		2	9.48	0.48		48.49
	5	1	390.30	5.49	6.11	109.77
		2	20.16	0.63		12.50
	10	1	677.10	9.26	10.08	92.56
		2	35.38	0.83		8.25
	20	1	1559.00	20.84	22.12	104.22
		2	69.49	1.27		6.37
	30	1	2516.00	33.42	35.87	111.39
		2	159.00	2.45		8.16
	40	1	2633.00	34.95	39.23	87.39
		2	297.90	4.27		10.69

Recovery of 2-FAL

Table 15 Recovery results for 2-FAL after two extractions indicating the total concentration recovered with the percentage that corresponded to the extraction.

TEMPERATURE	CONCENTRATION (ppm)	EXTRACTION	2-FAL		TOTAL CONC (ppm)	% RECOVERY
			PEAK AREA	CONC (ppm)		
60	0.1	1	4.37	0.56	1.10	561.59
		2	2.70	0.54		543.27
	0.5	1	9.50	0.62	1.14	123.57
		2	0.80	0.52		104.49
	1	1	1.56	0.53	1.10	53.08
		2	5.04	0.57		56.89
	5	1	66.60	1.24	2.11	24.88
		2	32.30	0.87		17.36
	10	1	121.10	1.84	3.14	18.42
		2	71.90	1.30		13.02
	20	1	300.40	3.81	5.62	19.04
		2	118.80	1.82		9.08
	30	1	428.60	5.21	8.73	17.38
		2	274.00	3.52		11.73
	40	1	613.70	7.24	10.85	18.11
		2	281.60	3.60		9.00
80	0.1	1	22.50	0.76	1.27	760.41
		2		0.51		513.66
	0.5	1	21.85	0.75	1.27	150.66
		2		0.51		102.73
	1	1	34.60	0.89	1.41	89.31
		2		0.51		51.37
	5	1	131.50	1.96	2.81	39.12
		2	31.46	0.86		17.17
	10	1	177.20	2.46	3.75	24.57
		2	71.12	1.29		12.94
	20	1	358.90	4.45	6.60	22.25
		2	149.20	2.15		10.75
	30	1	674.50	7.91	11.23	26.37
		2	256.00	3.32		11.07
	40	1	498.40	5.98	10.73	14.95
		2	386.70	4.75		11.89

Recovery of 2-ACF

Table 16 Recovery results for 2-ACF after two extractions indicating the total concentration recovered with the percentage that corresponded to the extraction.

TEMPERATURE	CONCENTRATION (ppm)	EXTRACTION	2-ACF		TOTAL CONC (ppm)	% RECOVERY	
			PEAK AREA	CONC (ppm)			
60	0.1	1	3.25	0.25	0.48	248.68	
		2	1.90	0.23		230.42	
	0.5	1	14.40	0.40	0.63	79.90	
		2	2.20	0.23		46.90	
	1	1	10.20	0.34	0.60	34.27	
		2	3.60	0.25		25.34	
	5	1	44.10	0.80	1.40	16.03	
		2	29.20	0.60		11.99	
	10	1	84.80	1.35	2.23	13.52	
		2	49.90	0.88		8.80	
	20	1	178.40	2.62	4.05	13.09	
		2	90.50	1.43		7.15	
	30	1	272.30	3.89	6.63	12.96	
		2	187.70	2.74		9.15	
	40	1	346.50	4.89	7.59	12.23	
		2	184.30	2.70		6.75	
	80	0.1	1	20.23	0.48	0.80	478.39
			2	8.30	0.32		317.00
0.5		1	17.61	0.44	0.77	88.59	
		2	9.20	0.33		65.84	
1		1	22.18	0.50	0.83	50.48	
		2	8.70	0.32		32.24	
5		1	66.91	1.11	1.56	22.20	
		2	18.32	0.45		9.05	
10		1	90.34	1.43	2.24	14.27	
		2	44.72	0.81		8.10	
20		1	195.90	2.85	4.33	14.27	
		2	93.60	1.47		7.35	
30		1	304.20	4.32	6.66	14.40	
		2	158.00	2.34		7.81	
40		1	245.80	3.53	7.04	8.83	
		2	244.30	3.51		8.77	

Recovery of 5-MEF

Table 17 Recovery results for 5-MEF after two extractions indicating the total concentration recovered with the percentage that corresponded to the extraction.

TEMPERATURE	CONCENTRATION (ppm)	EXTRACTION	5-MEF		TOTAL CONC (ppm)	% RECOVERY
			PEAK AREA	CONC (ppm)		
60	0.1	1	1.20	0.47	0.93	473.13
		2	0.40	0.46		461.02
	0.5	1	3.20	0.50	0.97	100.68
		2	0.50	0.46		92.51
	1	1	0.90	0.47	0.94	46.86
		2	1.10	0.47		47.16
	5	1	22.60	0.80	1.48	15.94
		2	14.90	0.68		13.61
	10	1	39.20	1.05	1.98	10.48
		2	31.60	0.93		9.33
	20	1	79.30	1.66	3.02	8.28
		2	59.90	1.36		6.81
	30	1	258.40	4.37	6.79	14.56
		2	130.00	2.42		8.08
	40	1	268.90	4.53	6.91	11.31
		2	127.40	2.38		5.96
80	0.1	1	13.58	0.66	1.17	660.54
		2	3.80	0.51		512.49
	0.5	1	9.96	0.61	1.11	121.15
		2	2.95	0.50		99.92
	1	1	12.36	0.64	1.22	64.21
		2	8.20	0.58		57.91
	5	1	41.37	1.08	1.73	21.62
		2	12.68	0.65		12.94
	10	1	50.75	1.22	2.14	12.23
		2	30.49	0.92		9.17
	20	1	99.20	1.96	3.31	9.78
		2	59.50	1.36		6.78
	30	1	254.50	4.31	6.17	14.36
		2	93.00	1.86		6.21
	40	1	158.60	2.86	5.47	7.14
		2	142.70	2.62		6.54

Recovery of FOL

Table 18 Recovery results for FOL after two extractions indicating the total concentration recovered with the percentage that corresponded to the extraction.

TEMPERATURE	CONCENTRATION (ppm)	EXTRACTION	FOL		TOTAL CONC (ppm)	% RECOVERY
			PEAK AREA	CONC (ppm)		
60	0.1	1	5.04	0.24	0.50	239.39
		2	5.90	0.26		256.24
	0.5	1	18.57	0.50	0.72	100.91
		2	3.70	0.21		42.63
	1	1	36.57	0.86	1.09	85.73
		2	4.76	0.23		23.39
	5	1	237.50	4.79	5.52	95.90
		2	29.60	0.72		14.41
	10	1	392.70	7.84	9.36	78.36
		2	70.60	1.52		15.24
	20	1	811.80	16.05	18.23	80.25
		2	104.20	2.18		10.91
	30	1	1161.80	22.91	27.99	76.36
		2	252.00	5.08		16.93
	40	1	1744.50	34.33	38.60	85.82
		2	211.00	4.28		10.69
80	0.1	1	10.57	0.35	0.79	347.76
		2	15.59	0.45		446.14
	0.5	1	26.73	0.66	0.96	132.89
		2	8.05	0.30		59.68
	1	1	39.32	0.91	1.05	91.12
		2		0.14		14.06
	5	1	211.30	4.28	4.78	85.63
		2	18.47	0.50		10.05
	10	1	378.94	7.57	8.51	75.67
		2	40.90	0.94		9.42
	20	1	847.30	16.74	18.83	83.72
		2	99.15	2.08		10.42
	30	1	1363.90	26.87	27.01	89.56
		2		0.14		0.47
	40	1	1171.70	23.10	30.67	57.76
		2	378.90	7.57		18.91

A.4 Discussion

As mentioned earlier, the insulation of a transformer mainly consists of cellulosic paper and mineral oil. Unavoidably, both components contain a good proportion, in different ratio, of water. When there is production of furanic compounds in the paper due to breakdown of cellulosic insulating material, it is believed that those compounds migrate from water molecules located in the paper to water molecules in the oil, until they reach an equilibrium state dependent on temperature. However, the ratio of that equilibrium state is not known. Although, that migration process some amount of furans remain in the cellulosic paper.

With that experiment is an attempt of reconstructing the movement of furanic compounds between a very hydrophilic phase, the paper, and a very hydrophobic phase, the oil. The pure water acts as a model for the water located in the paper, and when that water is mixed with the oil, which is already water-saturated (in order to avoid any absorption of the water by the oil and hence the furanic compounds), will give valuable information about how the furans are distributed in an oil water environment, and give information about the amount of furans that is possible to recover from an oil matrix.

Figure 38 shows the results for 5-HMF. It can be seen that this particular compound can be recovered after the first extraction in both temperatures investigated. That means that 5-HMF prefers the aqueous phase and there is no distribution of the compound between the water and the oil. The problem arises when it comes to the existing method where extraction of that compound comes from the oil. If there is no movement of the compound from the paper to the oil there is no detection of the compound and therefore no indication of the state of the degradation of the cellulosic paper.

2-FAL analysis (see Fig 39) showed that this compound is not able to recover the full amount even in the second extraction. Introducing more concentrated solution, results to greater loss of the compound at the end of the measurement. The

interesting observation was that the compound behaves the same at both temperatures, which means that this parameter does not affect of the migration and distribution of the compound. Also, a higher concentration of that compound in to the oil means, that $\frac{3}{4}$ of the initial concentration migrates to the oil. Only, up to 5 ppm is capable to recover after the second extraction. Those results in comparison with the existing method means, that although the compound distributed more towards the oil it is very difficult to recover the actual amount that the oil contains of that furanic compound. There is also, another possibility of that great loss, which is the degradation of the compound due to the high temperature (60 and 80°C). It was investigated earlier on, the degradation of 2-FAL in aqueous controlled environment and showed that the degradation is not immediate, at least not in the first hour, but in this case although the environment is aqueous is different when is mixed with the oil, therefore the parameters have changed and a relation factor is not possible.

Figure 40 and 41 shows the results for 2-ACF and 5-MEF respectively. Both compounds behave the same as with the case of 2-FAL with the only difference that 2-ACF is not able to fully recovered for concentrations higher than 1 ppm.

