New Methodology Development for Quantification of Additive in Polyolefins Using Infrared Spectroscopy and X-ray Fluorescence Spectroscopy Analytical Techniques

A Major Project Report submitted in partial fulfillment for the award of the degree

Of

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IN

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Submitted by

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CERTIFICATE

This is to certify that the M.Tech major project entitled **"New Methodology Development for Quantification of Additive in Polyolefins Using Infrared Spectroscopy and X-ray Fluorescence Spectroscopy Analytical Techniques"**, submitted by **Gautam Ahuja**, for the award of the degree of **"Master of Technology in Polymer Technology"** is a record of bonafide work carried out by him. Gautam Ahuja has worked under our guidance and supervision and has fulfilled the requirements for the submission of the dissertation. The project work has been carried out during the session 2012-2013.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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DATE: **GAUTAM AHUJA**

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ABSTRACT

To ensure that the specified amount of an additive or combination of additives is incorporated into a polymer after the extrusion process, a rapid and accurate analytical method is required. Quantification of additives in the polymer is necessary, since the additives may degrade and the amount of additives can influence the physical nature of the polymer. The accurate and reliable measurement of antioxidant content in polymers by chromatographic techniques, e.g., liquid chromatography (LC) is an important tool in quality and manufacturing control, troubleshooting, and material or vendor identification. The major difficulty in the characterization is usually not the analytical method but rather the separation of the antioxidants from the polymer matrix. Conventional extraction techniques for polymer additives, such as, Soxhlet or dissolution / precipitation are labor intensive, time consuming, expensive, and the optimal recovery is significantly less than 90 percent. Therefore, more complex and efficient methods with the possibility of working at elevated temperatures and pressures have been developed, i.e., microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). The present research employs MAE for the extraction of additives, i.e. Irganox 1010 and Irgafos 168 from high density polyethylene (HDPE) followed by HPLC/UV concentration analysis. Further, calibration models have been devised against the HPLC concentration (reference) for the additives using Infrared spectroscopy & X-Ray Fluorescence characterization techniques. These calibration curves can be used for swift analysis of quantification of additives in HDPE without undergoing tedious extraction and chromatographic procedures during quality control.

AIM & OBJECTIVES

Following are the important objectives of the present research work:

a) Successful extraction of the additives (anti-oxidants) from polymers to attain high recovery percentages & in lesser time consumption, in contrast to the primitive extraction procedures.

b) Actual concentration determination of the extracted additives via HPLC analysis, and also monitor the effect of calcium stearate (acid scavenger) on consumption of anti-oxidants.

c) Generation of calibration curves by means of FTIR & XRF analysis techniques while using the HPLC concentration as the reference amount.

d) Thus utilizing these calibration models for direct quantitative analysis of the concerned additives in future aimed at rapid, accurate & uncomplicated quality control.

CHAPTER 1

INTRODUCTION

1.1 ADDITIVES IN POLYMERS

The importance of polymeric materials for various applications in everyday life has continuously increased over the last decades. These materials provide significant benefits, such as being durable and lightweight with an excellent cost/ performance ratio. At a first glance, many technical polymers may seem to be of chemically simple composition, but polymeric materials can be complex samples containing numerous additives that are responsible for the final physical and chemical properties as well as for the long-term behavior. Among these additives are nucleating agents that provide control over the formation of crystals; antistatics that prevent build-up of static electricity by interacting with atmospheric moisture; slip and antiblocking agents for easier manipulation of the polymer; acid scavengers that protect manufacturing devices from corrosion; flame retardants; compounding ingredients including mineral fillers or glass fibers; color pigments; and stabilizers [1].

Stabilizers are of utmost importance because several polymers would be significantly impaired by degradation processes if no stabilizers were added. Typical stabilizers include phenolic antioxidants that scavenge radicals, organo-phosphites that decompose peroxides, and light stabilizers such as benzophenone derivatives, benzotriazol compounds, and hindered amine light stabilizers (HALS) that protect the material against photo-oxidation.

Performance additives such as antioxidants (AOs), heat and light stabilizers, antistatic agents and other functional additives used at relatively low concentrations, are growing in demand, though at different rates. Additives are becoming more technical, doing more work, offering greater value, and so commanding a higher price. PVC is still by far the largest user, in volume terms, but polyolefins have emerged as a growing second-runner and the development of engineering plastics has opened up a fast-growing market for specialty additives [2]. Given their high volume and susceptibility to oxidation, polyolefins (POs) consume over half of all the anti-oxidants (AOs) used for plastics, with about two-thirds of

AO's used at primary resin producers and one-third by compounders. For light stabilizers, over 60% are used by POs, 40% by polypropylene (PP) alone, and over half are added to resin by compounders.

The analysis of additives (and especially of stabilizers) can be approached at in two different ways:-

i. On the one hand, there is an obvious need for target analysis (quantitative determination of known additives) for quality control during the production process of polymers and polymeric materials, as the lifetime of a plastic component may be directly related to the presence of a sufficiently high concentration of a certain stabilizer [1].

ii. On the other hand, non-target analysis (qualitative and quantitative analysis of unknown species) becomes a matter of concern when products of competitors must be characterized or when degradation pathways of additives (stabilizers) are investigated in order to obtain a better understanding of the reaction mechanisms of stabilizers in a polymer. A better knowledge of degradation products helps to avoid an insufficient stabilizer performance and to select the most appropriate ones for a certain application.

1.2 SIGNIFICANCE OF ADDITIVE ANALYSIS

There are a number of reasons why the analysis of polymer additives is important:-

- Product composition control.
- Health and environmental considerations that arise from the use of plastics for an application such as food packaging.
- Possible leaching of the additives into the food requires the determination of the levels of additives in the plastic and the environment.
- Recent discoveries that some additives appear to have estrogenic properties, which have been linked to a drop in the male sperm count, have highlighted the environmental risks from these compounds.
- Product deformulation.

- Monitor levels of stabilizers (UV, antioxidants) and their degradation by-products to ensure product stability.
- Product quality control.
- Monitor additive stability during product processing and end product life.
- End product failure analysis.

Generally, the determination of additives and possibly unknown degradation products in plastic materials is a challenging task in analytical chemistry due to the widely differing chemical structures of additives. Difficulties in identifying and determining additives arise from three factors according to Wheeler [3]:

(a) High reactivity and low stability of certain additives.

(b) Low additive concentration (0.1 - 0.2%) within the polymer, and

(c) Relatively insoluble polymer matrix.

From the practical point of view, methods that can directly analyze additives in the solid sample without sample preparation would be most attractive. Unfortunately, such methods are not yet widely available or may not be sensitive enough to measure stabilizers typically present at concentration levels of a few tenths of a percent. In many cases, extraction of the analytes from the polymeric material or dissolution of the whole sample may be necessary. Due to the superior chemical stability of various technical polymeric materials, dissolution can become a main obstacle within the analysis. Even if sample preparation steps are available to get the analytes into solution, the subsequent determination step, typically based on chromatographic procedures, is far from trivial. Most additives are only slightly volatile and therefore not suitable for gas chromatographic (GC) analysis. Consequently, separation techniques operating in the liquid phase, including high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE), are preferred. Although HPLC methods have become a routine tool for determination of additives in technical polymers, there is still no single stationary phase or single detection mode that allows simultaneous separation of the whole range of chemically different additives typically used for polymers.

1.3 ANTIOXIDANTS AND HEAT STABILIZATION

Throughout the compounding, molding and extrusion processes they are exposed to, POs face conditions that tend to degrade their polymer chains and change their properties. The heat and stress of the processing environment can initiate oxidation and degradation processes in the polymer well before the finished product has been packed for shipment. Further, thermal exposure in the application itself gradually adds to the total "heat history" of the material, leading to degradation unless adequate heat stabilizers have been added. To maintain a resin's original molecular weight and mechanical properties throughout its planned processing and design lifetimes, AOs are essential ingredients in a PO compound.

1.3.1 AUTO-OXIDATION IN POLYMERS

In polymers, auto-oxidation is caused by the creation of free radicals (reactive molecular species with unpaired electrons). Auto-oxidation is a circular, self-propagating process that, unless interfered with by AOs, gradually leads to increasing degradation of the polymer. Such degradation is almost always unwanted, except when the material is intentionally designed to degrade after its service life is complete. Degradation mechanisms are complex and some are still not completely understood, although the property damaging effects of auto-oxidation are obvious.

POs are susceptible to degradation by free radicals via breaking or cleavage of their polymeric chains (that is, chain scission) or by cross-linking between chains. These reactions lead to changes in molecular weight, molecular-weight distribution, mechanical properties, and appearance. Because of molecular structure differences, the tendency toward chain scission is more pronounced in PP than in PE (leading to reduced molecular weight), while cross-linking tends to predominate especially in linear types of PE. Molecular weight changes in the polymer and degradation can also create changes in the resin's organoleptic properties (color, taste, and odor). Given that exposure to oxygen is greatest at the surface of a plastic product, a product's cosmetic properties are the most visibly affected, with oxidation creating a cracked and/or powdery, chalked surface. This can be particularly disastrous with films and fibers, which have relatively high surface area per volume [4].

Auto-oxidation via free radicals can be initiated by *heat, mechanical stress, metal catalyst residues and radiation*—conditions faced to differing degrees during resin production, compounding, processing, and throughout the lifetime of the product. Driven by heat and the presence of oxygen, auto-oxidation proceeds through a series of *initiation*, *propagation*, and *branching* chain reactions, summarized as follows:

(a) Heat, light, shear and catalyst residues tend to strip hydrogen from the polymer chain (RH) to form alkyl free radicals ($R^{\bullet}$).

$$R\text{-}R \rightarrow R^{\bullet} + R^{\bullet}$$

(b) Oxygen combines with the free-radical species to create new reactive species, including peroxy radicals and hydroperoxides:-

$$O_2 + R^{\bullet} \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

and other fragment species such as H_2O, H_2, H_2O_2.

(c) The hydroperoxides (ROOH), in turn, are themselves reactive, creating new free-radical species, such as hydroxy and alkoxy radicals:-

$$ROOH \rightarrow {}^{\bullet}OH + RO^{\bullet}$$

Depending on how effectively this self-initiating and self-propagating process is slowed and inhibited by AOs at certain points in the cycle, and on how much oxygen is available, it may slowly, progressively, and catastrophically degrade the polymer as the peroxy and alkoxy radicals decompose [4,5].

Propagation ultimately leads to chain scission or cross-linking. For example, when alkyl free radicals are near each other, enough to combine with each other, the result is cross-linking, which increases viscosity. Otherwise, the macromolecular chains are weakened and cut at their reactive free-radical points, lowering their average molecular weight and increasing melt flow. This destabilizing effect on melt-flow index usually becomes more and more pronounced after several extrusion passes. However, AOs help keep melt-flow properties stable.

1.3.2 TYPES OF ANTI-OXIDANTS

AOs tend to interfere with the propagation of free-radical reactions that break polymer chains. Primary AOs do so by "scavenging" or consuming free radicals, while secondary AOs react with secondary hydroperoxide species created during auto-oxidation, preventing them from further degrading the polymer.

A. PRIMARY AOs (RADICAL SCAVENGERS)

A primary AO stabilizes free radicals by donating a hydrogen atom, essentially covering the radical's unpaired electron and making the chemical species once again stable. The AO, in return, becomes a radical. But because of its structure, it is more stable than other radicals and prevents the chain reaction of radical propagation from continuing (and eventually it may react with other free radicals to form completely stable chemical species). Primary AOs act similarly on the products of auto-oxidation, including radicals, which have combined with additional oxygen atoms (alkoxy or peroxy radicals). Some primary AOs mainly supply melt-processing stability; others provide longer-term stability to protect the product over its lifetime. Few of the widely used primary AOs are as follows:-

i. HINDERED-PHENOL AOs

Hindered-phenol AOs are the most popular primary AOs. They are called "hindered" because each molecule's reactive hydroxyl (OH) group is attached to its phenolic ring at the point where it is sterically shielded by hydrocarbon units connected to each neighboring carbon atom in the ring. Its structure allows the molecule to donate a hydrogen atom from its OH group to deactivate free radicals, transforming itself into a stable, inactive phenoxy radical that prevents the initiation of new radicals in the polymer. Higher processing or application temperatures tend to require phenolic AOs with higher molecular weights (generally ranging from 200 to over 1000), added to the polymer in percentages up to 0.5%. Added at an adequate level where they can overwhelm the side-reactions that propel the free-radical degradation cycle, phenolic AOs can provide both melt-processing stability and long term thermal stability.

$$R^{\bullet} + AH \rightarrow RH + A^{\bullet}$$

However, as phenolic AOs are themselves oxidized, some unintended changes in the resin's properties become evident, such as gas fading or yellowing caused by prolonged processing or exposure to nitrogen oxide pollutants or gamma radiation. At high temperatures, hindered phenols can also react with oxygen to create peroxy radicals that cause degradation. Moreover, acidic metal catalyst residues left over from polymerization can also oxidize these AOs, unless acid scavengers are included in the additive package. For POs, these are typically hydrotalcite-based antacids and calcium stearate and zinc stearate.

ii.PHENOL-FREE STABILIZERS

Phenol-free stabilizers provide the benefits of phenolic-based AOs without the threat of discoloration from gas fading. These are often based on hindered amine chemistries, which serve as free-radical scavengers and are usually referred to as hindered amine light stabilizers (HALS) because of their specialized roles. As a "phenol-free" alternative, high molecular-weight HALS grades are also effective in providing long-term heat stability. HALS can be a more effective AO at low temperatures than phenolics. However, during service aging, HALS have been shown to create a gradual decline in mechanical properties (particularly in PP), rather than a sudden decline after a long period of little change, as with phenolic AOs (which are consumed by the auto-oxidation process).