Finally, FOL (see Fig 42) can be recovered fully from the first extraction at 60°C, but in the case of the mixture treated at 80°C temperature, the compound in the highest concentration of 40 ppm was not been able to be fully recovered. Therefore, there is a similar behaviour of FOL with 5-HMF.

Another explanation of why some of the furanic compounds prefer the movement towards the oil is the fact that the moisture content of the oil increases. Initially, the moisture content of the mineral oil was 4 ppm, after saturation the moisture increases to 80 ppm. When the samples treated to the designated temperatures the moisture from all the samples increased significantly to an extent of 280 ppm.

A.5 Conclusion

Furanic compounds are known as hydrophilic compounds moving through the water molecules between the insulating cellulosic paper and the oil. That experiment attempted to investigate and to explain that migration through the recovery process of a known amount of furans, when they are located in an oil water environment. The completion of the experiment showed that the furans are divided into two groups. The first group include the compounds which show preference towards the aqueous environment and there is no distribution of those compounds between the water and the oil. Those compounds are found to be 5-HMF and FOL. The second group involves the compounds that migrate and the majority of their presences prefer the oil. Those compounds are 2-FAL, 2-ACF and 5-MEF. An important parameter for the distribution of the furans and hence the migration of them from one state to the other, is the moisture content of the oil. It was found that at 60 and 80°C temperature the moisture content of the oil increases to an extent that accelerates and attracts more furanic compounds. However, that change of the moisture parameter seems to not affect all the furans.

APPENDIX B

APPENDIX A TABLES OF AGEING RESULTS FOR THE FIVE FURAN DERIVATIVES AT DIFFERENT CONDITIONS FOR 63 DAYS OF ANALYSIS.

Table 19 Ageing results for 5-HMF at pH 4.6 stored at 0 C for a period of 63 days

Table 20 Ageing results for 5-HMF at pH 6.8 stored at 0 C for a period of 63

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.94	0.01	0.10	2.85	28.83
01/08/2005	1	2.94	0.02	0.10	2.84	28.75
02/08/2005	2	2.90	0.02	0.09	2.81	28.37
03/08/2005	3	2.89	0.03	0.10	2.79	28.23
04/08/2005	4	2.90	0.02	0.10	2.79	28.21
05/08/2005	5	2.93	0.02	0.13	2.81	28.40
06/08/2005	6	2.93	0.05	0.14	2.79	28.22
07/08/2005	7	3.03	0.02	0.14	2.89	29.28
10/08/2005	10	3.02	0.43	0.44	2.59	25.98
13/08/2005	13	3.02	0.00	0.16	2.86	28.96
16/08/2005	16	2.90	0.03	0.09	2.80	28.35
19/08/2005	19	2.82	0.03	0.07	2.75	27.80
22/08/2005	21	2.91	0.03	0.06	2.84	28.78
30/08/2005	25	2.90	0.04	0.07	2.82	28.57
06/09/2005	31	2.88	0.02	0.06	2.81	28.45
09/10/2005	63	2.91	0.01	0.07	2.84	28.75

of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.94	0.02	0.09	2.85	28.88
01/08/2005	1	3.03	0.04	0.10	2.93	29.74
02/08/2005	2	3.00	0.01	0.09	2.91	29.52
03/08/2005	3	2.95	0.02	0.10	2.84	28.80
04/08/2005	4	2.96	0.03	0.11	2.85	28.86
05/08/2005	5	2.96	0.01	0.12	2.84	28.74
06/08/2005	6	2.97	0.02	0.13	2.84	28.78
07/08/2005	7	3.03	0.04	0.14	2.89	29.33
10/08/2005	10	3.24	0.03	0.43	2.81	28.40
13/08/2005	13	3.01	0.03	0.15	2.85	28.89
16/08/2005	16	2.92	0.03	0.09	2.83	28.64
19/08/2005	19	2.86	0.03	0.07	2.79	28.24
22/08/2005	21	2.86	0.03	0.07	2.80	28.28
30/08/2005	25	2.90	0.03	0.08	2.82	28.51
06/09/2005	31	2.94	0.02	0.07	2.87	29.07
09/10/2005	63	2.90	0.02	0.16	2.73	27.57

Days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30.00
31/07/2005	0	2.92	0.00	0.09	2.83	28.60
01/08/2005	1	2.97	0.02	0.09	2.88	29.20
02/08/2005	2	3.01	0.01	0.09	2.92	29.63
03/08/2005	3	2.97	0.04	0.11	2.86	28.96
04/08/2005	4	2.95	0.01	0.11	2.84	28.70
05/08/2005	5	2.96	0.01	0.12	2.84	28.79
06/08/2005	6	3.00	0.04	0.14	2.86	29.01
07/08/2005	7	3.02	0.03	0.14	2.88	29.14
10/08/2005	10	3.29	0.03	0.44	2.85	28.91
13/08/2005	13	3.03	0.01	0.16	2.87	29.07
16/08/2005	16	2.97	0.04	0.09	2.88	29.15
19/08/2005	19	2.89	0.02	0.07	2.82	28.48
22/08/2005	21	2.93	0.01	0.07	2.86	28.93
30/08/2005	25	2.91	0.03	0.08	2.83	28.65
06/09/2005	31	2.90	0.03	0.08	2.82	28.57
09/10/2005	63	2.94	0.03	0.14	2.79	28.22

Table 21 Ageing results for 5-HMF at pH 10 stored at 0 C for a period of 63 days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
31/07/2005	0	2.94	0.01	0.10	2.85	28.83
01/08/2005	1	2.98	0.04	0.10	2.88	29.22
02/08/2005	2	2.99	0.02	0.09	2.90	29.41
03/08/2005	3	2.99	0.03	0.10	2.88	29.24
04/08/2005	4	2.96	0.02	0.10	2.85	28.90
05/08/2005	5	2.97	0.01	0.12	2.86	28.94
06/08/2005	6	2.97	0.01	0.13	2.84	28.73
07/08/2005	7	3.08	0.06	0.13	2.95	29.94
10/08/2005	10	3.28	0.04	0.42	2.86	28.96
13/08/2005	13	3.02	0.02	0.15	2.87	29.09
16/08/2005	16	2.96	0.05	0.08	2.88	29.20
19/08/2005	19	2.92	0.02	0.06	2.86	29.01
22/08/2005	21	2.91	0.02	0.05	2.85	28.90
30/08/2005	25	2.92	0.01	0.05	2.87	29.07
06/09/2005	31	2.94	0.03	0.05	2.88	29.20
09/10/2005	63	2.93	0.02	0.08	2.86	28.93

Table 22 Ageing results for 5-HMF at pH 4.6 stored at 40 C for a period of 63 Days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
31/07/2005	0	2.94	0.02	0.09	2.85	28.88
01/08/2005	1	3.00	0.03	0.09	2.92	29.57
02/08/2005	2	3.01	0.03	0.09	2.91	29.55
03/08/2005	3	2.98	0.01	0.10	2.87	29.12
04/08/2005	4	2.96	0.04	0.11	2.86	28.95
05/08/2005	5	2.97	0.01	0.11	2.85	28.90
06/08/2005	6	2.99	0.02	0.13	2.86	29.01
07/08/2005	7	3.03	0.04	0.13	2.90	29.42
10/08/2005	10	3.25	0.02	0.45	2.80	28.27
13/08/2005	13	2.99	0.02	0.18	2.81	28.40
16/08/2005	16	2.93	0.02	0.12	2.80	28.33
19/08/2005	19	2.88	0.02	0.12	2.76	27.86
22/08/2005	21	2.90	0.02	0.14	2.76	27.85
30/08/2005	25	2.88	0.02	0.12	2.77	27.94
06/09/2005	31	2.91	0.01	0.12	2.79	28.22
09/10/2005	63	2.66	0.02	0.16	2.49	24.95

Table 23 Ageing results for 5-HMF at pH 6.8 stored at 40 C for a period of 63 days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
31/07/2005	0	2.92	0.00	0.09	2.83	28.60
01/08/2005	1	2.96	0.02	0.09	2.86	29.01
02/08/2005	2	2.96	0.01	0.10	2.86	28.99
03/08/2005	3	2.98	0.03	0.11	2.87	29.10
04/08/2005	4	2.95	0.03	0.11	2.84	28.75
05/08/2005	5	2.96	0.02	0.12	2.84	28.78
06/08/2005	6	3.00	0.03	0.14	2.86	29.00
07/08/2005	7	2.95	0.01	0.14	2.81	28.46
10/08/2005	10	3.24	0.02	0.44	2.80	28.33
13/08/2005	13	2.96	0.03	0.16	2.81	28.37
16/08/2005	16	2.87	0.03	0.10	2.78	28.05
19/08/2005	19	2.83	0.02	0.08	2.75	27.79
22/08/2005	21	2.80	0.03	0.08	2.73	27.52
30/08/2005	25	2.77	0.02	0.08	2.69	27.10
06/09/2005	31	2.72	0.02	0.08	2.64	26.53
09/10/2005	63	2.57	0.01	0.11	2.47	24.69

Table 24 Ageing results for 5-HMF at pH 10 stored at 40 C for a period of 63 Days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.94	0.01	0.10	2.85	28.83
01/08/2005	1	2.95	0.03	0.10	2.86	28.91
02/08/2005	2	3.01	0.02	0.09	2.91	29.57
03/08/2005	3	2.97	0.02	0.10	2.86	29.01
04/08/2005	4	2.96	0.02	0.10	2.86	28.98
05/08/2005	5	2.97	0.01	0.11	2.86	28.95
06/08/2005	6	3.01	0.01	0.13	2.88	29.17
07/08/2005	7	3.06	0.03	0.13	2.93	29.69
10/08/2005	10	3.30	0.02	0.43	2.87	29.12
13/08/2005	13	3.05	0.02	0.15	2.91	29.47
16/08/2005	16	2.96	0.02	0.08	2.88	29.18
19/08/2005	19	2.92	0.05	0.06	2.86	28.99
22/08/2005	21	2.92	0.02	0.05	2.87	29.07
30/08/2005	25	2.92	0.04	0.06	2.86	28.94
06/09/2005	31	2.94	0.01	0.06	2.88	29.21
09/10/2005	63	2.94	0.03	0.13	2.81	28.38