A HALS's effect on properties might be explained by its AO mechanism. After the HALS molecule oxidizes and loses its reactive hydrogen atom from its hindered amine location, the resulting active nitroxide (nitroxyl radical) then interrupts the auto-oxidation cycle through a series of reactions. In these reactions, the nitroxyl species partially regenerates itself until it gradually loses its radical-scavenging efficiency.

- **IRGANOX 1010**

The primary anti-oxidant used in the present research work is Irganox 1010. Irganox 1010 is a sterically hindered phenolic antioxidant – is a highly effective, non discoloring stabilizer for organic substrates such as plastics, synthetic fibers, elastomers, adhesives, waxes, oils and fats. It protects these substrates against thermo-oxidative degradation.

Chemical Name – Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenol)propionate).

Chemical Structure:

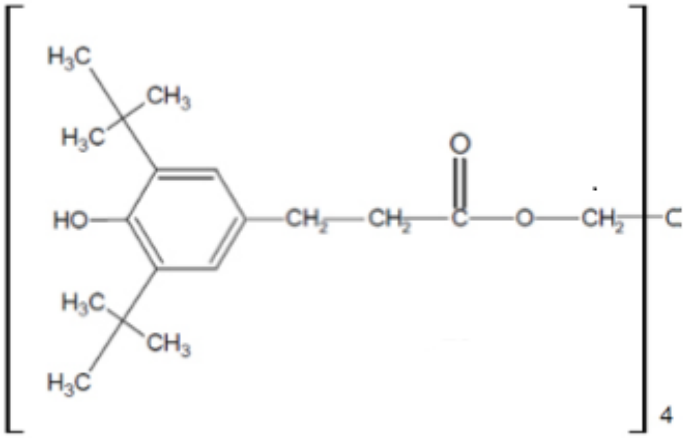


Fig 1.1: Chemical Structure of Irganox 1010

APPLICATIONS

Irganox 1010 can be applied in polyolefins, such as polyethylene, polypropylene, polybutene and olefin copolymers such as ethylene-vinylacetate copolymers. Also, its use is recommended for the processing of polymers such as polyacetals, polyamides and polyurethanes, polyesters, PVC, styrene homo- and copolymers, ABS, elastomers such as butyl rubber (IIR), SBS, SEBS, EPM and EPDM as well as other synthetic rubbers, adhesives, natural and synthetic tackifier resins, and other organic substrates [6].

SOLUBILITY DATA

Table 1.1: Solubility Data of Irganox 1010

SOLVENT	SOLUBILITY (g/100ml solution) (at 20°C)
ACETONE	47
CHLOROFORM	71
ETHANOL	1.5
ETHYLACETATE	37
CYCLOHEXANE	0.3
METHANOL	0.9
METHYLENE CHLORIDE	63

Melting Range: 110 – 125°C

Molecular weight: 1178 g/mol

B. SECONDARY AOs (PEROXIDE DECOMPOSERS)

The propagating reaction of autoxidation creates hydroperoxides (ROOH), a relatively unstable species which must be reduced by AOs into more-stable alcohol (ROH) forms. Secondary AOs decompose these species by allowing themselves to become oxidized (taking the oxygen from the ROOH). Used in combination with primary AOs, secondary AOs are often referred to as "*synergists*", because their interaction with primary AOs greatly enhances the protection the polymer receives. Secondary AOs become cost-effective when they can lower the required amount of more-expensive primary AOs.

i. PHOSPHITE-BASED AOs

Phosphite-based AOs support melt-processing stability by accepting oxygen atoms from hydroperoxides, becoming themselves phosphates and leaving behind stable alcohol species. However, they are susceptible to reactions with water (hydrolysis) to form acids, causing melt-flow changes, black specks, corrosion, and breakdowns of other additives or materials encountered in service or in processing.

Accordingly, different kinds of phosphites are available with bulky molecular structures that hinder their phosphorous atoms and resist hydrolysis. Generally, phosphites with higher-phosphorous content are more active and provide better process stability than lower-phosphorous grades [5]. In combination with primary AOs in POs, phosphites help retain the melt-flow properties and color stability through repeated processing passes better than each AO can do alone. This helps limit the amount of primary AO that is consumed in processing dramatically. Moreover, phosphites and hindered-phenol AOs can be combined as dry blends to simplify handling and feeding.

$$ROOH + P(OR)_3 \rightarrow ROH + O{=}P(OR)_3$$

ii. THIOESTER-BASED AOs

Thioester-based AOs are sulfur-based secondary AOs that are often called "thiosynergists" when combined with primary AOs. Like phosphites, thiosynergists transform reactive peroxide groups into alcohol groups, supporting long term thermal

stabilization. However, due to the odors they create, sulfur-based AOs tend to be used less than phosphites.

- **IRGAFOS 168**

Irgafos 168 is the secondary anti-oxidant used in the present research work. It is a hydrolytically stable phosphite processing stabilizer. As a secondary antioxidant, Irgafos 168 reacts during processing with hydroperoxides formed by auto-oxidation of polymers preventing process induced degradation and extending the performance of primary antioxidants.

Chemical name- Tris(2,4-ditert-butylphenyl)phosphate

Chemical Structure:

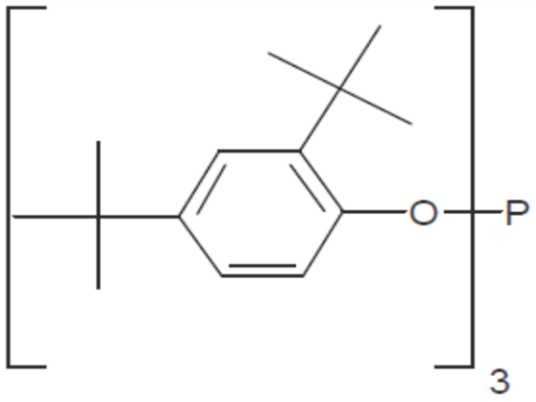


Fig 1.2: Chemical Structure of Irgafos 168

APPLICATIONS

The application range of Irgafos-168 synergistically combined with other anti-oxidants comprises polyolefins and olefin-copolymers such as polyethylene (e.g. HDPE, LLDPE), polypropylene, polybutene and ethylene-vinylacetate copolymers as well as polycarbonates and polyamides. The blends can also be used in polyesters, styrene homo- and copolymers, adhesives and natural and synthetic tackifier resins, elastomers such as BR, SEBS, SBS, and other organic substrates. Irgafos 168 blends can be used in combination with light stabilizers of the tinuvin and chimassorb range.

FEATURES

Irgafos 168 is an organo-phosphite of low volatility and is particularly resistant to hydrolysis. It protects polymers which are prone to oxidation, during the processing steps (compounding/ pelletizing, fabrication and recycling) from molecular weight change (e.g. chain scission/ crosslinking) and prevents discoloration. Irgafos 168 performs best when combined with other antioxidants. Blends of Irgafos 168 with antioxidants of the Irganox range and with Hydroxylamine FS042 are particularly effective. The Irganox range antioxidants additionally provide storage stability and give the polymer long term protection against thermo-oxidative degradation [7].

SOLUBILITY DATA

Table 1.2: Solubility Data of Irgafos 168

SOLVENT	SOLUBILITY (g/100ml solution) (at 20°C)
ACETONE	1
CHLOROFORM	36
ETHANOL	0.1
ETHYLACETATE	4
CYCLOHEXANE	16
METHANOL	< 0.01
METHYLENE CHLORIDE	36
TOLUENE	30
WATER	< 0.01

Melting Range = 183 – 186°C

Molecular weight = 646.9 g/mol

1.3.3 FACTORS DETERMINING AO SELECTION

In materials-selection situations of all kinds, decisions about additives often come down to making compromises between desired performance and cost. Notably, decisions about AOs and stabilizers for POs are complicated by a number of factors, including:

I. The basic application requirements, such as the anticipated melt processing and service temperatures, whether an AO is needed more for melt stability or for long-term heat stability in service (or both), whether the resin will be in contact with food or not, and aesthetic concerns (such as restrictions of discoloration or odors).

II. The additive's performance in terms of PO type (e.g., PP homopolymer or copolymer; HDPE, LDPE, LLDPE, and so on) and on the product form the PO is processed into (film, sheet, injection-molded part, rotationally molded part, etc.).

III. Interactions between an AO and other additives, including synergistic effects (in which two additives provide greater performance than the sum of each), and antagonistic effects (in which the summed effect is lessened as one co-additive reduces the effectiveness of another).

IV. The physical forms in which an additive is available (e.g., liquid, powder, or preblended forms), and how this form cost-effectively integrates with the point in the production process where the additive is added.

V. The potential environmental or health hazards of an additive during processing or in the final product—whether they be well-documented threats or suggested/perceived potential threats that are causing the industry to avoid using a given type of additive.

Traditional stabilizer systems for polyolefins are based on a combination of a phenolic anti-oxidant and a phosphorus-based melt processing stabilizer, the phenolic providing melt processing stability as a donor of hydrogen atoms and a scavenger of free radicals, and a level of thermal stability. The phosphorus-based additive functions as a hydroperoxide decomposer during the melt compounding stage.

1.4 ACID SCAVENGERS

Catalysts are used to increase the efficiency and economy of the polymerization process used to produce polypropylene (PP) and polyethylene (PE) resins. Most of the catalysts used today for PP and PE synthesis are of the Ziegler- Natta type; the names refer to the original discoverers of commercial PP catalysts. Ziegler-Natta catalysts utilize transition metals (titanium, chromium, etc.) and chlorine-based co-catalysts. The transition metals have many available electron sites that aid in polymerization. The chlorine-based co-catalysts increase the efficiency of the Ziegler-Natta catalysts.

While the presence of transition metals and chlorine-based materials are essential for viable commercial PP and PE polymerization, these catalyst residues can promote the degradation of the polymer chains in the finished material. Transition metals are known to catalyze the free-radical decomposition of hydroperoxides which are formed by the reaction of atmospheric oxygen with the carbon-hydrogen bond in the polymer. The decomposition of the hydroperoxide [ROOH] by the transition metals [M^{+m} or M^{+n}] is believed to proceed by the following mechanisms:

$$ROOH + M^{+n} \rightarrow ROO^{\bullet} + H^{+} + M^{+m}$$

$$ROOH + M^{+m} \rightarrow RO^{\bullet} + OH^{-} + M^{+n}$$

where; m = n-1

The mechanism by which the transition metal decomposes the hydroperoxide, and thus furthers the autoxidation process, also regenerates the transition metal so that the process can continue indefinitely. To combat this process, scavengers are added to the PP and PE reactor powder during pelletization which bind to the transition metals and deactivate them [8].

➢ CALCIUM STEARATE

The most commonly used transition metal scavenger is calcium stearate [$Ca(O_2C_{18}H_{37})_2$]. Calcium stearate is a molecule consisting of a central calcium ion with two stearate groups attached. The stearate group is essentially a long-chain carbon molecule. As such, the stearate group is similar to, and therefore soluble in, the polymer chains. Calcium stearate attacks the

transition metals, usually found in the form of metal chlorides [MCl_2] by the following reaction:

$$Ca(O_2C_{18}H_{37})_2 + MCl_2 \rightarrow CaCl_2 + MSt_2$$

The large stearate groups bond with the transition metal rendering the metal essentially inactive. The presence of chloride ions in PP and PE can result in the formation of hydrochloric acid [HCI] and other acids if not properly scavenged. Hydrochloric acid can degrade the polymer and produce unwanted color formation (yellowing) in the pellets.

The following figure shows the manner in which inhibition of auto-oxidation occurs in polymers by different mechanisms:

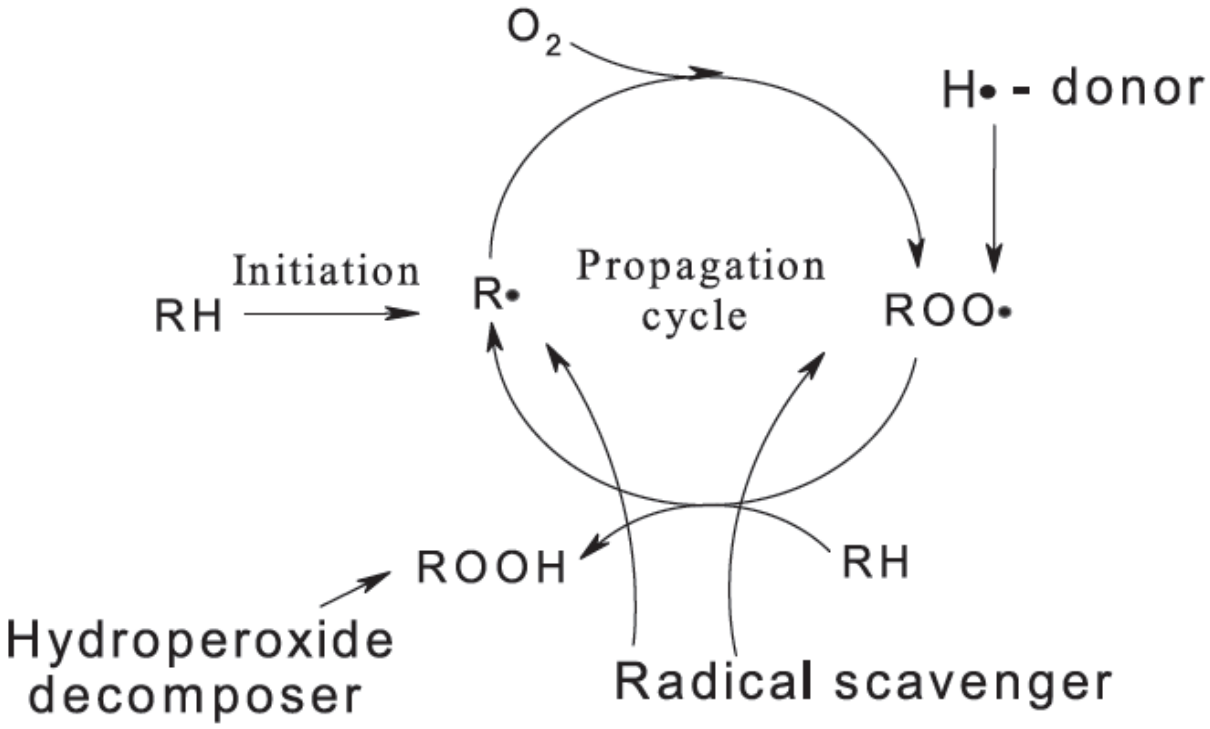


Fig 1.3: Inhibition of auto-oxidation by different mechanisms

1.5 LABORATORY TECHNIQUES

Following are the important laboratory techniques used in the present research work:

1.5.1 MICROWAVE ASSISTED EXTRACTION

Microwaves are non-ionizing electromagnetic waves of frequency between 300 MHz to 300 GHz and positioned between the X- ray and infrared rays in the electromagnetic spectrum.

MAE is the process of heating solvents in contact with a sample with microwave energy to partition compounds of analytical interest from the sample matrix into the solvent. The approach is a direct descendant of closed vessel microwave acid digestions & solvent extraction of organic analytes from solid samples. These two concepts have been united: the result is a rapid sample preparation technique that enables extractions with reduces amounts of common laboratory solvents in closed vessels with elevated temperatures & temperature control of the extraction process.

The principle of heating using microwave is based upon its direct impact with polar materials/solvents and is governed by two phenomenons: *ionic conduction and dipole rotation*, which in most cases occurs simultaneously.

- ***Ionic conduction*** refers to the electrophoretic migration of ions under the influence of the changing electric field. The resistance offered by the solution to the migration of ions generates friction, which eventually heats up the solution.
- ***Dipole rotation*** means realignment of the dipoles of the molecule with the rapidly changing electric field **[9]**.

The system enables the laboratory analyst to accomplish multiple quantitative sample extraction within minutes, with enhanced reproducibility & reduced exposure of solvents to the laboratory, personnel & environment.

The process is a partitioning of compounds of interest from the sample matrix into the solvent, with the kinetics driven by elevated temperature & choice of solvent or solvent mixtures. Using closed vessel to contain the sample & the solvent, combined with the ability

to heat the solvent directly through the vessel, extends & improves the traditional solvent extraction to a controlled science.

The closed vessel MAE approach can be contrasted to extractions in devices like Soxhlet, which are subject to atmospheric pressure. When using solvents in open devices, temperature possible is determined by the boiling point of the solvent at atmospheric pressure. The temperature will in general be consistent unless there is a significant change in atmospheric pressure. However, in closed vessels, the solvents can be heated to comparatively elevated temperatures by microwave energy, limited only by vessel's pressure specifications **[10].**

In comparison with the traditional extraction methodologies, MAE offers the following advantages:-

i. Use of solvents with lower toxicity & environmental adverse effects.
ii. Less solvent is required. Because no evaporation occurs, there is no need continually to add solvent to maintain the volume. Also, the risk of contamination is avoided as a result there is little or no risk of airborne contamination.
iii. Fast & total recovery of either difficult or highly polar compounds.
iv. No coagulation, washing and concentration required prior to HPLC analysis.
v. The fumes produced during an acid microwave extraction are contained within the vessel, therefore, no provision for handling potentially hazardous fumes needs to be made.
vi. Appreciable accuracy improvement of analytical evaluations.
vii. Negligible decomposition of stabilizers.
viii. Extraction of a very wide dipolarity range of organic compounds **[11].**

➢ SELECTION OF SOLVENTS FOR MAE

A proper selection of organic solvents is the most important key to successful extraction of additives from polymer matrices. The efficiency with which different solvents heat up under microwave depends on the dissipation factor (**tan δ**), which is indeed the measure of the

ability of the solvent to absorb microwave energy and pass it on as heat to the surrounding molecules. The dissipation factor is given by the equation:

$$\mathbf{Tan\ \delta = \varepsilon'' / \varepsilon'}$$

where; **ε"** = The dielectric loss which indicates the efficiency of converting microwave energy into heat [9].

ε' = The dielectric constant which is the measure of the ability to absorb microwave energy.

Table 1 lists the dielectric constants and dissipation factors for solvents commonly used in MAE. The table shows that both ethanol and methanol will undergo lesser microwave absorption than water due to their lower **ε'** value but the overall heating efficiency for both the solvents will remain higher than water (due to increased **tan δ** value). Whereas on the other hand hexane and other less polar solvents like chloroform will remain transparent to microwave, thus producing no heat.

Table 1.3: Dissipation factor & dielectric constants for some solvents used in MAE

SOLVENT	DIELECTRIC CONSTANT	DIELECTRIC LOSS (ε")
ACETONE	20.7	-
ACETONITRILE	37.5	-
ETHANOL	24.3	2500
HEXANE	1.89	-
METHANOL	32.6	6400
2-PROPANOL	19.9	6700
WATER	78.3	1570

Therefore, in binary solvent mixtures, one apolar component (n-hexane or n-heptane), gives high swelling-melting power to polymer but does not heat under microwave irradiation. The second polar component (acetone, isopropyl alcohol & ethyl acetate) has a sufficient dipole moment to facilitate heating under the microwave field & produces a shrinkage effect on the polymer macrostructure, preventing its salvation. Hence, the right ratio of two solvents

is necessary for optimal swelling and good extraction.

Thus the solvent properties which determine its selection can be listed as follows:-

a. The solubilization capacity for compounds of interest.
b. The microwave absorption capacity and the ability to convert electromagnetic energy to thermal energy.
c. Lowest possible toxicity.
d. The ability to cause the right degree of polymer swelling at elevated temperature.
e. The tendency to dissolve smallest quantity of polymer at room temperature **[11].**

- The tetraphenolic primary stabilizer Irganox 1010, because it is the most commercially common anti-oxidant for polyolefins, and since it has accentuated dipolarity, shows poor solubility in hydrocarbon solvent. It therefore needs a high swelling grade of polymeric matrix to be completely extracted which can be assured by presence of cyclohexane.

- The phosphate aromatic secondary stabilizer Irgafos 168 is not difficult to extract but has a high level of anti-oxidant activity as hydrogen peroxide decomposer & suffers a fast degradation at temperatures greater than 140ºC. It decays via oxidation to give the phosphonate by-product, and less frequently, via hydrolysis to give 2,4-di-tert-butylphenol (2,4-DTBP).

1.5.2 CRYOGENIC GRINDING

The analysis of the additives in polymers is usually done with chromatographic methods (HPLC-UV, GC-MS). First it is necessary to extract the compounds in question from the test material, e.g. by solvent extraction. To facilitate the extraction and obtain a small but representative sample quantity, the material has to be ground to a very fine particle size. The fact that the polyolefins are rubbery in nature at room temperature & above (T_g for HDPE = -60^oC), and are also heat-sensitive at high temperatures, this poses an extra

challenge for the size reduction process. Moreover, it must be ensured that volatile components of the sample are not expelled by the warmth which is usually generated during grinding.

Cryogenic grinding technology can efficiently grind most tough & difficult to grind materials. Cryogenic grinding employs a cryogenic process (cold energy available from liquid nitrogen) to embrittle and grind materials to achieve consistent particle size for a wide range of products. All materials which due to their specific properties at ambient temperatures are elastic, have low melting points, contain volatile or oily substances, have low combustion temperatures and are sensitive to oxygen, are ideal candidates for cryogenic size reduction.

The CryoMill is an impact ball mill specifically designed for cryogenic grinding. It features an integrated cooling system which continually cools the grinding jar with liquid nitrogen (-196^{o}C) before and during the grinding process. Thus the sample is embrittled and volatile components are preserved. The combination of impact and friction leads to substantially finer grind sizes compared to other cryogenic mills. Usually, grinding in the CryoMill only takes a few minutes so that the sample does not get warm during the process. If, however, longer grinding times are required, it is also possible to pre-select periods of intermediate cooling and the number of cryogenic cycles [12].

1.5.3 HIGH PRESSURE LIQUID CHROMATOGRAPHY

Chromatography is a separation process in which the components to be separated are distributed between two phases, a stationary phase and a mobile phase. Components of the sample mixture separate when they have differential migration in the column. Differential migration depends on the equilibrium distribution of the sample components between the stationary and mobile phase. Compounds whose molecules are found to reside most of the time in the mobile phase will elute first. Compounds whose molecules spend most of their time in the stationary phase will move through the column more slowly and elute at later retention times.

HPLC is a physical separation technique in which a sample dissolved in a liquid is injected into a column packed with small particles and it is separated into its constituent components. It is probably the most important and widely used analytical technique for quantitative analysis of organics and biomolecules. The analytes to be separated are distributed between two phases:

a. Mobile phase (a flowing solvent)

b. Stationary phase (a column packed with porous particles)

An on-line detector thus monitors the concentration the concentration of each eluting component & generates a trace called the chromatogram.

Commonly used solvents in reversed phase HPLC in the order of increasing elution strength are stated below:-

I. Water

II. Methanol

III. Acetonitrile

IV. Isopropanol

V. Dioxane

VI. Tetrahydrofuran

The components of a high performance liquid chromatography include:

i. Solvent reservoirs.

ii. A pumping system to provide accurate compositions, flows and the pressure necessary to push the mobile phase through the tightly packed column.

iii. A sample delivery mechanism which will not interrupt the flow of mobile phase.

iv. A column where the separation takes place.

v. The detector to sense the presence of individual sample components.