Table 25 Ageing results for 5-HMF at pH 4.6 stored at 60 C for a period of 63 days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.94	0.02	0.09	2.85	28.88
01/08/2005	1	2.98	0.03	0.09	2.90	29.37
02/08/2005	2	2.99	0.02	0.10	2.89	29.28
03/08/2005	3	2.96	0.05	0.10	2.85	28.91
04/08/2005	4	2.95	0.02	0.10	2.85	28.82
05/08/2005	5	2.95	0.01	0.11	2.84	28.75
06/08/2005	6	2.97	0.01	0.13	2.84	28.77
07/08/2005	7	3.02	0.02	0.13	2.89	29.28
10/08/2005	10	3.25	0.03	0.43	2.82	28.57
13/08/2005	13	2.96	0.03	0.15	2.82	28.48
16/08/2005	16	2.92	0.01	0.08	2.84	28.71
19/08/2005	19	2.87	0.03	0.06	2.81	28.44
22/08/2005	21	2.88	0.02	0.05	2.83	28.59
30/08/2005	25	2.90	0.04	0.06	2.84	28.73
06/09/2005	31	2.90	0.02	0.06	2.84	28.75
09/10/2005	63	2.84	0.02	0.08	2.76	27.85

Table 26 Ageing results for 5-HMF at pH 6.8 stored at 60 C for a period of 63 days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
31/07/2005	0	2.92	0.00	0.09	2.83	28.60
01/08/2005	1	2.91	0.02	0.09	2.82	28.53
02/08/2005	2	2.88	0.02	0.10	2.78	28.12
03/08/2005	3	2.79	0.01	0.11	2.68	27.03
04/08/2005	4	2.72	0.01	0.11	2.61	26.23
05/08/2005	5	2.65	0.01	0.12	2.53	25.37
06/08/2005	6	2.58	0.02	0.14	2.44	24.42
07/08/2005	7	2.52	0.02	0.14	2.38	23.73
10/08/2005	10	2.59	0.01	0.43	2.16	21.32
13/08/2005	13	2.11	0.01	0.15	1.96	19.10
16/08/2005	16	1.86	0.01	0.09	1.77	17.02
19/08/2005	19	1.61	0.00	0.07	1.54	14.58
22/08/2005	21	1.36	0.00	0.07	1.30	11.91
30/08/2005	25	1.16	0.00	0.07	1.09	9.59
06/09/2005	31	1.06	0.08	0.07	0.99	8.49
09/10/2005	63	0.60	0.01	0.10	0.51	3.24

Table 27 Ageing results for 5-HMF at pH 10 stored at 60 C for a period of 63 days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
31/07/2005	0	2.94	0.01	0.10	2.85	28.83
01/08/2005	1	3.06	0.05	0.10	2.96	30.08
02/08/2005	2	3.00	0.02	0.10	2.91	29.47
03/08/2005	3	2.96	0.02	0.11	2.85	28.88
04/08/2005	4	2.97	0.02	0.11	2.86	28.94
05/08/2005	5	2.97	0.01	0.12	2.85	28.83
06/08/2005	6	3.01	0.03	0.15	2.86	28.95
07/08/2005	7	3.07	0.05	0.15	2.92	29.65
10/08/2005	10	3.29	0.01	0.47	2.82	28.57
13/08/2005	13	2.99	0.03	0.20	2.79	28.20
16/08/2005	16	2.96	0.03	0.14	2.82	28.54
19/08/2005	19	2.93	0.03	0.13	2.80	28.36
22/08/2005	21	2.91	0.02	0.14	2.77	27.93
30/08/2005	25	2.96	0.02	0.18	2.77	28.03
06/09/2005	31	2.96	0.03	0.18	2.78	28.06
09/10/2005	63	2.94	0.02	0.08	2.86	28.96

Table 28 Ageing results for 5-HMF at pH 4.6 stored at 80 C for a period of 63 days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
31/07/2005	0.00	2.94	0.02	0.09	2.85	28.88
01/08/2005	1.00	2.98	0.03	0.09	2.89	29.30
02/08/2005	2.00	3.00	0.02	0.13	2.87	29.11
03/08/2005	3.00	2.98	0.03	0.12	2.86	28.98
04/08/2005	4.00	2.95	0.03	0.12	2.83	28.66
05/08/2005	5.00	2.96	0.01	0.13	2.83	28.68
06/08/2005	6.00	2.98	0.02	0.14	2.84	28.71
07/08/2005	7.00	3.06	0.06	0.15	2.91	29.50
10/08/2005	10.00	3.22	0.04	0.44	2.78	28.08
13/08/2005	13.00	2.97	0.02	0.16	2.81	28.38
16/08/2005	16.00	2.91	0.01	0.09	2.82	28.52
19/08/2005	19.00	2.89	0.01	0.08	2.82	28.51
22/08/2005	21.00	2.90	0.03	0.07	2.84	28.70
30/08/2005	25.00	2.86	0.02	0.08	2.78	28.13
06/09/2005	31.00	2.88	0.01	0.08	2.79	28.25
09/10/2005	63.00	2.81	0.01	0.10	2.71	27.32

Table 29 Ageing results for 5-HMF at pH 6.8 stored at 80 C for a period of 63 days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
31/07/2005	0	2.92	0.00	0.09	2.83	28.60
01/08/2005	1	2.28	0.01	0.09	2.18	21.58
02/08/2005	2	1.71	0.01	0.09	1.62	15.42
03/08/2005	3	1.31	0.00	0.10	1.21	10.89
04/08/2005	4	1.03	0.00	0.11	0.92	7.82
05/08/2005	5	0.84	0.00	0.12	0.72	5.61
06/08/2005	6	0.71	0.00	0.13	0.57	3.99
07/08/2005	7	0.66	0.00	0.14	0.52	3.36
10/08/2005	10	0.80	0.00	0.45	0.35	1.51
13/08/2005	13	0.45	0.00	0.18	0.27	0.68
16/08/2005	16	0.32	0.00	0.13	0.19	-0.16
19/08/2005	19	0.30	0.00	0.13	0.17	-0.47
22/08/2005	21	0.30	0.00	0.16	0.14	-0.75
30/08/2005	25	0.32	0.01	0.18	0.14	-0.74
06/09/2005	31	0.27	0.00	0.05	0.21	0.03
09/10/2005	63	0.00	0.00	0.00	0.00	-2.29

Table 30 Ageing results for 5-HMF at pH 10 stored at 80 C for a period of 63 Days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	3.25	0.06	0.09	3.16	29.21
02/08/2005	1	3.30	0.02	0.11	3.19	29.48
03/08/2005	2	3.22	0.05	0.10	3.11	28.70
04/08/2005	3	3.21	0.07	0.12	3.09	28.50
05/08/2005	4	3.27	0.00	0.23	3.04	27.97
06/08/2005	5	3.33	0.09	0.17	3.16	29.16
07/08/2005	6	3.32	0.09	0.18	3.13	28.91
08/08/2005	7	3.35	0.05	0.18	3.17	29.32
12/08/2005	11	3.27	0.04	0.20	3.07	28.24
15/08/2005	14	3.11	0.01	0.09	3.02	27.81
18/08/2005	17	3.14	0.05	0.13	3.01	27.62
23/08/2005	22	3.23	0.03	0.10	3.14	28.93
08/09/2005	37	3.14	0.05	0.10	3.04	28.02
09/10/2005	67	3.18	0.04	0.11	3.07	28.30

Table 31 Ageing results for 2-FAL at pH 4.6 stored at 0 C for a period of 63 days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	3.20	0.01	0.10	3.10	28.57
02/08/2005	1	3.24	0.02	0.11	3.13	28.87
03/08/2005	2	3.24	0.00	0.11	3.13	28.85
04/08/2005	3	3.21	0.05	0.13	3.08	28.42
05/08/2005	4	3.26	0.03	0.14	3.12	28.81
06/08/2005	5	3.34	0.02	0.16	3.19	29.43
07/08/2005	6	3.27	0.06	0.17	3.10	28.57
08/08/2005	7	3.32	0.06	0.17	3.14	28.99
12/08/2005	11	3.19	0.02	0.18	3.01	27.70
15/08/2005	14	3.15	0.05	0.09	3.06	28.15
18/08/2005	17	3.13	0.02	0.13	3.00	27.54
23/08/2005	22	3.20	0.04	0.09	3.11	28.69
08/09/2005	37	3.14	0.05	0.10	3.04	27.98
09/10/2005	67	3.11	0.04	0.18	2.93	26.86

Table 32 Ageing results for 2-FAL at pH 6.8 stored at 0 C for a period of 63 days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	3.24	0.01	0.09	3.14	29.00
02/08/2005	1	3.31	0.06	0.11	3.20	29.61
03/08/2005	2	3.25	0.02	0.11	3.14	29.01
04/08/2005	3	3.24	0.03	0.13	3.12	28.72
05/08/2005	4	3.30	0.04	0.14	3.16	29.17
06/08/2005	5	3.31	0.05	0.16	3.15	29.09
07/08/2005	6	3.30	0.06	0.17	3.13	28.90
08/08/2005	7	3.37	0.02	0.17	3.20	29.54
12/08/2005	11	3.26	0.02	0.19	3.07	28.30
15/08/2005	14	3.20	0.06	0.09	3.11	28.70
18/08/2005	17	3.16	0.03	0.12	3.04	27.96
23/08/2005	22	3.23	0.06	0.08	3.14	28.98
08/09/2005	37	3.13	0.02	0.09	3.04	27.95
09/10/2005	67	3.18	0.05	0.16	3.03	27.84

Table 33 Ageing results for 2-FAL at pH 10 stored at 0 C for a period of 63 days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	3.25	0.06	0.09	3.16	29.21
02/08/2005	1	3.30	0.06	0.10	3.20	29.55
03/08/2005	2	3.23	0.06	0.10	3.13	28.91
04/08/2005	3	3.25	0.06	0.12	3.13	28.89
05/08/2005	4	3.32	0.02	0.14	3.18	29.35
06/08/2005	5	3.33	0.07	0.15	3.18	29.41
07/08/2005	6	3.36	0.06	0.16	3.20	29.56
08/08/2005	7	3.32	0.05	0.16	3.16	29.19
12/08/2005	11	3.29	0.05	0.17	3.12	28.75
15/08/2005	14	3.19	0.05	0.07	3.12	28.79
18/08/2005	17	3.14	0.04	0.10	3.04	27.95
23/08/2005	22	3.23	0.03	0.07	3.17	29.22
08/09/2005	37	3.12	0.03	0.07	3.05	28.02
09/10/2005	67	3.23	0.02	0.09	3.14	28.98

Table 34 Ageing results for 2-FAL at pH 4.6 stored at 40 C for a period of 63 Days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
01/08/2005	0	3.20	0.01	0.10	3.10	28.57
02/08/2005	1	3.26	0.04	0.11	3.15	29.12
03/08/2005	2	3.29	0.05	0.10	3.18	29.39
04/08/2005	3	3.20	0.04	0.12	3.09	28.42
05/08/2005	4	3.28	0.05	0.14	3.15	29.04
06/08/2005	5	3.36	0.07	0.15	3.22	29.75
07/08/2005	6	3.28	0.06	0.16	3.12	28.80
08/08/2005	7	3.31	0.04	0.17	3.15	29.02
12/08/2005	11	3.23	0.02	0.21	3.02	27.77
15/08/2005	14	3.17	0.05	0.12	3.04	28.01
18/08/2005	17	3.12	0.06	0.16	2.96	27.17
23/08/2005	22	3.21	0.03	0.14	3.08	28.36
08/09/2005	37	3.12	0.03	0.16	2.96	27.18
09/10/2005	67	3.20	0.01	0.20	3.00	27.57

Table 35 Ageing results for 2-FAL at pH 6.8 stored at 40 C for a period of 63 days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
01/08/2005	0	3.24	0.01	0.09	3.14	29.00
02/08/2005	1	3.33	0.05	0.11	3.22	29.78
03/08/2005	2	3.22	0.05	0.11	3.12	28.73
04/08/2005	3	3.24	0.04	0.13	3.11	28.67
05/08/2005	4	3.29	0.03	0.14	3.15	29.11
06/08/2005	5	3.31	0.05	0.15	3.15	29.11
07/08/2005	6	3.27	0.03	0.17	3.11	28.64
08/08/2005	7	3.30	0.04	0.17	3.13	28.86
12/08/2005	11	3.27	0.06	0.19	3.08	28.33
15/08/2005	14	3.17	0.05	0.10	3.07	28.28
18/08/2005	17	3.16	0.01	0.14	3.02	27.80
23/08/2005	22	3.22	0.02	0.09	3.13	28.85
08/09/2005	37	3.09	0.05	0.10	2.99	27.44
09/10/2005	67	3.12	0.02	0.11	3.01	27.69

Table 36 Ageing results for 2-FAL at pH 10 stored at 40 C for a period of 63 Days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	3.25	0.06	0.09	3.16	29.21
02/08/2005	1	3.30	0.06	0.11	3.19	29.50
03/08/2005	2	3.25	0.02	0.11	3.14	28.96
04/08/2005	3	3.23	0.01	0.12	3.11	28.66
05/08/2005	4	3.28	0.05	0.13	3.15	29.08
06/08/2005	5	3.34	0.05	0.14	3.20	29.52
07/08/2005	6	3.35	0.07	0.16	3.19	29.47
08/08/2005	7	3.30	0.07	0.16	3.14	28.93
12/08/2005	11	3.27	0.04	0.17	3.10	28.60
15/08/2005	14	3.17	0.03	0.07	3.09	28.49
18/08/2005	17	3.17	0.04	0.10	3.07	28.22
23/08/2005	22	3.26	0.06	0.07	3.19	29.46
08/09/2005	37	2.46	0.01	0.09	2.37	21.30
09/10/2005	67	2.21	0.03	0.16	2.05	18.05

Table 37 Ageing results for 2-FAL at pH 4.6 stored at 60 C for a period of 63 days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	3.20	0.01	0.10	3.10	28.57
02/08/2005	1	3.31	0.04	0.11	3.20	29.61
03/08/2005	2	3.24	0.05	0.11	3.14	28.93
04/08/2005	3	3.24	0.07	0.12	3.11	28.71
05/08/2005	4	3.28	0.02	0.13	3.15	29.06
06/08/2005	5	3.26	0.04	0.15	3.12	28.75
07/08/2005	6	3.29	0.05	0.16	3.13	28.89
08/08/2005	7	3.27	0.07	0.16	3.11	28.67
12/08/2005	11	3.26	0.07	0.17	3.09	28.43
15/08/2005	14	3.14	0.04	0.08	3.06	28.20
18/08/2005	17	3.09	0.03	0.11	2.98	27.40
23/08/2005	22	3.19	0.06	0.07	3.12	28.73
08/09/2005	37	2.38	0.01	0.08	2.31	20.64
09/10/2005	67	2.19	0.04	0.09	2.10	18.54

Table 38 Ageing results for 2-FAL at pH 6.8 stored at 60 C for a period of 63 Days of analysis.

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	3.24	0.01	0.09	3.14	29.00
02/08/2005	1	3.29	0.07	0.11	3.18	29.39
03/08/2005	2	3.24	0.05	0.11	3.12	28.80
04/08/2005	3	3.19	0.04	0.12	3.07	28.24
05/08/2005	4	3.23	0.03	0.14	3.09	28.46
06/08/2005	5	3.23	0.06	0.15	3.08	28.34
07/08/2005	6	3.17	0.06	0.16	3.00	27.61
08/08/2005	7	3.14	0.03	0.17	2.97	27.32
12/08/2005	11	2.85	0.02	0.18	2.67	24.30
15/08/2005	14	2.49	0.01	0.08	2.41	21.66
18/08/2005	17	2.28	0.01	0.12	2.16	19.20
23/08/2005	22	1.96	0.01	0.08	1.87	16.31
08/09/2005	37	0.72	0.00	0.09	0.63	3.88
09/10/2005	67	0.74	0.00	0.13	0.60	3.61

Table 39 Ageing results for 2-FAL at pH 10 stored at 60 C for a period of 63 days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	3.25	0.06	0.09	3.16	29.21
02/08/2005	1	3.35	0.03	0.10	3.25	30.04
03/08/2005	2	3.25	0.06	0.12	3.13	28.88
04/08/2005	3	3.27	0.03	0.14	3.13	28.86
05/08/2005	4	3.30	0.08	0.15	3.15	29.09
06/08/2005	5	3.34	0.02	0.18	3.17	29.24
07/08/2005	6	3.34	0.03	0.19	3.15	29.08
08/08/2005	7	3.36	0.09	0.23	3.14	28.95
12/08/2005	11	3.26	0.06	0.25	3.01	27.71
15/08/2005	14	3.12	0.04	0.16	2.96	27.18
18/08/2005	17	3.13	0.03	0.33	2.79	25.50
23/08/2005	22	3.23	0.06	0.20	3.04	27.95
08/09/2005	37	3.09	0.05	0.20	2.90	26.55
09/10/2005	67	3.03	0.04	0.19	2.85	26.05

Table 40 Ageing results for 2-FAL at pH 4.6 stored at 80 C for a period of 63 Days of analysis.

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
01/08/2005	0	3.20	0.01	0.10	3.10	28.57
02/08/2005	1	3.29	0.05	0.15	3.15	29.05
03/08/2005	2	3.24	0.04	0.12	3.12	28.80
04/08/2005	3	3.20	0.03	0.13	3.07	28.27
05/08/2005	4	3.27	0.00	0.15	3.13	28.83
06/08/2005	5	3.29	0.04	0.16	3.13	28.83
07/08/2005	6	3.24	0.04	0.17	3.07	28.28
08/08/2005	7	3.29	0.03	0.18	3.11	28.67
12/08/2005	11	3.19	0.03	0.19	3.00	27.60
15/08/2005	14	3.15	0.04	0.09	3.05	28.09
18/08/2005	17	3.12	0.03	0.14	2.98	27.38
23/08/2005	22	3.23	0.05	0.09	3.13	28.92
08/09/2005	37	3.08	0.02	0.10	2.98	27.37
09/10/2005	67	3.07	0.04	0.11	2.96	27.13

Table 41 Ageing results for 2-FAL at pH 6.8 stored at 80 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM 30
01/08/2005	0	3.24	0.01	0.09	3.14	29.00
02/08/2005	1	2.97	0.01	0.12	2.85	26.03
03/08/2005	2	2.28	0.01	0.11	2.17	19.23
04/08/2005	3	1.79	0.01	0.13	1.66	14.13
05/08/2005	4	1.28	0.00	0.15	1.13	8.85
06/08/2005	5	1.00	0.00	0.16	0.83	5.91
07/08/2005	6	0.85	0.00	0.18	0.68	4.36
08/08/2005	7	0.76	0.00	0.19	0.57	3.23
12/08/2005	11	0.52	0.00	0.24	0.28	0.38
15/08/2005	14	0.37	0.00	0.18	0.19	-0.54
18/08/2005	17	0.30	0.00	0.24	0.07	-1.78
23/08/2005	22	0.44	0.00	0.29	0.15	-0.97
08/09/2005	37	0.31	0.00	0.06	0.24	0.00
09/10/2005	67	0.00	0.00	0.00	0.00	0.00

Table 42 Ageing results for 2-FAL at pH 10 stored at 80 C for a period of 63 days of analysis.