A schematic layout of HPLC is as given below:

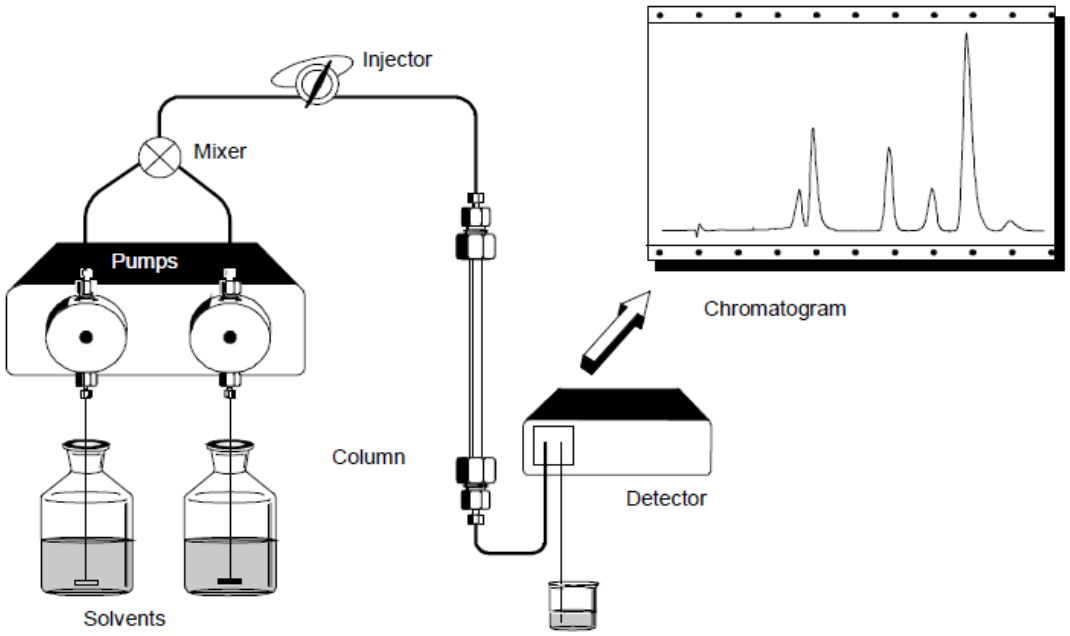


Fig 1.4: Schematic Layout of HPLC

Following are the different modes for operating liquid chromatography [13]:

Table 1.4: Different Operating Modes for HPLC

TYPES OF COMPOUNDS SEPARATED	MODE	STATIONARY PHASE	MOBILE PHASE
Neutrals, Weak Acids, Weak Bases	Reversed Phase	C-18, C-8, C-4, C-2	Water/Organic Modifiers
Ionics, Bases, Acids	Ion Pair	C-18, C-8	Water/Organic Ion Pair Reagent
Organic isomers	Normal Phase	Silica, Amino, Cyano, Diol	Organics
Ionics, Inorganic Ions	Ion Exchange	Anion or Cation Exchange Resin	Aqueous/Buffer Counter Ion
High Molecular Weight Compounds	Size Exclusion	Polystyrene, Silica Polymers	Gel Filtration-Aqueous, Gel Permeation- Organic

Some of the few important advantages of HPLC are as follows:

a) HPLC provides a very high resolution.

b) The technique is amenable to diverse samples including organics, biomolecules & ions.

c) Using an auto-sampler & data system, the technique provides for an automated analysis.

d) HPLC also provides a high sensitivity detection alogwith a rapid & precise analysis.

1.5.4 INFRARED SPECTROSCOPY

Infrared spectroscopy is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. The IR region is commonly divided into three smaller areas:

- Near IR— 780-2500 nm (12,800-4000 cm^{-1})
- Mid IR— 2500-50,000 nm (4000-200 cm^{-1})
- Far IR— 50-1000 nm (200-10 cm^{-1})

It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption information is generally presented in the form of a spectrum with wavelength or wavenumber as the x-axis and absorption intensity or percent transmittance as the y-axis [14]. Transmittance, *T*, is the ratio of radiant power transmitted by the sample (*I*) to the radiant power incident on the sample (I_o). Absorbance (*A*) is the logarithm to the base 10 of the reciprocal of the transmittance (*T*).

$$A = \log_{10}(1/T) = -\log_{10}(T) = -\log_{10}(I / I_o)$$

The figure below is a typical layout of FTIR:

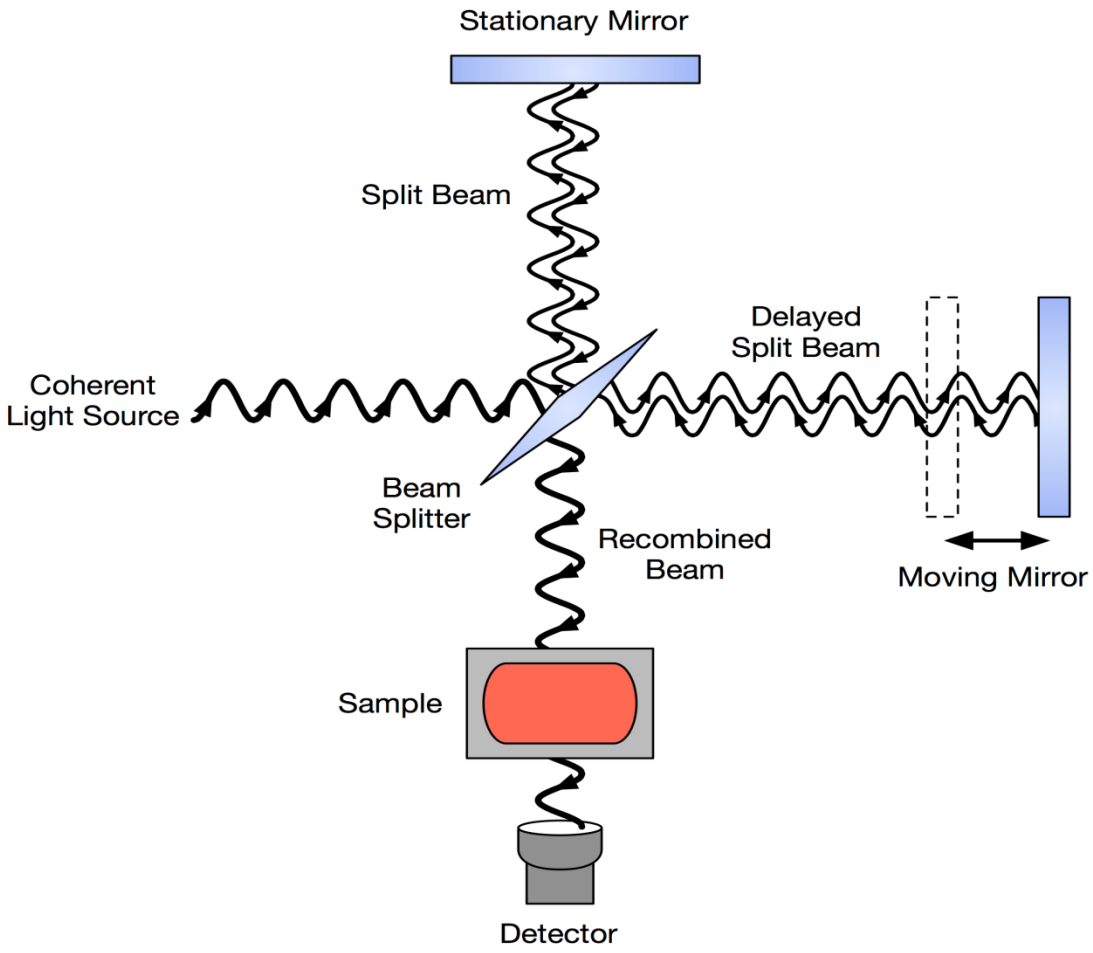


Fig 1.5: Typical layout of FTIR

➢ QUANTITATIVE ANALYSIS USING IR

The intensities of spectral bands are used for quantitative IR analysis. The capacity of any component to absorb IR radiation is constant. This capacity is termed its molar absorptivity. Additionally, the intensity of any specific absorption band in relation to another is constant, because the intensity of an absorption band is directly proportional to the rate of change in the dipole moment of that particular vibration. A large change in the dipole moment of the atoms during a vibration will produce an intense band. Thus, very polar functional groups, such as those containing halogens, will exhibit intense absorption bands. An intense absorption band can also be produced by the presence of multiple functional groups within the molecule, such as CH_2 groups in paraffin wax, that each have the same vibrational

energy, such that an additive effect is created. There is a linear quantitative relationship between absorbance and concentration of absorbing molecules (Beer-Lambert's law):

$$A = \varepsilon.b.c = \log_{10}(1/T)$$

where;

A = Absorbance

ε = Molar absorptivity (a constant for the molecule)

b = Path length

c = Concentration of the molecule

T = Transmittance

The equation shows that there is a one-to-one relationship between the height, or intensity (in absorbance units), of an absorption band and the concentration of that molecule. Note that the linear relationship holds for absorbance and not for transmittance, which has a logarithmic relationship. Thus, for quantitative work, spectra are usually plotted in absorbance units [15].

All quantitative IR analysis are done by comparing the intensity of a specific absorption band, in absorbance units, of the unknown material with the absorbance, or band height, of the same material in a standard of known concentration. In a mixture of materials, the absorbances are additive; thus, the total absorbance at any given wavelength is the sum of the absorptions of the individual components. Therefore, for quantitative analysis of a material, it is advantageous to select an absorption band that not only is characteristic of that material but also is isolated from absorption bands due to other materials in the sample.

Beer's law shows that sample path length is also a factor in the measurement. For one quantitative method, direct calculation of concentration, the path length must be either known or fixed. Thus, direct measurement is normally limited to liquids or solutions that can be analyzed in a fixed-path length liquid cell. In this method, the unknown concentration of an identified single component can be calculated from a calibration curve. The calibration curve is prepared by analysis of the same component in solutions, or mixtures, of at least four different concentrations. An absorption band is selected that is characteristic of the

component of interest and that is free from interferences. Then a plot is made of the absorbance value for that band versus the concentration of the component in each solution. The concentration of the sample is determined by comparing the intensity of that particular band in its spectrum with the calibration curve. The intensity of the band is measured as the absorbance difference from its maximum to its baseline. Because the path length cannot be determined precisely, this method is not used for films and pellets.

The ***"absorbance ratio"*** method is used when the path length of the sample cannot be readily determined. The method works well for films, pellets, and diffuse or internal reflection measurements. For this method, at least two components (A and B) must be in the sample matrix, and each must have an absorbance band that exhibits minimum interference. Because the components are present in the same sample, the path length is the same and is no longer a variable. The calibration curve is generated from at least four spectra obtained from mixtures of the components in different proportions. The ratio of the intensities of the two bands of interest (I_A/I_B) is plotted versus the ratio of their concentrations (C_A/C_B). Once the curve is generated, the ratio of the concentration of the components in the unknown sample can be determined, since the sum of their concentrations equals unity, or 100 %. Thus, the specific concentrations for each component can be easily calculated.

- **PARTIAL LEAST SQUARES ANALYSIS (PLS)**

Partial least squares is a popular method for soft modeling in scientific applications. Research in science often involves using controllable and/or easy-to-measure variables (factors) to explain, regulate, or predict the behavior of other variables (responses). For example, spectrographs are often used to estimate the amount of different compounds in a chemical sample. In this case, the factors are the measurements that comprise the spectrum; they can number in the hundreds but are likely to be highly collinear. The responses are component amounts that the researcher wants to predict in future samples. Partial least squares (PLS) is a method for constructing predictive models when the factors are many and highly collinear.

The emphasis is on predicting the responses and not necessarily on trying to understand the underlying relationship between the variables. Each spectrum is comprised of

measurements at 1,000 different frequencies; these are the factor levels, and the responses are the component concentrations [16].

PLS statistical analysis module performs model construction and prediction of activity/property using the Partial Least Squares (PLS) regression technique. It is based on linear transition from a large number of original descriptors to a small number of orthogonal factors (latent variables) providing the optimal linear model in terms of predictivity (characterized by the value of statistical performance parameters, such as correlation coefficient, MSEP, SEP etc).

1.5.5 X-RAY FLUORESCENCE SPECTROSCOPY (XRF)

X-ray is a type of electromagnetic waves such as visible light ray, but the key difference is its extremely short wavelength, measuring from *100A to 0.1 A*. And compared to normal electromagnetic waves, X-ray easily passes through material and it becomes stronger as the material's atomic number decreases. X-ray fluorescence analysis is a method that uses the characteristic X-ray (fluorescent X-ray) that is generated when X-ray is irradiated on a substance**.** The fluorescent X-ray is the excess energy irradiated as electro-magnetic field, which is generated when the irradiated X-ray forces the constituent atom's inner-shell electrons to the outer shell and the vacant space (acceptor) falls on the outer-shell electrons. These rays possess energy characteristic to each element, and qualitative analysis using Mosley's Equation and quantitative analysis using the energy's X-ray intensity (number of photons) are possible [17].

Easy sample preparation, multi-element determination, and the possibility to screen completely unknown samples are the significant advantages of XRF. For XRF samples, quantities between 3 and 8 gm are typical. This is very important for inhomogeneous samples where more sample material reduces the influence of the inhomogeneity.