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.43	0.02	0.05	2.38	28.42
02/08/2005	1	2.41	0.02	0.13	2.28	27.32
03/08/2005	2	2.40	0.01	0.09	2.32	27.69
04/08/2005	3	2.52	0.02	0.15	2.36	28.25
05/08/2005	4	2.44	0.02	0.17	2.28	27.21
06/08/2005	5	2.47	0.03	0.17	2.30	27.50
07/08/2005	6	2.47	0.02	0.18	2.30	27.45
08/08/2005	7	2.49	0.01	0.18	2.31	27.60
12/08/2005	11	2.45	0.01	0.19	2.26	27.06
15/08/2005	14	2.46	0.02	0.10	2.35	28.15
18/08/2005	17	2.35	0.01	0.17	2.18	26.06
23/08/2005	22	2.43	0.01	0.10	2.34	27.95
08/09/2005	37	2.42	0.01	0.10	2.33	27.83
09/10/2005	67	2.49	0.01	0.12	2.37	28.38

Table 43 Ageing results for 2-ACF at pH 4.6 stored at 0 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.42	0.02	0.05	2.38	28.42
02/08/2005	1	2.42	0.01	0.12	2.30	27.50
03/08/2005	2	2.39	0.02	0.09	2.31	27.60
04/08/2005	3	2.54	0.01	0.14	2.40	28.75
05/08/2005	4	2.54	0.02	0.15	2.39	28.63
06/08/2005	5	2.55	0.02	0.16	2.39	28.62
07/08/2005	6	2.55	0.01	0.17	2.38	28.52
08/08/2005	7	2.53	0.02	0.17	2.37	28.31
12/08/2005	11	2.50	0.00	0.18	2.31	27.67
15/08/2005	14	2.31	0.01	0.10	2.22	26.49
18/08/2005	17	2.21	0.00	0.15	2.06	24.63
23/08/2005	22	2.12	0.01	0.09	2.04	24.34
08/09/2005	37	1.98	0.01	0.09	1.89	22.57
09/10/2005	67	1.84	0.01	0.23	1.61	19.16

Table 44 Ageing results for 2-ACF at pH 6.8 stored at 0 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.40	0.01	0.05	2.35	28.15
02/08/2005	1	2.39	0.01	0.11	2.28	27.21
03/08/2005	2	2.53	0.01	0.06	2.46	29.48
04/08/2005	3	2.55	0.01	0.14	2.41	28.87
05/08/2005	4	2.56	0.01	0.15	2.42	28.92
06/08/2005	5	2.56	0.02	0.16	2.40	28.66
07/08/2005	6	2.59	0.01	0.16	2.42	28.97
08/08/2005	7	2.57	0.01	0.17	2.40	28.70
12/08/2005	11	2.55	0.02	0.18	2.37	28.37
15/08/2005	14	2.46	0.01	0.09	2.37	28.32
18/08/2005	17	2.48	0.01	0.14	2.34	27.97
23/08/2005	22	2.49	0.01	0.08	2.41	28.78
08/09/2005	37	2.42	0.01	0.09	2.34	27.97
09/10/2005	67	2.46	0.02	0.16	2.29	27.40

Table 45 Ageing results for 2-ACF at pH 10 stored at 0 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.43	0.02	0.05	2.38	28.42
02/08/2005	1	2.55	0.01	0.12	2.43	29.03
03/08/2005	2	2.51	0.01	0.08	2.43	29.09
04/08/2005	3	2.55	0.03	0.13	2.42	28.96
05/08/2005	4	2.55	0.02	0.14	2.41	28.85
06/08/2005	5	2.57	0.02	0.15	2.41	28.88
07/08/2005	6	2.56	0.00	0.16	2.40	28.70
08/08/2005	7	2.53	0.01	0.15	2.38	28.45
12/08/2005	11	2.55	0.01	0.16	2.38	28.52
15/08/2005	14	2.45	0.01	0.08	2.38	28.42
18/08/2005	17	2.45	0.02	0.13	2.32	27.70
23/08/2005	22	2.44	0.01	0.07	2.37	28.38
08/09/2005	37	2.42	0.01	0.07	2.35	28.05
09/10/2005	67	2.48	0.02	0.09	2.39	28.57

Table 46 Ageing results for 2-ACF at pH 4.6 stored at 40 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.42	0.02	0.05	2.38	28.42
02/08/2005	1	2.53	0.02	0.12	2.41	28.79
03/08/2005	2	2.50	0.01	0.08	2.42	28.89
04/08/2005	3	2.54	0.03	0.13	2.42	28.89
05/08/2005	4	2.53	0.01	0.14	2.39	28.64
06/08/2005	5	2.56	0.01	0.15	2.41	28.81
07/08/2005	6	2.57	0.01	0.16	2.41	28.78
08/08/2005	7	2.48	0.13	0.18	2.30	27.51
12/08/2005	11	2.53	0.01	0.21	2.32	27.70
15/08/2005	14	2.45	0.02	0.14	2.31	27.62
18/08/2005	17	2.43	0.02	0.18	2.25	26.92
23/08/2005	22	2.42	0.01	0.12	2.30	27.47
08/09/2005	37	2.36	0.02	0.15	2.22	26.48
09/10/2005	67	2.40	0.02	0.21	2.18	26.08

Table 47 Ageing results for 2-ACF at pH 6.8 stored at 40 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.40	0.01	0.05	2.35	28.15
02/08/2005	1	2.57	0.01	0.11	2.46	29.42
03/08/2005	2	2.51	0.01	0.07	2.44	29.25
04/08/2005	3	2.55	0.02	0.14	2.41	28.86
05/08/2005	4	2.55	0.03	0.15	2.40	28.75
06/08/2005	5	2.56	0.01	0.16	2.40	28.72
07/08/2005	6	2.55	0.01	0.16	2.39	28.57
08/08/2005	7	2.54	0.02	0.17	2.38	28.41
12/08/2005	11	2.55	0.03	0.18	2.36	28.28
15/08/2005	14	2.43	0.01	0.10	2.33	27.87
18/08/2005	17	2.45	0.01	0.15	2.30	27.47
23/08/2005	22	2.42	0.01	0.09	2.32	27.79
08/09/2005	37	2.40	0.02	0.10	2.30	27.50
09/10/2005	67	2.42	0.02	0.14	2.29	27.34

Table 48 Ageing results for 2-ACF at pH 10 stored at 40 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.43	0.02	0.05	2.38	28.42
02/08/2005	1	2.56	0.02	0.12	2.44	29.17
03/08/2005	2	2.52	0.02	0.09	2.43	29.09
04/08/2005	3	2.60	0.02	0.13	2.47	29.59
05/08/2005	4	2.56	0.01	0.14	2.42	28.98
06/08/2005	5	2.55	0.02	0.15	2.40	28.69
07/08/2005	6	2.54	0.02	0.15	2.38	28.51
08/08/2005	7	2.55	0.03	0.15	2.40	28.66
12/08/2005	11	2.54	0.02	0.16	2.38	28.50
15/08/2005	14	2.44	0.02	0.08	2.36	28.21
18/08/2005	17	2.44	0.01	0.14	2.30	27.50
23/08/2005	22	2.43	0.02	0.07	2.35	28.16
08/09/2005	37	2.39	0.01	0.08	2.30	27.54
09/10/2005	67	2.42	0.01	0.16	2.26	27.00

Table 49 Ageing results for 2-ACF at pH 4.6 stored at 60 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.42	0.02	0.05	2.38	28.42
02/08/2005	1	2.54	0.01	0.12	2.42	28.99
03/08/2005	2	2.50	0.01	0.08	2.42	28.91
04/08/2005	3	2.56	0.01	0.13	2.43	29.06
05/08/2005	4	2.53	0.01	0.14	2.39	28.57
06/08/2005	5	2.56	0.01	0.15	2.41	28.83
07/08/2005	6	2.56	0.02	0.16	2.40	28.69
08/08/2005	7	2.54	0.02	0.15	2.39	28.62
12/08/2005	11	2.53	0.03	0.16	2.36	28.27
15/08/2005	14	2.43	0.02	0.08	2.34	28.03
18/08/2005	17	2.43	0.01	0.13	2.30	27.56
23/08/2005	22	2.41	0.01	0.07	2.34	27.96
08/09/2005	37	2.37	0.01	0.07	2.30	27.46
09/10/2005	67	2.39	0.02	0.10	2.29	27.35

Table 50 Ageing results for 2-ACF at pH 6.8 stored at 60 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.40	0.01	0.05	2.35	28.15
02/08/2005	1	2.54	0.02	0.11	2.43	29.10
03/08/2005	2	2.50	0.02	0.05	2.45	29.29
04/08/2005	3	2.52	0.02	0.14	2.38	28.52
05/08/2005	4	2.50	0.01	0.14	2.35	28.16
06/08/2005	5	2.48	0.01	0.16	2.32	27.76
07/08/2005	6	2.50	0.02	0.16	2.33	27.89
08/08/2005	7	2.50	0.02	0.16	2.34	27.93
12/08/2005	11	2.44	0.01	0.17	2.27	27.08
15/08/2005	14	2.30	0.01	0.09	2.21	26.45
18/08/2005	17	2.26	0.01	0.14	2.12	25.31
23/08/2005	22	2.20	0.01	0.08	2.12	25.38
08/09/2005	37	2.00	0.01	0.09	1.92	22.86
09/10/2005	67	1.76	0.00	0.13	1.63	19.46

Table 51 Ageing results for 2-ACF at pH 10 stored at 60 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.43	0.02	0.05	2.38	28.42
02/08/2005	1	2.57	0.01	0.12	2.45	29.27
03/08/2005	2	2.51	0.01	0.09	2.43	29.04
04/08/2005	3	2.55	0.02	0.14	2.40	28.74
05/08/2005	4	2.53	0.02	0.17	2.36	28.24
06/08/2005	5	2.54	0.01	0.18	2.36	28.28
07/08/2005	6	2.52	0.01	0.20	2.33	27.84
08/08/2005	7	2.52	0.02	0.20	2.32	27.71
12/08/2005	11	2.52	0.02	0.23	2.29	27.33
15/08/2005	14	2.41	0.02	0.17	2.23	26.69
18/08/2005	17	2.39	0.01	0.13	2.26	27.02
23/08/2005	22	2.37	0.02	0.17	2.20	26.29
08/09/2005	37	2.28	0.01	0.15	2.13	25.49
09/10/2005	67	1.93	0.03	0.09	1.84	21.99