With XRF all elements between '*Na and U'* can be analyzed. For the elements from '*Na to Ce'*, K-lines are used; and for all elements from '*Pr to U'*, L-lines are used. The analysis of the elements '*Be to F'* is limited to just a few special applications. The reason for this is

the depth of analysis. These elements show low energy x-rays that are easily absorbed by air or a simple polypropylene film [18]. The following figure depicts a typical XRF layout:

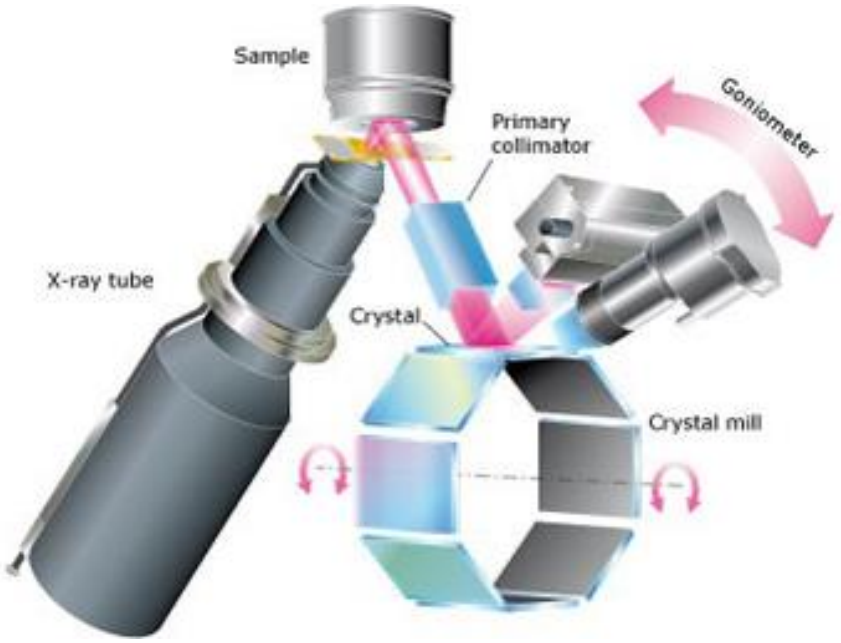


Fig 1.6: Schematic Layout of XRF

➢ BRAGG'S EQUATION

When parallel X-rays strike a pair of parallel lattice planes, every atom within the planes acts as a scattering centre and emits a secondary wave. All of the secondary waves combine to form a reflected wave. The same occurs on the parallel lattice planes for only very little of the X-ray wave is absorbed within the lattice plane distance, "***d***". All these reflected waves interfere with each other. If the amplification condition: "*phase difference = a whole multiple of wavelengths*" ($\Delta\lambda = n\lambda$) is not precisely met, the reflected wave will interfere such that cancellation occurs [19]. All that remains is the wavelength for which the amplification condition is precisely met. For a defined wavelength and a defined lattice plane distance, this is only given with a specific angle, the *Bragg angle* (θ).

Bragg's equation is given as:-

$$n\lambda = 2d \sin\theta$$

where;

n = Reflection order (1,2,3..); d = Lattice plane distance

λ = Wavelength of X-ray; θ = Bragg's angle

This provides the basis for two measuring techniques for the quantitative and qualitative determination of chemical elements and crystalline structures, depending on whether the wavelength 'λ' or the '2d' value is identified by measuring the angle 'θ' as given below:

- In X-ray diffraction (**XRD**) the sample is excited with monochromatic radiation of a known wavelength (λ) in order to evaluate the lattice plane distances (d) as per Bragg's equation.
- In **XRF,** the '*d*'-value of the analyzer crystal is known and we can solve Bragg's equation for the element characteristic wavelength (λ).

Table 1.5: Parameters in XRF and XRD

KNOWN	SOUGHT	MEASURED	METHOD	INSTRUMENT TYPE
d	λ	θ	**X-ray fluorescence**	Spectrometer
λ	d	θ	**X-ray diffraction**	Diffractometer

CHAPTER 2

LITERATURE REVIEW

Kriston et.al. studied the role of a phenolic and three phosphorous (phosphite, phosphonite and phosphine) antioxidants in the melt stabilization of a Phillips type polyethylene by multiple extrusions. The functional groups (methyl, vinyl, vinylidene, trans-vinylene and carbonyl) of polyethylene and the residual amount of phosphorous antioxidants were analyzed quantitatively by FTIR method. They observed that the phenolic antioxidant itself does not hinder the formation of long chain branches. It reduces the rate of oxidation of the various phosphorous stabilizers hence decreasing their consumption [20].

Systematic analysis of organic additives in polyolefins using microwave assisted extraction and direct chromatographic evaluation of extract by high-performance liquid chromatography coupled with ultraviolet and evaporative light scattering detection was carried out by Marcato & Vianello. They proposed two microwave-assisted processes: the "One-step MAE", useful for additives with low to medium di-polarity (like stabilizers, flame retardant, anti-statics, slip and processing agents), and the "Two-step MAE", useful for additives with either high di-polarity (like organic salts, anti-gas fading, antacid, nucleating agent) or high molecular mass (like polymeric hindered amine light stabilizers). Both the proposed processes were tested on representative additives in five commercially common polymeric matrices, demonstrating their satisfactory analytical results, in terms of repeatability and percentage recoveries, and their good performances, in terms of safety and time/ solvent consumption, in comparison with those of traditional extraction methods [11].

Camacho & Karlsson in their work made use of the partial least square regression to generate a calibration model that can be used for the prediction of additives in polymers. The compounded samples were analyzed by near infrared (NIR) spectroscopy in the diffuse reflectance mode [21]. They concluded that NIR is a suitable method for quantification of antioxidants in polyethylene. The standard error of prediction is almost comparable to the error of wet methods, i.e., extraction plus liquid chromatography.

Karstang & Henriksen compared the different calibration and scaling techniques for the quantitative analysis of three additives and one degradation product (phosphate) in one high-density polyethylene polymer product. A calibration model was also combined with background correction techniques for the quantification of one of the additives in three other high-density polyethylene products. Their results indicated that the optimized scaling and the approach using normalization based on selective regions followed by PLS regression give comparable results. The same model complexity and prediction errors were obtained from cross-validation of the calibration set and the separate test set. This means that the model is well suited for quantification of additives in real production samples. By applying background correction techniques, a calibration model designed for one high-density polyethylene product can be used on other qualities with only a small loss in predictive power [22].

In recent years, analysis with supercritical fluids (SFs) has emerged as an alternative analytical technique because SFs afford higher diffusivity and lower viscosity. The extraction of antioxidant additives, such as, Irganox 1076 and Irgafos 168, from low-density polyethylene (LDPE) and Irganox 1010, Irgafos 168 from high-density polyethylene (HDPE) using supercritical fluid extraction (SFE) working in constant pressure, conventional reflux, and automatic Soxhlet system (Soxtec) was carried out by Monica & co-workers [23]. SFE extractions of polymer were successfully carried out and these were associated with better recoveries (>94.9%), simplicity and speed of the extraction process. The time required to conduct the overall procedure (viz., extraction and HPLC analysis) was significantly different (viz., 25 min with the SFE method versus 80 min with the conventional reflux extraction and 540 min with soxtec extraction method). Thus, SFE was found to be the most advantageous technique in terms of simplicity, cost-effectiveness and speed in comparison to conventional reflux and Soxtec procedures. Although it is not an expensive technique, the high-pressure technology involved in SFE is a potential disadvantage regarding the maintenance of equipment.

Amongst other techniques for extraction of additives, ultrasonic extraction with chloroform at 60 °C has been applied for the isolation of Chimassorb 944 from commercial low density poly(ethylene) film with a thickness of 150mm as well as for the isolation of Irganox 1010 and Irgafos 168 from commercial medium density poly(ethylene) film with a

thickness of 25 mm; a fast and total recovery of these additives was achieved. Quantitative analysis of the additives was performed by UV spectroscopy and HPLC. Total recovery was reached after 15 min, 45 min and 60 min at 60 °C for Irgafos 168, Irganox 1010 and Chimassorb 944, respectively. Ultrasonic extraction from LDPE and MDPE films resulted in a fast and complete recovery of the additives without any noticeable degradation [24].

Nielson investigated some ways to extract the additives from HDPE, LDPE & PP using MAE & ultrasonic bath techniques. It was observed that the extraction times are 20-25 mins for MAE and 40-60 mins for ultrasonic extraction with recoveries greater than 90% being obtained [25].

Frietag & John also studied the extraction of additives from polyolefins using MAE. The polymer samples were kept in cleaned vessels & irradiated in a laboratory microwave oven. Fairly quantitative (> 90% of the expected content) extraction of stabilizers from powdered polymer was achieved between 3 to 6 mins using 1,1,1-trichloroethane or the 1:1 mixture of acetone & n-heptane as extracting solvent. They also observed that Irganox 1010 being bulkiest of all the additives examined, migrates slowly. Faster extractions were obtained with 1,1,1-trichloroethane, but the toxic & environmental properties of this solvent are less favorable compared to acetone/n-heptane mixture [26].

The processing stabilising performance of various phosphorous antioxidants in polyolefins is affected significantly by their chemical composition. In order to explore the mechanism of stabilisation, Kriston et al. investigated the reactions of a hindered aryl phosphite [tris(2,4-di-tert-butylphenyl)phosphite (DTBPP)] at temperatures corresponding to polyethylene processing. The thermal and thermo-oxidative stability of the additive was determined by differential scanning calorimetric (DSC) and thermogravimetric methods. DTBPP was heat treated under argon and oxygen at 200 and 240 ^{o}C. The stabiliser was reacted at 200 ^{o}C with azobisisobutyronitrile (AIBN) in oxygen-free environment and under oxygen. The reaction products were identified by FT-IR and HPLC-MS. The results revealed that besides the known reactions of hindered aryl phosphites, thermal decomposition and recombination reactions also take place above the melting point of the antioxidant. DTBPP does not react with molecular oxygen, but its decomposition is accelerated by oxygen and especially by radicals. Thus, they concluded that the heat-stability of phosphorous stabilizers

also has to be taken into account in their application, as it is one of the factors which influence the processing stabilization of polyolefins [27].

Eva et al. in their research identified the degradation products of antioxidants in polyolefins by liquid chromatography combined with atmospheric pressure photo-ionization mass spectrometry. They investigated the degradation pathways of six common antioxidants. While ADK Stab, Kinox 30, Everfos 168, and Irganox 1076 turned out to be thermally stable at 115 ºC, Irganox 3114 and Cyanox 1790 were partly degraded by oxidation. In the presence of talcum, which is a widely used inorganic filler for polyolefins, additional degradation reactions such as the cleavage of ester bonds and the loss of tert-butyl groups were observed at elevated temperature. Hence, they concluded that the general underestimation of stabilizers in polyolefins may be (partly) ascribed to reactions of the stabilizers already occurring during the production of a compounded polymer sample. Typically, such reactions include the loss tert-butyl groups and the cleavage of ester bonds, whereby the presence of mineral fillers can have an impact on the degradation pathways [28].

The thermal performances of two commercial phenol/phosphite (Anox-Great Lakes) and three commercial phenol/ phosphite/ lactone (Ciba Specialty Chemicals) packages have been determined in HDPE in the absence and presence of two processing aids, calcium stearate and oleamide by Norman et al. Stabilities were assessed using FTIR, thermal analysis and mechanical property changes (tensile, elongation and impact). In terms of thermal stabilization, the phenol/phosphite blends are found to be superior to the tris–phenol/phosphite/lactone blends. In the presence of calcium stearate strong synergism was observed with the Irganox blends and this may be associated with an exchange interaction/complexation between the calcium and the phosphite derivatives. These complexes appear to have high performance in thermal stabilization possibly through hydroperoxide decomposition and inhibition of carbonyl formation [29].

Rudolf reviewed that in parallel to the growth of polyolefins, the polymer industry has seen a dramatic improvement of additive performance especially in the processing stabilizer/antioxidants and light stabilizer area, either through new chemical structures or through synergistic effects. He stated that a well-known example of improved processing stability is the combination of phosphites (e.g. Irgafos 168) and phenolic antioxidants (e.g.

Irganox 1010) outperforming the performance of the individual components. This combination can be even further improved by using as a third component a benzofuranone derivative (e.g. Irganox HP 136), which is a very powerful radical scavenger and proves its efficiency at the increased processing temperatures, commonly used today [30].

Lucas et al. in their work evaluated MAE prior to HPLC for determination of additives in polyolefins. They investigated several different solvents and solvent mixtures in a monomode microwave reaction system at different extraction temperatures. They observed that ethyl acetate showed the best extraction performance with respect to easy and rapid sample preparation. For this solvent, a systematic and comprehensive survey of time- and temperature-dependence of extraction efficiency was carried out. Extractions utilizing ethyl acetate for 30 min at 130^{o}C showed the best overall performance for all investigated analytes. They concluded that by choosing the correct solvent, the problem of partially dissolving polymer or oligomer can be overcome, which enables skipping the precipitation step and reduces the chance of random errors caused by co-precipitation of analytes [31].