Table 52 Ageing results for 2-ACF at pH 4.6 stored at 80 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.42	0.02	0.05	2.38	28.42
02/08/2005	1	2.55	0.02	0.11	2.44	29.21
03/08/2005	2	2.46	0.03	0.08	2.38	28.44
04/08/2005	3	2.55	0.02	0.15	2.40	28.69
05/08/2005	4	2.50	0.02	0.16	2.34	28.00
06/08/2005	5	2.53	0.00	0.17	2.35	28.16
07/08/2005	6	2.53	0.01	0.18	2.35	28.11
08/08/2005	7	2.49	0.02	0.17	2.32	27.72
12/08/2005	11	2.47	0.02	0.18	2.29	27.39
15/08/2005	14	2.39	0.01	0.09	2.30	27.52
18/08/2005	17	2.35	0.02	0.14	2.21	26.45
23/08/2005	22	2.31	0.01	0.09	2.22	26.55
08/09/2005	37	2.28	0.02	0.09	2.18	26.08
09/10/2005	67	2.21	0.01	0.12	2.09	24.90

Table 53 Ageing results for 2-ACF at pH 6.8 stored at 80 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
	0					30
01/08/2005	0	2.40	0.01	0.05	2.35	28.15
02/08/2005	1	2.52	0.01	0.11	2.40	28.75
03/08/2005	2	2.41	0.02	0.08	2.34	27.92
04/08/2005	3	2.18	0.01	0.14	2.04	24.36
05/08/2005	4	2.07	0.01	0.16	1.91	22.84
06/08/2005	5	1.98	0.01	0.17	1.81	21.60
07/08/2005	6	1.87	0.01	0.18	1.69	20.13
08/08/2005	7	1.80	0.02	0.19	1.60	19.10
12/08/2005	11	1.51	0.00	0.22	1.29	15.32
15/08/2005	14	1.20	0.00	0.17	1.03	12.17
18/08/2005	17	0.99	0.00	0.24	0.75	8.77
23/08/2005	22	0.87	0.01	0.26	0.61	7.09
08/09/2005	37	0.55	0.00	0.07	0.49	5.59
09/10/2005	67	0.00	0.00	0.00	0.00	-0.28

Table 54 Ageing results for 2-ACF at pH 10 stored at 80 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.10	2.34	29.64
02/08/2005	1	2.40	0.02	0.10	2.30	29.06
03/08/2005	2	2.45	0.01	0.11	2.34	29.55
04/08/2005	3	2.52	0.02	0.15	2.36	29.87
05/08/2005	4	2.44	0.02	0.17	2.28	28.77
06/08/2005	5	2.47	0.03	0.17	2.30	29.08
07/08/2005	6	2.47	0.02	0.18	2.30	29.03
08/08/2005	7	2.49	0.01	0.18	2.31	29.18
12/08/2005	11	2.45	0.01	0.19	2.26	28.61
15/08/2005	14	2.46	0.02	0.10	2.35	29.76
18/08/2005	17	2.35	0.01	0.17	2.18	27.56
23/08/2005	22	2.43	0.01	0.10	2.34	29.55
08/09/2005	37	2.42	0.01	0.10	2.33	29.42
09/10/2005	67	2.49	0.01	0.12	2.37	30.01

Table 55 Ageing results for 5-MEF at pH 4.6 stored at 0 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.29	28.94
02/08/2005	1	2.51	0.01	0.11	2.40	30.37
03/08/2005	2	2.52	0.02	0.12	2.40	30.33
04/08/2005	3	2.54	0.01	0.14	2.40	30.40
05/08/2005	4	2.54	0.02	0.15	2.39	30.27
06/08/2005	5	2.55	0.02	0.16	2.39	30.26
07/08/2005	6	2.55	0.01	0.17	2.38	30.15
08/08/2005	7	2.53	0.02	0.17	2.37	29.93
12/08/2005	11	2.50	0.00	0.18	2.31	29.26
15/08/2005	14	2.31	0.01	0.10	2.22	28.01
18/08/2005	17	2.21	0.00	0.15	2.06	26.06
23/08/2005	22	2.12	0.01	0.09	2.04	25.75
08/09/2005	37	1.98	0.01	0.09	1.89	23.88
09/10/2005	67	1.84	0.01	0.23	1.61	20.29

Table 56 Ageing results for 5-MEF at pH 6.8 stored at 0 C for a period of 63 of days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.30	29.05
02/08/2005	1	2.52	0.02	0.11	2.41	30.53
03/08/2005	2	2.54	0.02	0.12	2.41	30.54
04/08/2005	3	2.55	0.02	0.14	2.41	30.52
05/08/2005	4	2.56	0.02	0.15	2.42	30.57
06/08/2005	5	2.56	0.02	0.16	2.40	30.30
07/08/2005	6	2.59	0.03	0.16	2.42	30.63
08/08/2005	7	2.57	0.02	0.17	2.40	30.34
12/08/2005	11	2.55	0.02	0.18	2.37	30.00
15/08/2005	14	2.46	0.01	0.09	2.37	29.94
18/08/2005	17	2.48	0.01	0.14	2.34	29.57
23/08/2005	22	2.49	0.02	0.08	2.41	30.42
08/09/2005	37	2.42	0.02	0.09	2.34	29.58
09/10/2005	67	2.46	0.01	0.16	2.29	28.98

Table 57 Ageing results for 5-MEF at pH 10 stored at 0 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.10	2.34	29.64
02/08/2005	1	2.53	0.01	0.10	2.43	30.75
03/08/2005	2	2.53	0.01	0.11	2.42	30.66
04/08/2005	3	2.55	0.03	0.13	2.42	30.61
05/08/2005	4	2.55	0.02	0.14	2.41	30.50
06/08/2005	5	2.57	0.02	0.15	2.41	30.53
07/08/2005	6	2.56	0.00	0.16	2.40	30.34
08/08/2005	7	2.53	0.01	0.15	2.38	30.08
12/08/2005	11	2.55	0.01	0.16	2.38	30.15
15/08/2005	14	2.45	0.01	0.08	2.38	30.05
18/08/2005	17	2.45	0.02	0.13	2.32	29.29
23/08/2005	22	2.44	0.01	0.07	2.37	30.01
08/09/2005	37	2.42	0.01	0.07	2.35	29.66
09/10/2005	67	2.48	0.02	0.09	2.39	30.21

Table 58 Ageing results for 5-MEF at pH 4.6 stored at 40 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.29	28.94
02/08/2005	1	2.52	0.01	0.10	2.41	30.52
03/08/2005	2	2.52	0.01	0.11	2.41	30.43
04/08/2005	3	2.54	0.03	0.13	2.42	30.54
05/08/2005	4	2.53	0.01	0.14	2.39	30.27
06/08/2005	5	2.56	0.01	0.15	2.41	30.45
07/08/2005	6	2.57	0.01	0.16	2.41	30.43
08/08/2005	7	2.48	0.13	0.18	2.30	29.09
12/08/2005	11	2.53	0.01	0.21	2.32	29.28
15/08/2005	14	2.45	0.02	0.14	2.31	29.21
18/08/2005	17	2.43	0.02	0.18	2.25	28.47
23/08/2005	22	2.42	0.01	0.12	2.30	29.05
08/09/2005	37	2.36	0.02	0.15	2.22	28.00
09/10/2005	67	2.40	0.02	0.21	2.18	27.58

Table 59 Ageing results for 5-MEF at pH 6.8 stored at 40 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.30	29.05
02/08/2005	1	2.48	0.01	0.11	2.38	30.03
03/08/2005	2	2.52	0.01	0.12	2.39	30.28
04/08/2005	3	2.55	0.02	0.14	2.41	30.51
05/08/2005	4	2.55	0.03	0.15	2.40	30.39
06/08/2005	5	2.56	0.01	0.16	2.40	30.37
07/08/2005	6	2.55	0.01	0.16	2.39	30.20
08/08/2005	7	2.54	0.02	0.17	2.38	30.04
12/08/2005	11	2.55	0.03	0.18	2.36	29.90
15/08/2005	14	2.43	0.01	0.10	2.33	29.47
18/08/2005	17	2.45	0.01	0.15	2.30	29.05
23/08/2005	22	2.42	0.01	0.09	2.32	29.39
08/09/2005	37	2.40	0.02	0.10	2.30	29.07
09/10/2005	67	2.42	0.02	0.14	2.29	28.91

Table 60 Ageing results for 5-MEF at pH 10 stored at 40 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.10	2.34	29.64
02/08/2005	1	2.52	0.01	0.10	2.42	30.54
03/08/2005	2	2.53	0.02	0.11	2.41	30.52
04/08/2005	3	2.60	0.02	0.13	2.47	31.28
05/08/2005	4	2.56	0.01	0.14	2.42	30.63
06/08/2005	5	2.55	0.02	0.15	2.40	30.33
07/08/2005	6	2.54	0.02	0.15	2.38	30.14
08/08/2005	7	2.55	0.03	0.15	2.40	30.30
12/08/2005	11	2.54	0.02	0.16	2.38	30.13
15/08/2005	14	2.44	0.02	0.08	2.36	29.82
18/08/2005	17	2.44	0.01	0.14	2.30	29.08
23/08/2005	22	2.43	0.02	0.07	2.35	29.77
08/09/2005	37	2.39	0.01	0.08	2.30	29.12
09/10/2005	67	2.42	0.01	0.16	2.26	28.55

Table 61 Ageing results for 5-MEF at pH 4.6 stored at 60 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.29	28.94
02/08/2005	1	2.50	0.02	0.10	2.39	30.25
03/08/2005	2	2.53	0.02	0.12	2.42	30.54
04/08/2005	3	2.56	0.01	0.13	2.43	30.72
05/08/2005	4	2.53	0.01	0.14	2.39	30.20
06/08/2005	5	2.56	0.01	0.15	2.41	30.48
07/08/2005	6	2.56	0.02	0.16	2.40	30.33
08/08/2005	7	2.54	0.02	0.15	2.39	30.26
12/08/2005	11	2.53	0.03	0.16	2.36	29.89
15/08/2005	14	2.43	0.02	0.08	2.34	29.63
18/08/2005	17	2.43	0.01	0.13	2.30	29.14
23/08/2005	22	2.41	0.01	0.07	2.34	29.56
08/09/2005	37	2.37	0.01	0.07	2.30	29.04
09/10/2005	67	2.39	0.02	0.10	2.29	28.92

Table 62 Ageing results for 5-MEF at pH 6.8 stored at 60 C for period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.30	29.05
02/08/2005	1	2.49	0.01	0.11	2.38	30.06
03/08/2005	2	2.51	0.01	0.12	2.38	30.13
04/08/2005	3	2.52	0.02	0.14	2.38	30.15
05/08/2005	4	2.50	0.01	0.14	2.35	29.77
06/08/2005	5	2.48	0.01	0.16	2.32	29.36
07/08/2005	6	2.50	0.02	0.16	2.33	29.49
08/08/2005	7	2.50	0.02	0.16	2.34	29.53
12/08/2005	11	2.44	0.01	0.17	2.27	28.64
15/08/2005	14	2.30	0.01	0.09	2.21	27.97
18/08/2005	17	2.26	0.01	0.14	2.12	26.77
23/08/2005	22	2.20	0.01	0.08	2.12	26.85
08/09/2005	37	2.00	0.01	0.09	1.92	24.19
09/10/2005	67	1.76	0.00	0.13	1.63	20.61

Table 63 Ageing results for 5-MEF at pH 10 stored at 60 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.10	2.34	29.64
02/08/2005	1	2.51	0.00	0.12	2.39	30.27
03/08/2005	2	2.54	0.01	0.13	2.41	30.47
04/08/2005	3	2.55	0.02	0.14	2.40	30.39
05/08/2005	4	2.53	0.02	0.17	2.36	29.86
06/08/2005	5	2.54	0.01	0.18	2.36	29.90
07/08/2005	6	2.52	0.01	0.20	2.33	29.44
08/08/2005	7	2.52	0.02	0.20	2.32	29.30
12/08/2005	11	2.52	0.02	0.23	2.29	28.90
15/08/2005	14	2.41	0.02	0.17	2.23	28.23
18/08/2005	17	2.39	0.01	0.13	2.26	28.57
23/08/2005	22	2.37	0.02	0.17	2.20	27.81
08/09/2005	37	2.28	0.01	0.15	2.13	26.96
09/10/2005	67	1.93	0.03	0.09	1.84	23.28

Table 64 Ageing results for 5-MEF at pH 4.6 stored at 80 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.29	28.94
02/08/2005	1	2.48	0.01	0.13	2.35	29.72
03/08/2005	2	2.52	0.01	0.13	2.39	30.22
04/08/2005	3	2.55	0.02	0.15	2.40	30.33
05/08/2005	4	2.50	0.02	0.16	2.34	29.61
06/08/2005	5	2.53	0.00	0.17	2.35	29.77
07/08/2005	6	2.53	0.01	0.18	2.35	29.72
08/08/2005	7	2.49	0.02	0.17	2.32	29.31
12/08/2005	11	2.47	0.02	0.18	2.29	28.96
15/08/2005	14	2.39	0.01	0.09	2.30	29.10
18/08/2005	17	2.35	0.02	0.14	2.21	27.97
23/08/2005	22	2.31	0.01	0.09	2.22	28.08
08/09/2005	37	2.28	0.02	0.09	2.18	27.59
09/10/2005	67	2.21	0.01	0.12	2.09	26.34

Table 65 Ageing results for 5-MEF at pH 6.8 stored at 80 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.44	0.01	0.15	2.30	29.05
02/08/2005	1	2.37	0.01	0.11	2.26	28.56
03/08/2005	2	2.28	0.01	0.13	2.16	27.25
04/08/2005	3	2.18	0.01	0.14	2.04	25.77
05/08/2005	4	2.07	0.01	0.16	1.91	24.17
06/08/2005	5	1.98	0.01	0.17	1.81	22.86
07/08/2005	6	1.87	0.01	0.18	1.69	21.32
08/08/2005	7	1.80	0.02	0.19	1.60	20.22
12/08/2005	11	1.51	0.00	0.22	1.29	16.25
15/08/2005	14	1.20	0.00	0.17	1.03	12.93
18/08/2005	17	0.99	0.00	0.24	0.75	9.34
23/08/2005	22	0.87	0.01	0.26	0.61	7.57
08/09/2005	37	0.55	0.00	0.07	0.49	6.00
09/10/2005	67	0.00	0.00	0.00	0.00	-0.19

Table 66 Ageing results for 5-MEF at pH 10 stored at 80 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.48862	0.014	1.8409	0.64772	9.9965385
01/08/2005	1	2.4694	0.013	1.8747	0.5947	8.9769231
02/08/2005	2	2.4806	0.017	1.8957	0.5849	8.7884615
03/08/2005	3	2.55792	0.009	1.9026	0.65532	10.142692
04/08/2005	4	2.48616	0.014	1.8333	0.65286	10.095385
05/08/2005	5	2.5014	0.008	1.799	0.7024	11.048077
06/08/2005	6	2.5166	0.014	1.804	0.7126	11.244231
07/08/2005	7	2.54786	0.024	1.8074	0.74046	11.78
10/08/2005	10	2.53974	0.020	1.7204	0.81934	13.296923
13/08/2005	13	2.43758	0.012	1.7083	0.72928	11.565
16/08/2005	16	2.44942	0.018	1.5284	0.92102	15.252308
19/08/2005	19	2.32178	0.029	1.4707	0.85108	13.907308
22/08/2005	21	2.41804	0.013	1.4561	0.96194	16.039231
30/08/2005	25	2.42456	0.030	1.3724	1.05216	17.774231
06/09/2005	31	2.44452	0.015	1.4662	0.97832	16.354231
09/10/2005	63	2.45	0.020	1.4294	1.0206	17.167308

Table 67 Ageing results for FOL at pH 4.6 stored at 0 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	1.80052	0.015	0.069	1.73152	30.838846
01/08/2005	1	1.97308	0.014	0.2143	1.75878	31.363077
02/08/2005	2	2.01756	0.017	0.2272	1.79036	31.970385
03/08/2005	3	2.0966	0.015	0.3171	1.7795	31.761538
04/08/2005	4	2.07552	0.013	0.3959	1.67962	29.840769
05/08/2005	5	2.03994	0.004	0.4063	1.63364	28.956538
06/08/2005	6	2.04824	0.008	0.5318	1.51644	26.702692
07/08/2005	7	2.04734	0.014	0.6179	1.42944	25.029615
10/08/2005	10	2.08842	0.010	0.7405	1.34792	23.461923
13/08/2005	13	1.99668	0.023	0.9039	1.09278	18.555385
16/08/2005	16	2.01286	0.010	0.8353	1.17756	20.185769
19/08/2005	19	1.8242	0.014	0.8761	0.9481	15.773077
22/08/2005	21	1.92942	0.009	0.9474	0.98202	16.425385
30/08/2005	25	1.9854	0.007	0.9282	1.0572	17.871154
06/09/2005	31	1.99878	0.007	1.0266	0.97218	16.236154
09/10/2005	63	2.01418	0.014	1.1182	0.89598	14.770769

Table 68 Ageing results for FOL at pH 6.8 stored at 0 C for a period 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
31/07/2005	0	2.3119	0.024	1.0981	1.2138	20.882692
01/08/2005	1	2.33102	0.012	0.9223	1.40872	24.631154
02/08/2005	2	2.33766	0.015	0.965	1.37266	23.937692
03/08/2005	3	2.37826	0.014	0.87798	1.50028	26.391923
04/08/2005	4	2.32758	0.010	0.7942	1.53338	27.028462
05/08/2005	5	2.33726	0.009	0.7995	1.53776	27.112692
06/08/2005	6	2.3399	0.016	0.7215	1.6184	28.663462
07/08/2005	7	2.35756	0.022	0.7406	1.61696	28.635769
10/08/2005	10	2.35236	0.018	0.6619	1.69046	30.049231
13/08/2005	13	2.27722	0.023	0.6196	1.65762	29.417692
16/08/2005	16	2.29408	0.007	0.4525	1.84158	32.955385
19/08/2005	19	2.1265	0.010	0.4131	1.7134	30.490385
22/08/2005	21	2.24818	0.006	0.3578	1.89038	33.893846
30/08/2005	25	2.25766	0.015	0.3565	1.90116	34.101154
06/09/2005	31	2.27986	0.008	0.3435	1.93636	34.778077
09/10/2005	63	2.31926	0.013	0.3496	1.96966	35.418462

Table 69 Ageing results for FOL at pH 10 stored at 0 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.48862	0.014	1.8409	0.64772	9.9965385
02/08/2005	1	2.39616	0.023	1.8689	0.52726	7.68
03/08/2005	2	2.50348	0.027	1.8994	0.60408	9.1573077
04/08/2005	3	2.52472	0.019	1.9463	0.57842	8.6638462
05/08/2005	4	2.49676	0.008	1.922	0.57476	8.5934615
06/08/2005	5	2.52124	0.003	1.9085	0.61274	9.3238462
07/08/2005	6	2.54578	0.030	1.9358	0.60998	9.2707692
10/08/2005	9	2.52704	0.021	1.9626	0.56444	8.395
13/08/2005	10	2.56706	0.022	1.9312	0.63586	9.7684615
16/08/2005	15	2.4911	0.025	1.9885	0.5026	7.2057692
19/08/2005	18	2.47894	0.015	1.831	0.64794	10.000769
22/08/2005	21	2.33652	0.024	1.8128	0.52372	7.6119231
30/08/2005	28	2.43722	0.022	1.7861	0.65112	10.061923
06/09/2005	31	2.45264	0.036	1.7966	0.65604	10.156538
09/10/2005	63	2.45302	0.023	1.8132	0.63982	9.8446154