Utilizing an advanced analysis technique, Himmelsbach et al. investigated the determination of polymer additives like antioxidants, UV absorbers and processing stabilizers. They employed liquid chromatography (LC) coupled with atmospheric pressure photoionization mass spectrometry (APPI–MS). Ion source parameters were optimized regarding temperatures, gas flow rates, and voltages applied. Detection limits were determined using APPI with or without dopant and were compared with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). The optimized method yielded detection limits between 0.001 mg L^{-1} and 0.022 mg L^{-1} for 15 different analytes. Linear calibration plots could be obtained for all solutes over a wide concentration range showing satisfying repeatability with standard deviations of peak areas between 3.4% and 7.6%. The results indicated that the developed method could be regarded as suitable for the quantitative determination of polymer additives even at low concentration levels [32].

C. Block et al. carried out the identification of polymer additives by liquid chromatography-mass spectrometry. LC-MS at different experimental conditions was used to construct a library of MS spectra of polymer additives. Combination of retention time information derived from the chromatogram with molecular mass and fragment ion

information derived from MS and MS/MS was used for the identification of 20 additives. Mixtures of different additives and extracts of LDPE films were prepared and analyzed as unknowns. They concluded that all 20 additives could be identified, 15 with 100% certainty [33].

Victoria et al. also reviewed the determination of polyolefin additives by reverse phase liquid chromatography. They examined the contribution of liquid chromatography to the study of polyolefin additives commonly used to obtain improved environmental resistance (antioxidants, ultraviolet light stabilizers, anti-statics, and so on) and appearance enhancements (*e.g.* colorants). Several reversed-phase liquid chromatographic methods & analyte extraction techniques were summarized. In addition, ways of applying these methods to analyze food contact materials and plastic toys were also emphasized. They concluded that the combination of extraction and HPLC methods allows knowledge on the performance of additives; for example the behavior of antioxidants during processing and plastics shelf life. Nevertheless, more research is required for the evaluation of strategies that focus on improving the determination of some other polyolefin additives such as anti-statics [34].

A. Ritter et al in their report presented the results obtained from two inter-laboratory tests performed by participants mainly from industry and research institutes analyzing two different antioxidants in four polymer matrices. The measured data were collected and evaluated using a robust statistical method. Samples of non-stabilised polyolefins were homogeneously doped with accurate well-known quantities of Irgafos 168 and Irganox 1010. Prior to concentration analysis, different sample preparation procedures such as soxhlet, solution & precipitation, Schoniger digestion, MAE, ASE were employed by different participants. For concentration analysis, techniques such as Pyrolysis/ GC/ MS, GC, GC/MS, XRF & HPLC were used, HPLC being the most common. The relative repeatability of the determinations was between 1.3 and 5.5%, and the relative reproducibility was in-between 12 and 28% for both antioxidants. For both Irganox 1010 and Irgafos 168, considerable differences between measured and ‘true’ contents were detected. The reasons could be thermal degradation of additives during compounding and ambiguity in analysis techniques itself. It was concluded that HPLC was the method of choice when the pre-treatment was optimized, which is very important to get reliable results [35].

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

a. HDPE:

High Density Polyethylene (HDPE) has been used as the base polymer resin. Following are its important properties:

- Density = 0.954 g/cm^3
- MFI = 1.2 g/10min

It is a bimodal resin grade with very good processability, good balance of stiffness, ESCR and impact properties.

b. IRGANOX 1010:

It is the most widely used primary anti-oxidant in polyolefins. Irganox 1010 been used in the present research is a manufacturing product of *BASF*.

c. IRGAFOS 168:

Irgafos 168 used has also been manufactured by *BASF*.

d. CALCIUM STEARATE (CaSt):

CaSt used as an acid scavenger is a product of *Peter Greven*. It is commonly used in polyolefin, PVC & plastic masterbatches, rubber and building material etc.

e. SOLVENTS:

i. Xylene used as dispersion solvent for particle size determination was LR grade (purity > 99.0 %) manufactured by Samir Tech Chem Pvt. Ltd.

ii. Acetone & cyclohexane employed for solvent extraction were HPLC grade (purity > 99.7%) and were a make of RFCL-Rankem.

iii. Acetonitrile & isopropyl alcohol used in chromatographic procedure were also HPLC grade (purity > 99.7%). They too were a product of RFCL-Rankem.

iv. Milli-Q Water used for HPLC analysis.

3.2 METHODS

Typically the following three steps are employed in the analytical methods for additive analysis:

1. Separation of additives from solid polymer samples.
2. Fractionate extract to obtain separate components. (typically by HPLC or SEC)
3. Identify/quantify the individual components (additives, degradation products). Methods include MS, FTIR, NMR.

3.2.1 COMPOUNDING

The above stated materials have been used to prepare the following twelve formulations weighing each one of them accurately:-

Table 3.1: Formulations of compounded HDPE in absence of CaSt.

Batch Size = 2kg

FORMULATION	HDPE (g)	AO 1010 (ppm)	AO168 (ppm)
F1	1998.8	300	300
F2	1997.6	600	600
F3	1996.4	900	900
F4	1995.2	1200	1200
F5	1994.0	1500	1500
F6	1992.8	1800	1800

Table 3.2: Formulations of compounded HDPE in presence of CaSt.

Batch Size = 2kg

FORMULATION	HDPE (g)	AO 1010 (ppm)	AO168 (ppm)	CaSt (ppm)
F1	1994.8 g	300	300	2000
F2	1993.6 g	600	600	2000
F3	1992.4 g	900	900	2000
F4	1991.2 g	1200	1200	2000
F5	1990.0 g	1500	1500	2000
F6	1988.8 g	1800	1800	2000

The formulations were first mixed manually in a plastic tumbler for 10 min each. Compounding was next done in laboratory co-rotating twin screw extruder (*Labtech Engineering Co.*) under Nitrogen blanket. The extruder specifications are mentioned below:

Screw Diameter = 26 mm

L/D = 40:1

Maximum Barrel Temperature = 400 ºC

Screw Rotation Speed = 0 – 800 rpm

The following were the important extrusion parameters:-

Temperature Profile (ºC):

Table 3.3: Extrusion Temperature Profile.

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	DIE
140	145	150	155	160	165	170	175	180	180

Screw speed = 200 rpm

Feeder output rate = 2.5 kg/hr

Die pressure = 65 bar

Pelletizer speed = 8 m/min

Pellet length = 2.5 mm

Fig 3.1: Labtech Engineering Co-rotating Twin Screw Extruder

3.2.2 CRYOGENIC GRINDING PROCESS

Cryogenic grinding of the compounded pellets was performed in a CryoMill (*Retsch Gmbh Co.*). Liquid nitrogen (-196^{o}C) was used as the cryogenic fluid. The operation parameters have been stated below:

Table 3.4: Operational parameters for Cryogenic Grinding.

OPERATION	TIME (min)	FREQUENCY (s^{-1})
PRE COOLING	8	5
GRINDING	2.5	25
INTERMEDIATE	2	5

Number of Grinding cycles	=	3
Nitrogen pressure	=	0.5 bar

4 – 4.5gm pellets of each formulation were grinded individually. After grinding, the sample vial was allowed to attain room temperature so that the powdered sample gets devoid of any moisture.

Fig 3.2: Retsch Cryogenic Ball Mill

3.2.3 PARTICLE SIZE ANALYSIS

Particle size measurement of the powdered sample was done by Wet Method using *Malvern Mastersizer-2000* equipment. The instrument determines the particle size based on the phenomena of laser diffraction. Significant equipment details are listed as follows:

Size Range	=	0.02µm to 2000µm
Measurement Principle	=	Mie scattering
Detection systems	=	Red light: forward scattering, side scattering, back scattering Blue light: wide angle forward and back scattering

Light sources = Red light: helium-neon laser

Blue light: solid-state light source

Xylene was used as the dispersing solvent. Background measurement was first performed in absence of powder sample. Agitation was done at 2000rpm & the powder sample added till the desired obscuration range (10 – 20) was obtained, after which measurement was done.

Fig 3.3: Malvern Particle Size Analyzer

3.2.4 ADDITIVE EXTRACTION (ASTM D7210)

'Mars Xpress' equipment from *CEM Corporation* was used for microwave assisted solvent extraction of the additives from the grinded polymer powder. A total of 40 samples could be extracted at once. Mixture of acetone & cyclohexane (70:30) was used as the extraction solvent taking into consideration the solubility, polarity, toxicity & dissipation factor of the available solvents.

500 ml extraction solution was prepared containing 0.025 gm of internal standard compound (Songsorb 2908). Further, 10% w/v solutions of each powder sample were prepared (2.5 gm in 25ml of extraction solution) accurately.

Following were the extraction parameters:

Extraction solution	=	Acetone: Cyclohexane (70:30)
Preheat time	=	10 min
Extraction temperature	=	125 ºC
Microwave power	=	1600 W
Holding time	=	25 min

The extracted samples were then allowed to cool to room temperature.

Fig 3.4: CEM Microwave Assisted Extraction Equipment

3.2.5 CHROMATOGRAPHIC ANALYSIS (HPLC-UV) (ASTM D6953)

Chromatographic analysis was performed in a reversed phase HPLC column (*Dionex Ultimate 3000*) packed with C_{18} microspheres (5µm) as stationary phase, and equipped with an auto-sampler, UV-Vis detector. Calibration was done using an internal standard compound (Songsorb 2908). A suitable amount of extraction solution was filtered by a micro-porous PTFE membrane syringe filter directly into HPLC vials for analysis of extracted additives. Following were the operating parameters:

Solvent A = Acetonitrile (HPLC grade)

Solvent B = Water (HPLC grade)

Solvent C = Isopropylalcohol (HPLC grade)

Parameters for gradient elution:

Table 3.5: Gradient elution parameters for HPLC analysis

TIME (min)	FLOW (ml/min)	%A	%B	%C
0	2	88	12	0
0.1	2	65	5	30
15	2	65	5	30
15.1	2	88	12	0

Wavelength = 278 nm

Column Temperature = 50 ºC

Injection volume = 20 µl

The identification of each compound present in the sample solution was done by comparing its retention time with that of the corresponding peak in the standard solution. Repeated trials were run for all the extracted samples for the confirmation of the results.

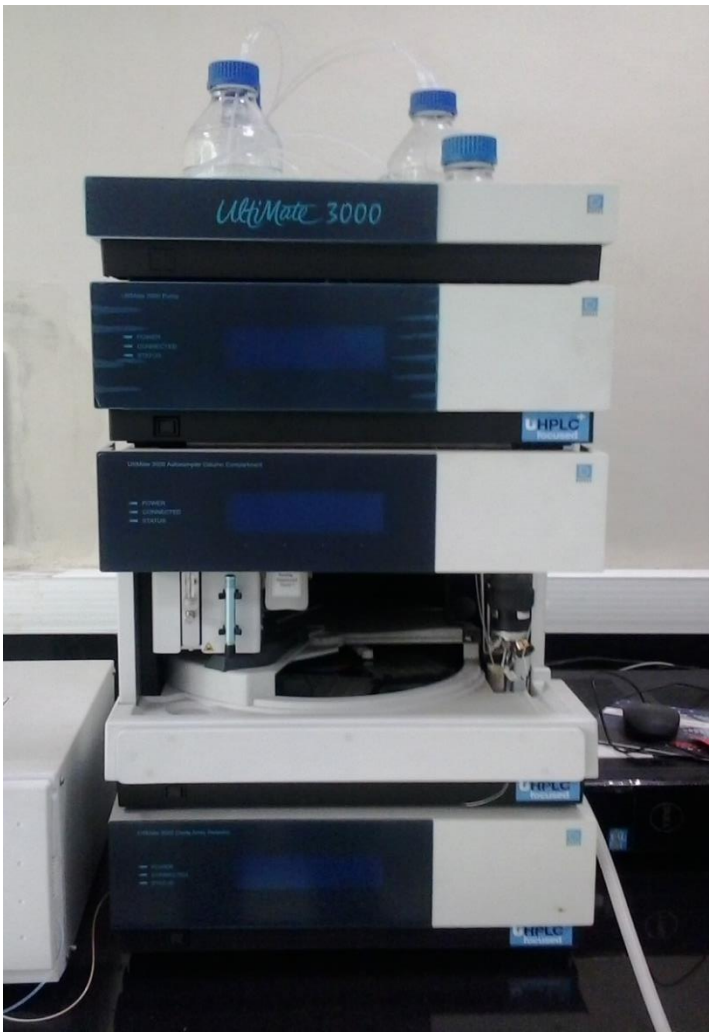


Fig 3.5: Dionex HPLC equipment

3.2.6 COMPRESSION MOLDING (SAMPLE PREPARATION)

Compression molding of all the formulated pellets had been carried out in a laboratory platen press (*Collin P 400 P/M*) to prepare samples for IR & XRF analysis. Machine specifications are given below:

Size of Platen = 400 x 400 mm^2

Maximum Platen Temperature = 450 ºC

Press Capacity = 500 kN

Quantity of material required was calculated using volume of mould & density of HDPE resin.

The following were the operating parameters:-

Molding temperature = 180 ºC

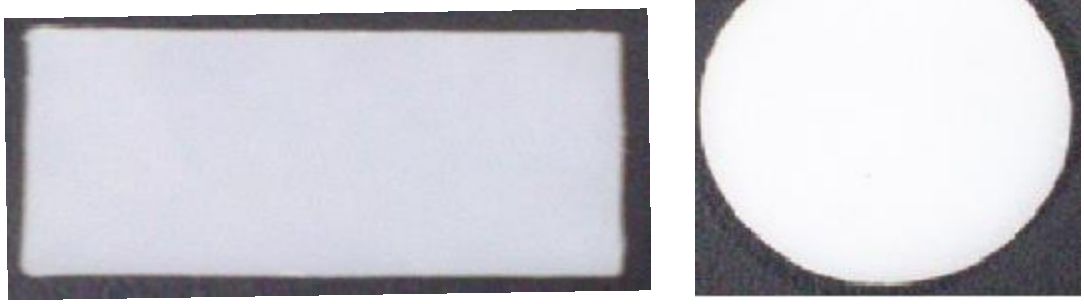
Operating pressure = 100 bar

Cooling rate = 15 K/min

Total cycle time = 2200 secs

Thus the following samples were obtained:

- 2mm thick rectangular samples for IR.
- 3mm thick disc shaped samples for XRF.



a) FTIR sample b) XRF sample

Fig 3.6: Compression molded samples for FTIR & XRF analysis

Fig 3.7: Collin Laboratory Platen Press

3.2.7 FOURIER TRANSFORM INFRARED SPECTRAL ANALYSIS (FTIR)

IR analysis was performed on a "*Shimadzu: IR Prestige-21*" spectrophotometer, using 3 test samples for each kind of formulation. The molded samples were mounted directly in the holder without any pre-treatment required. The following were the important test parameters:

Source = He-Ne laser

Scan Range = 4000-400 cm^{-1}

Resolution = 4 cm^{-1}

Mirror speed = 2.8 mm/sec

Mode = Absorbance

Carbonyl group (ester carbonyl) and Phosphate group (P-O) respectively corresponding to Irganox 1010 and Irgafos 168 were detected using instrument's IR-solution software. The overlapping IR absorption bands in the spectrum require a multivariate mathematical procedure such as partial least squares (PLS) in order to take full advantage of the benefits of the high signal to noise ratios, irrespective of the overlapping bands. In order to create a suitable calibration model, standards are required that reflect the expected variance of the analytical samples.

Thus, the PLS regression analysis method was used to predict the concentration of the additives by correlating the spectral intensities with the reference HPLC concentration. Following were the parameters for PLS analysis model:

Table 3.6: Parameters for PLS analysis model.

PARAMETER	IRGANOX 1010	IRGAFOS 168
Algorithm	PLS 1	PLS 1
No: of components	1	1
No: of standards	54 (6*3*3)	54 (6*3*3)
No: of factors	3	3
Spectral Region	1689 – 1782 cm^{-1} (ester carbonyl)	a.1204 – 1219 cm^{-1} b.1182 – 1199 cm^{-1} (P-O linkage)

To improve the PLS calibration, all spectra were centered and baseline corrected using the IR-solution software. The IR-solution software provides the reference parameters versus the spectroscopically obtained parameters. Calibration plot was next drawn between "Actual (HPLC Reference)" v/s "PLS Predicted" concentration values.

Fig 3.8: Shimadzu FTIR spectroscopy equipment

3.2.8 X-RAY FLUORESCENCE SPECTRAL ANALYSIS (XRF)

XRF spectroscopy analysis had been performed using "*Panalytical Axios WDXRF*" equipment having a maximum power output of 4kW and equipped with an auto-sampler. The disc shaped samples were directly analyzed using a sample cup without requiring any pre-treatment. Vacuum path was used to remove any discrepancy that would have been caused by reduction of fluorescent x-ray intensity if helium or air were used as optical path environment.

Following were the operating parameters:

Tube Voltage	=	30 kV
Tube Current	=	125 mA
Analyzing Crystal	=	Ge (111), 2d = 6.53 A
Optical Path	=	Vacuum
Detector	=	F.C
Spectral Line	=	P (Kα)

Three samples for each formulation were tested to obtain average results. Phosphorus element was detected using instrument's software & its characteristic wavelength 'λ' calculated. Further the peak intensities (counts per sec or cps) were determined for all samples by using wavelength value. 'Peak intensity' v/s 'HPLC Concentration (Reference)' calibration curve for Irgafos 168 was then generated.

Fig 3.9: PANalytical XRF spectroscopy equipment

CHAPTER 4

RESULTS & DISCUSSION

The following important results have been obtained from the various analytical tests carried out:-

4.1 PARTICLE SIZE DISTRIBUTION

The following results have been obtained from particle size analysis of compounded resin after it was grinded cryogenically:

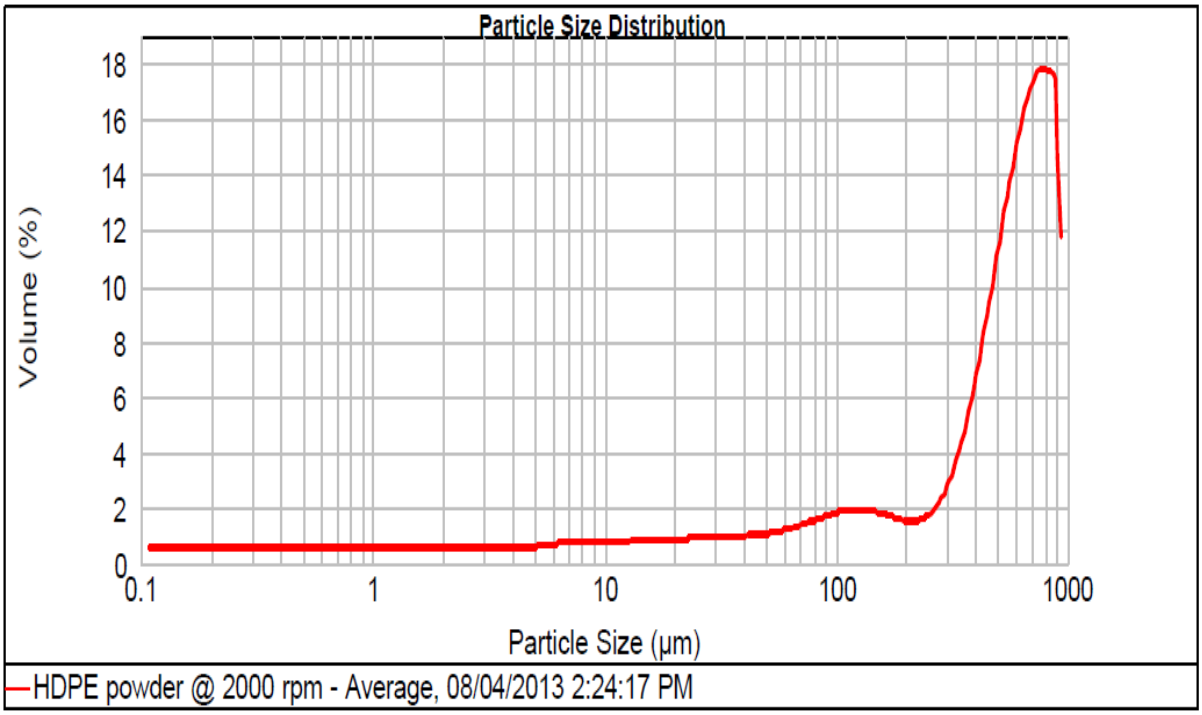


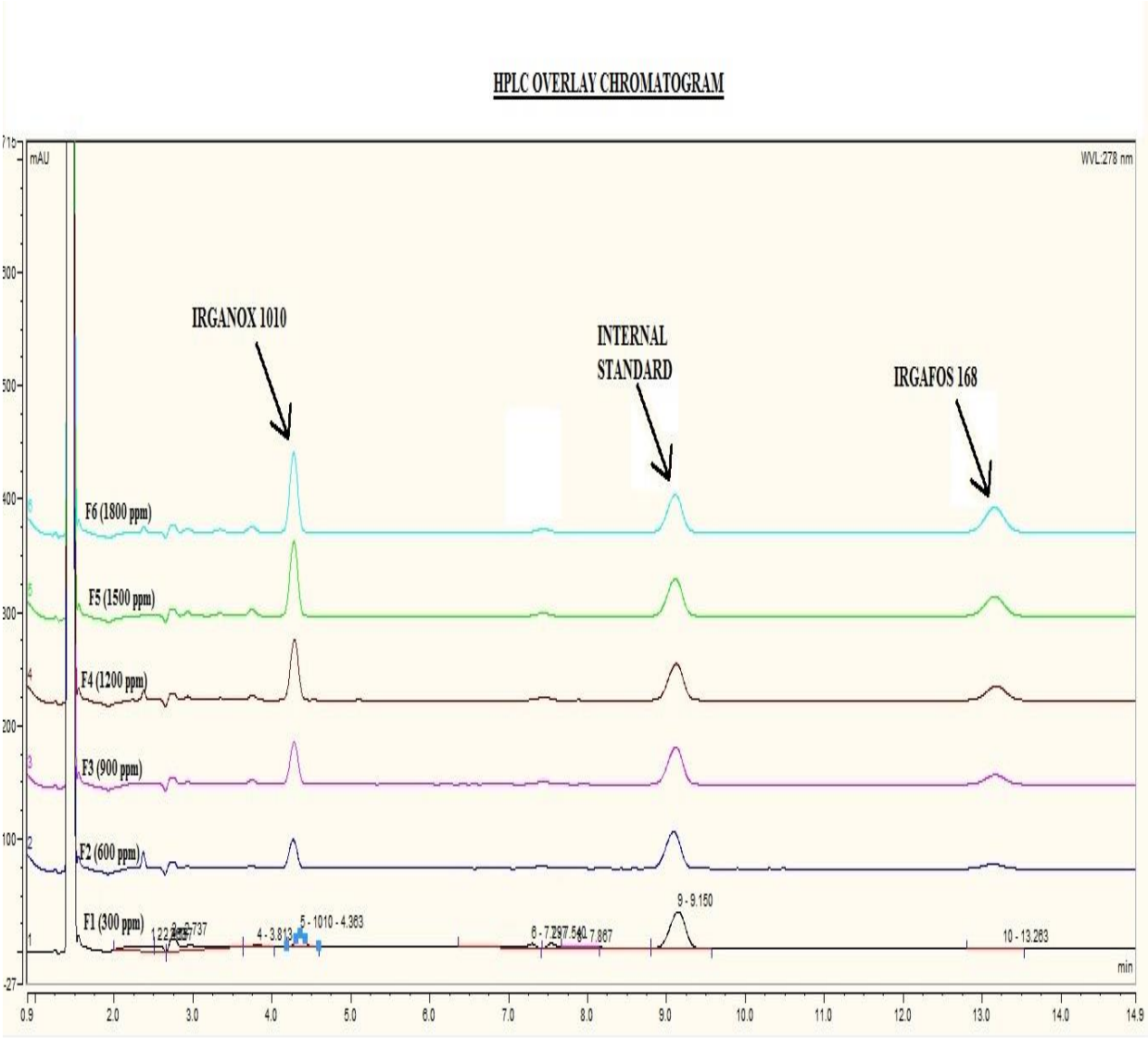
Fig 4.1: Particle size distribution of compounded HDPE.

D(0.5) < 1000 µm

Since, the instrument can measure maximum particle size upto 1000 microns only, exact D(0.5) value cannot be calculated. D(0.5) is the median value for particle size based on volume distribution. It is the size in microns that splits the distribution with half above and half below this diameter. Such a small average particle size renders the material to be conducive for microwave assisted solvent extraction process.

4.2 HIGH PRESSURE LIQUID CHROMATOGRAPH

The figure below shows the HPLC chromatogram of extracts from various formulations prepared in presence of Calcium Stearate.



F1: Additive Concentration- 300ppm
F2: Additive Concentration- 600ppm
F3: Additive Concentration- 900ppm
F4: Additive Concentration- 1200ppm
F5: Additive Concentration- 1500ppm
F6: Additive Concentration- 1800ppm

Fig 4.2: HPLC Overlay Chromatograph for all formulations.