Table 70 Ageing results for FOL at pH 4.6 stored at 40 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	1.80052	0.015	0.069	1.73152	30.838846
02/08/2005	1	2.00702	0.011	0.1755	1.83152	32.761923
03/08/2005	2	2.04046	0.004	0.2246	1.81586	32.460769
04/08/2005	3	2.07448	0.009	0.2117	1.86278	33.363077
05/08/2005	4	2.06124	0.004	0.2304	1.83084	32.748846
06/08/2005	5	2.0364	0.003	0.2458	1.7906	31.975
07/08/2005	6	2.04828	0.010	0.2832	1.76508	31.484231
10/08/2005	9	2.05172	0.012	0.3469	1.70482	30.325385
13/08/2005	10	2.06056	0.013	0.3819	1.67866	29.822308
16/08/2005	15	2.00346	0.007	0.4635	1.53996	27.155
19/08/2005	18	1.98524	0.012	0.3618	1.62344	28.760385
22/08/2005	21	1.8196	0.010	0.3871	1.4325	25.088462
30/08/2005	25	1.93192	0.005	0.4408	1.49112	26.215769
06/09/2005	31	1.95228	0.011	0.3744	1.57788	27.884231
09/10/2005	63	1.95	0.011	0.4523	1.4977	26.34

Table 71 Ageing results for FOL at pH 6.8 stored at 40 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.3119	0.024	1.0981	1.2138	20.882692
02/08/2005	1	2.31026	0.015	0.9223	1.38796	24.231923
03/08/2005	2	2.35634	0.008	0.8897	1.46664	25.745
04/08/2005	3	2.3502	0.024	0.9314	1.4188	24.825
05/08/2005	4	2.3359	0.014	0.9147	1.4212	24.871154
06/08/2005	5	2.35366	0.009	0.9309	1.42276	24.901154
07/08/2005	6	2.34626	0.009	0.9301	1.41616	24.774231
10/08/2005	9	2.36026	0.010	0.9551	1.40516	24.562692
13/08/2005	10	2.38094	0.011	0.9698	1.41114	24.677692
16/08/2005	15	2.29032	0.015	0.9588	1.33152	23.146538
19/08/2005	18	2.30116	0.017	0.8327	1.46846	25.78
22/08/2005	21	2.11402	0.005	0.8008	1.31322	22.794615
30/08/2005	25	2.25958	0.021	0.7752	1.48438	26.086154
06/09/2005	31	2.28052	0.010	0.7717	1.50882	26.556154
09/10/2005	63	2.2574	0.021	0.8229	1.4345	25.126923

Table 72 Ageing results for FOL at pH 10 stored at 40 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.48862	0.014	1.8409	0.64772	9.9965385
02/08/2005	1	2.41058	0.016	1.904	0.50658	7.2823077
03/08/2005	2	2.51262	0.013	1.9725	0.54012	7.9273077
04/08/2005	3	2.54842	0.013	1.9601	0.58832	8.8542308
05/08/2005	4	2.51518	0.032	1.9738	0.54138	7.9515385
06/08/2005	5	2.52848	0.009	1.965	0.56348	8.3765385
07/08/2005	6	2.5489	0.013	1.9944	0.5545	8.2038462
10/08/2005	9	2.56202	0.018	2.0646	0.49742	7.1061538
13/08/2005	10	2.56614	0.024	2.0623	0.50384	7.2296154
16/08/2005	15	2.4799	0.020	2.1035	0.3764	4.7788462
19/08/2005	18	2.49778	0.016	2.0125	0.48528	6.8726923
22/08/2005	21	2.35924	0.018	2.0173	0.34194	4.1161538
30/08/2005	28	2.46872	0.016	2.0415	0.42722	5.7561538
06/09/2005	31	2.48522	0.022	2.2069	0.27832	2.8926923
09/10/2005	63	2.49522	0.024	2.2742	0.22102	1.7907692

Table 73 Ageing results for FOL at pH 4.6 stored at 60 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	1.80052	0.015	0.069	1.73152	30.838846
02/08/2005	1	1.97578	0.010	0.1495	1.82628	32.661154
03/08/2005	2	2.02646	0.015	0.1825	1.84396	33.001154
04/08/2005	3	2.06574	0.011	0.1974	1.86834	33.47
05/08/2005	4	2.0633	0.012	0.2063	1.857	33.251923
06/08/2005	5	2.0294	0.002	0.2302	1.7992	32.140385
07/08/2005	6	2.03488	0.008	0.2489	1.78598	31.886154
10/08/2005	9	2.05742	0.013	0.3074	1.75002	31.194615
13/08/2005	10	2.04866	0.004	0.282	1.76666	31.514615
16/08/2005	15	1.96766	0.012	0.31	1.65766	29.418462
19/08/2005	18	1.977	0.008	0.1785	1.7985	32.126923
22/08/2005	21	1.8073	0.007	0.1801	1.6272	28.832692
30/08/2005	25	1.92836	0.005	0.1568	1.77156	31.608846
06/09/2005	31	1.93058	0.012	0.1609	1.76968	31.572692
09/10/2005	63	1.93108	0.009	0.1872	1.74388	31.076538

Table 74 Ageing results for FOL at pH 6.8 stored at 60 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.3119	0.024	1.0981	1.2138	20.882692
02/08/2005	1	2.31008	0.003	0.9223	1.38778	24.228462
03/08/2005	2	2.34186	0.019	0.9545	1.38736	24.220385
04/08/2005	3	2.3407	0.020	0.9602	1.3805	24.088462
05/08/2005	4	2.34302	0.006	0.9888	1.35422	23.583077
06/08/2005	5	2.34918	0.007	0.9715	1.37768	24.034231
07/08/2005	6	2.36166	0.015	0.9919	1.36976	23.881923
10/08/2005	9	2.35676	0.015	1.0118	1.34496	23.405
13/08/2005	10	2.3917	0.007	1.0613	1.3304	23.125
16/08/2005	15	2.29816	0.008	1.0517	1.24646	21.510769
19/08/2005	18	2.28784	0.019	0.9429	1.34494	23.404615
22/08/2005	21	2.13628	0.011	0.9293	1.20698	20.751538
30/08/2005	25	2.2568	0.017	0.8956	1.3612	23.717308
06/09/2005	31	2.28542	0.012	0.9468	1.33862	23.283077
09/10/2005	63	2.2675	0.025	0.9028	1.3647	23.784615

Table 75 Ageing results for FOL at pH 10 stored at 60 C for a period of 63 days of analysis

PH 4.6						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.48862	0.014	1.8409	0.64772	9.9965385
02/08/2005	1	2.42418	0.014	1.8577	0.56648	8.4342308
03/08/2005	2	2.53476	0.022	1.9827	0.55206	8.1569231
04/08/2005	3	2.55482	0.020	2.0684	0.48642	6.8946154
05/08/2005	4	2.56966	0.025	2.0904	0.47926	6.7569231
06/08/2005	5	2.57518	0.010	2.0985	0.47668	6.7073077
07/08/2005	6	2.60736	0.025	2.2222	0.38516	4.9473077
10/08/2005	9	2.61906	0.031	2.2806	0.33846	4.0492308
13/08/2005	10	2.64646	0.021	2.4921	0.15436	0.5088462
16/08/2005	15	2.59904	0.030	2.5919	0.00714	-2.3223077
19/08/2005	18	2.60384	0.015	2.5177	0.08614	-0.8030769
22/08/2005	21	2.45194	0.031	2.33889	0.11305	-0.2855769
30/08/2005	28	2.57132	0.016	2.5868	-0.01548	-2.7573077
06/09/2005	31	2.65134	0.025	2.6807	-0.02936	-3.0242308
09/10/2005	63	2.62634	0.018	2.6505	-0.02416	-2.9242308

Table 76 Ageing results for FOL at pH 4.6 stored at 80 C for a period of 63 days of analysis

PH 6.8						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	1.80052	0.015	0.069	1.73152	30.838846
02/08/2005	1	1.96916	0.006	0.1682	1.80096	32.174231
03/08/2005	2	2.03392	0.012	0.1875	1.84642	33.048462
04/08/2005	3	2.07342	0.011	0.1969	1.87652	33.627308
05/08/2005	4	2.05588	0.011	0.2169	1.83898	32.905385
06/08/2005	5	2.03486	0.008	0.2412	1.79366	32.033846
07/08/2005	6	2.03442	0.006	0.2622	1.77222	31.621538
10/08/2005	9	2.05696	0.018	0.3203	1.73666	30.937692
13/08/2005	10	2.05016	0.007	0.2989	1.75126	31.218462
16/08/2005	15	1.9935	0.015	0.3199	1.6736	29.725
19/08/2005	18	2.01042	0.017	0.1775	1.83292	32.788846
22/08/2005	21	1.87114	0.006	0.1818	1.68934	30.027692
30/08/2005	25	1.97938	0.014	0.1561	1.82328	32.603462
06/09/2005	31	2.0491	0.014	0.1654	1.8837	33.765385
09/10/2005	63	2.00466	0.006	0.2011	1.80356	32.224231

Table 77 Ageing results for FOL at pH 6.8 stored at 80 C for a period of 63 days of analysis

PH 10.0						
DATE OF MEASUREMENT	NO OF DAYS	MEAN OF ABS	STANDARD DEVIATION	ABS OF BUFFER	CORRECTED ABS	CONC PPM
01/08/2005	0	2.3119	0.024	1.0981	1.2138	20.882692
02/08/2005	1	2.37694	0.015	0.9223	1.45464	25.514231
03/08/2005	2	2.34028	0.016	0.9941	1.34618	23.428462
04/08/2005	3	2.3425	0.022	1.0111	1.3314	23.144231
05/08/2005	4	2.34154	0.019	1.0229	1.31864	22.898846
06/08/2005	5	2.34594	0.007	1.0361	1.30984	22.729615
07/08/2005	6	2.36812	0.003	1.086	1.28212	22.196538
10/08/2005	9	2.35394	0.021	1.1061	1.24784	21.537308
13/08/2005	10	2.39286	0.032	1.4171	0.97576	16.305
16/08/2005	15	2.31422	0.020	1.5972	0.71702	11.329231
19/08/2005	18	2.32952	0.020	1.7296	0.59992	9.0773077
22/08/2005	21	2.20646	0.016	2.0194	0.18706	1.1376923
30/08/2005	25	2.32484	0.022	2.509	-0.18416	-6.0011538
06/09/2005	31	2.49928	0.030	2.6999	-0.20062	-6.3176923
09/10/2005	63	2.37316	0.013	2.2159	0.15726	0.5646154

Table 78 Ageing results for FOL at pH 10 stored at 80 C for a period of 63 days of analysis