The following components are eluted in the order of increasing retention time based on their interaction with C-18 column:

Table 4.1: Retention time of anti-oxidants based on interaction with C-18 column

S.NO	COMPONENT	RETENTION TIME
1	IRGANOX 1010	4.3
2	OXIDIZED IRGAFOS 168	7.2
3	INTERNAL STANDARD	9.1
4	IRGAFOS 168	13.2

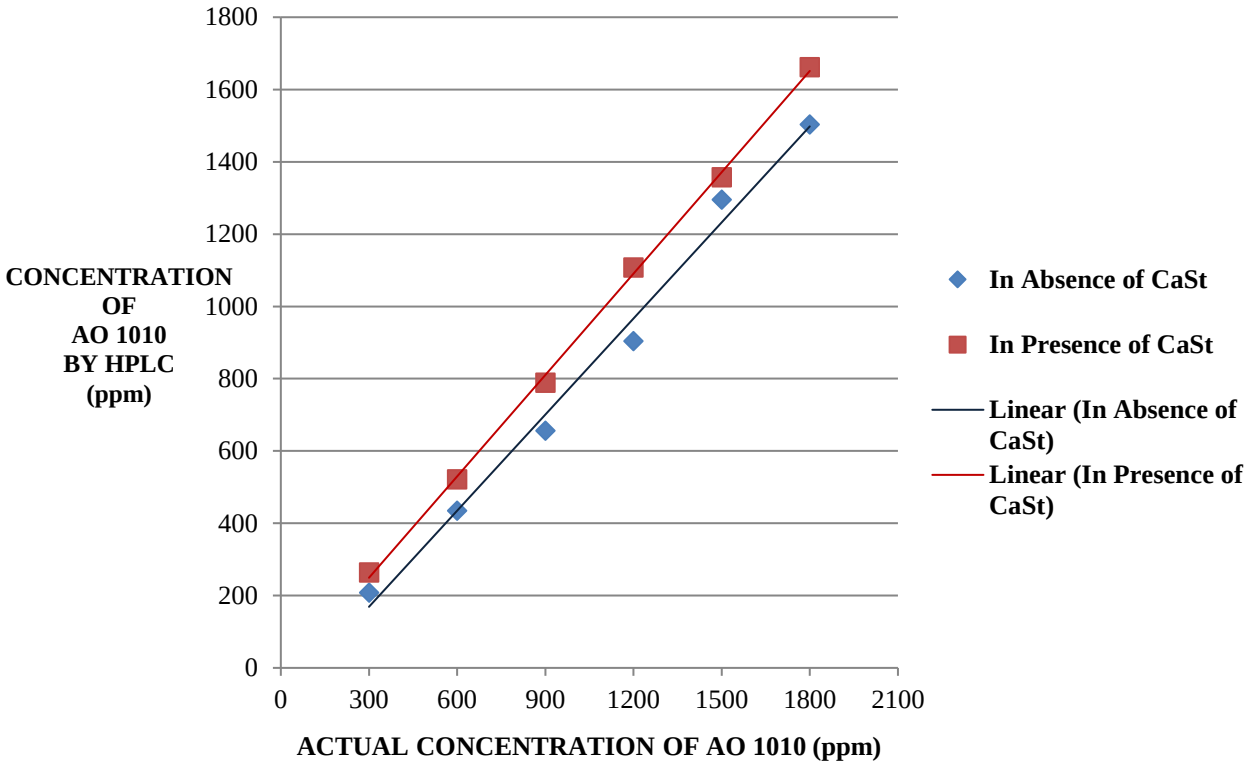
The above peaks were determined by comparison with the calibration solution containing mixture of Irganox 1010, Irgafos 168 and Internal Standard. Careful solvent selection & gradient elution has led to a visibly good resolution. Further, it is evident that the peak height increases with the greater concentration of additives from formulation F-1 to F6.

The concentrations of the additives as determined after thorough calculation have been tabulated further. The concentration obtained is average of 4 measurements.

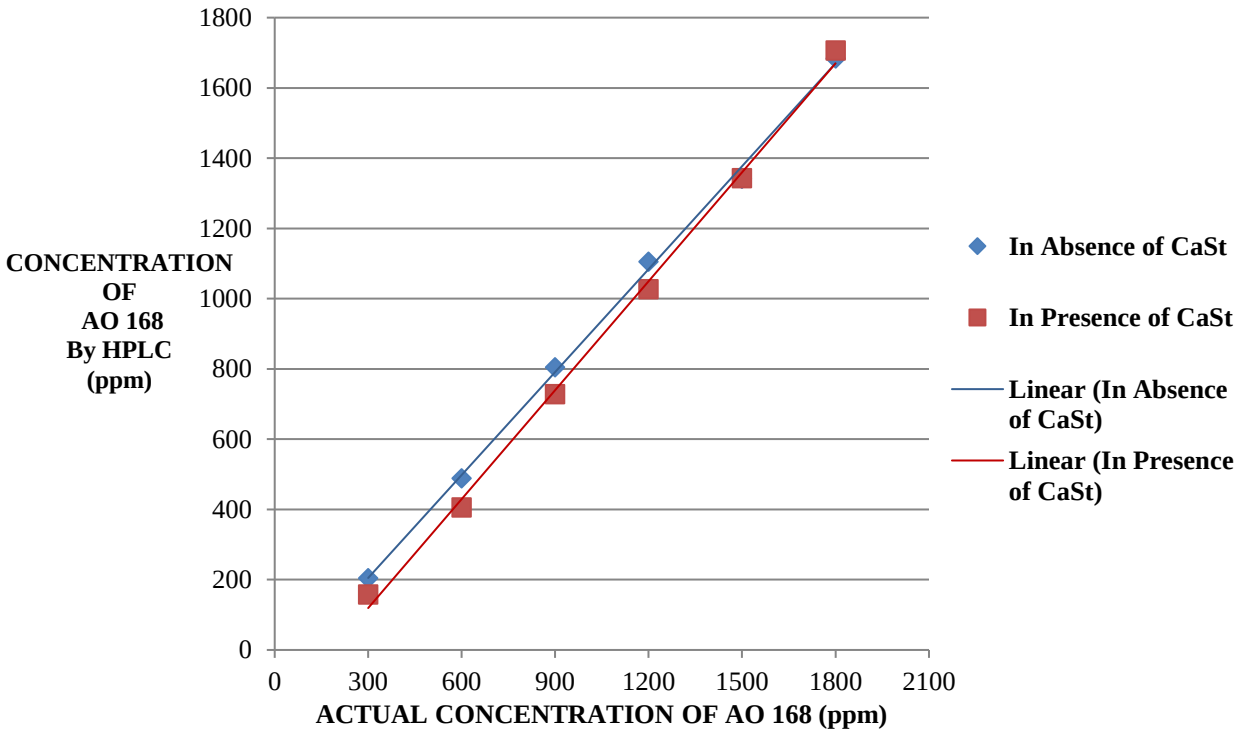
Table 4.2: Concentration of anti-oxidants from HPLC analysis

S.NO	ACTUAL CONCENTRATION OF THE ADDITIVES (ppm)	FORMULATIONS IN ABSENCE OF CALCIUM STEARATE		FORMULATIONS IN PRESENCE OF CALCIUM STEARATE	
		AO 1010 (ppm)	AO 168 (ppm)	AO 1010 (ppm)	AO 168 (ppm)
F1	300	208	204	264	158
F2	600	435	488	522	405
F3	900	656	804	789	728
F4	1200	904	1105	1108	1027
F5	1500	1295	1341	1357	1343
F6	1800	1503	1683	1662	1706

Graphical representation corresponding to the above tabulated values is plotted ahead:



Graph 4.1: HPLC v/s Actual added Concentration of Irganox 1010



Graph 4.2: HPLC v/s Actual added Concentration of Irgafos 168

It can be seen from the data that the values of Irganox 1010 and Irgafos 168 experimentally determined by HPLC are lower than the theoretical compounded values. This shows that anti-oxidants are consumed to some extent during the compounding process.

However, the above results also show that there is a significant decrease in the consumption of primary anti-oxidant, i.e. Irganox 1010 when the formulations are prepared in the presence of calcium stearate as an acid scavenger. It is reported in the literature that if acid scavengers are not incorporated into polyolefins, the acidic residues left in the polymer will de-alkylate the tertiary butyl groups present in hindered phenolic antioxidant.

Henceforth, in further analysis, only formulations containing calcium stearate have been tested for additive concentration to make calibration model for various additives by infra-red spectroscopy. The calcium stearate content has been kept constant (2000 ppm) in all the formulations.

Further, as seen from Table 4.2 there is uniform difference (F-1 – F-6) in the actual concentration of additives added into polymer during compounding and concentration values as determined by HPLC. The difference of the concentration is around 100 – 150 ppm. The probable reason for this observation is as follows:

- 100 – 150 ppm each of Irganox 1010 and Irgafos 168 is consumed during the compounding
- During extraction, small amount of additive may not be successfully extracted from the polymer matrix

4.3 X-RAY FLUORESCENCE SPECTRA

X-ray spectra (Intensity v/s 2Theta) of compounded HDPE disc sample for full range scan is given below:

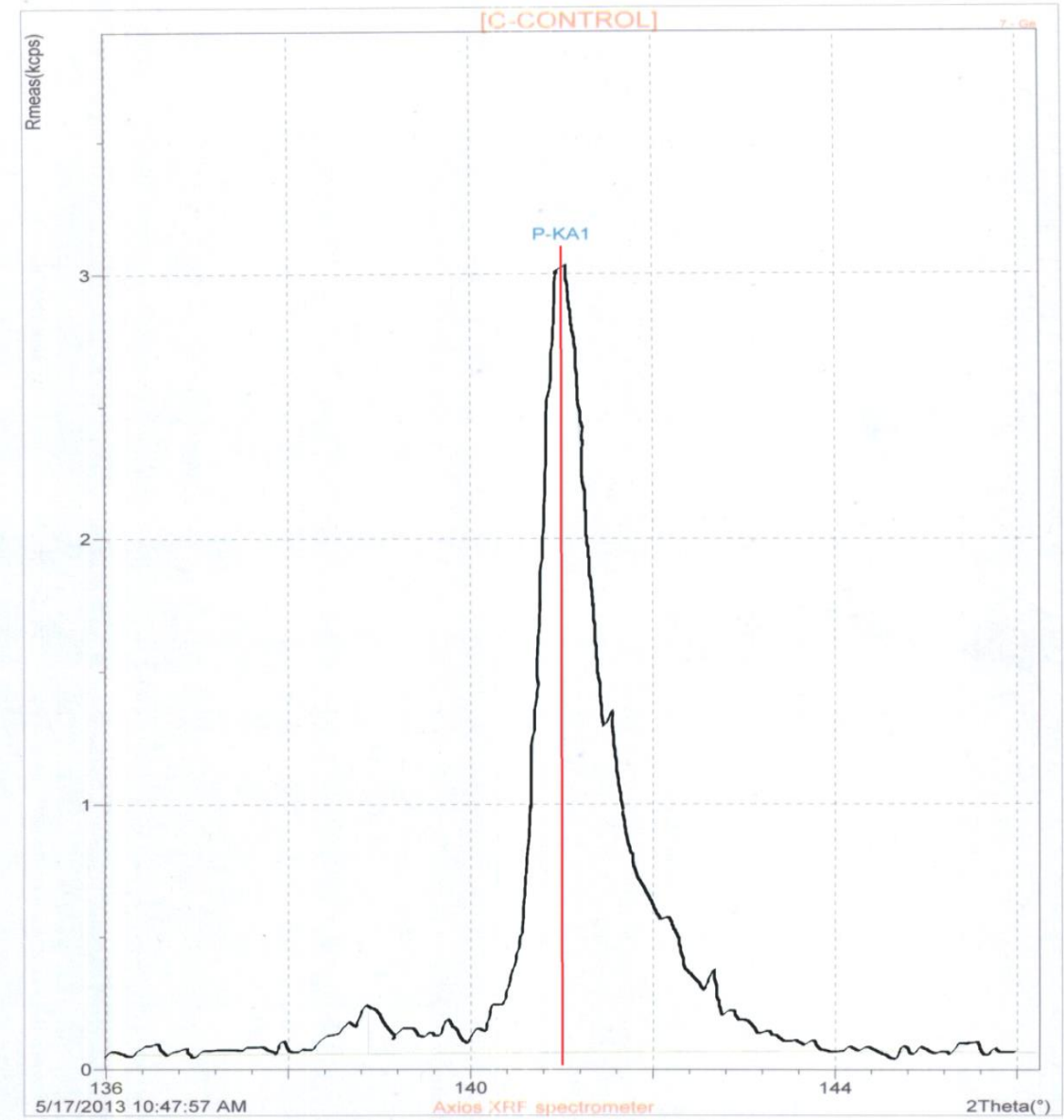


Fig 4.3: XRF spectra of compounded HDPE

The 'Kα' line for phosphorus(P) element as detected by system software has been clearly shown. The '2θ' value for the phosphorus peak from the spectral plot is 141º in presence of Ge(111) crystal.

The characteristic wavelength value "λ" can be calculated from the Bragg's law as follows:

Bragg's equation: $n\lambda = 2d \sin\theta$

where;

n = 1

2d = 6.53 A (for Ge crystal)

θ = 70.5^{o}

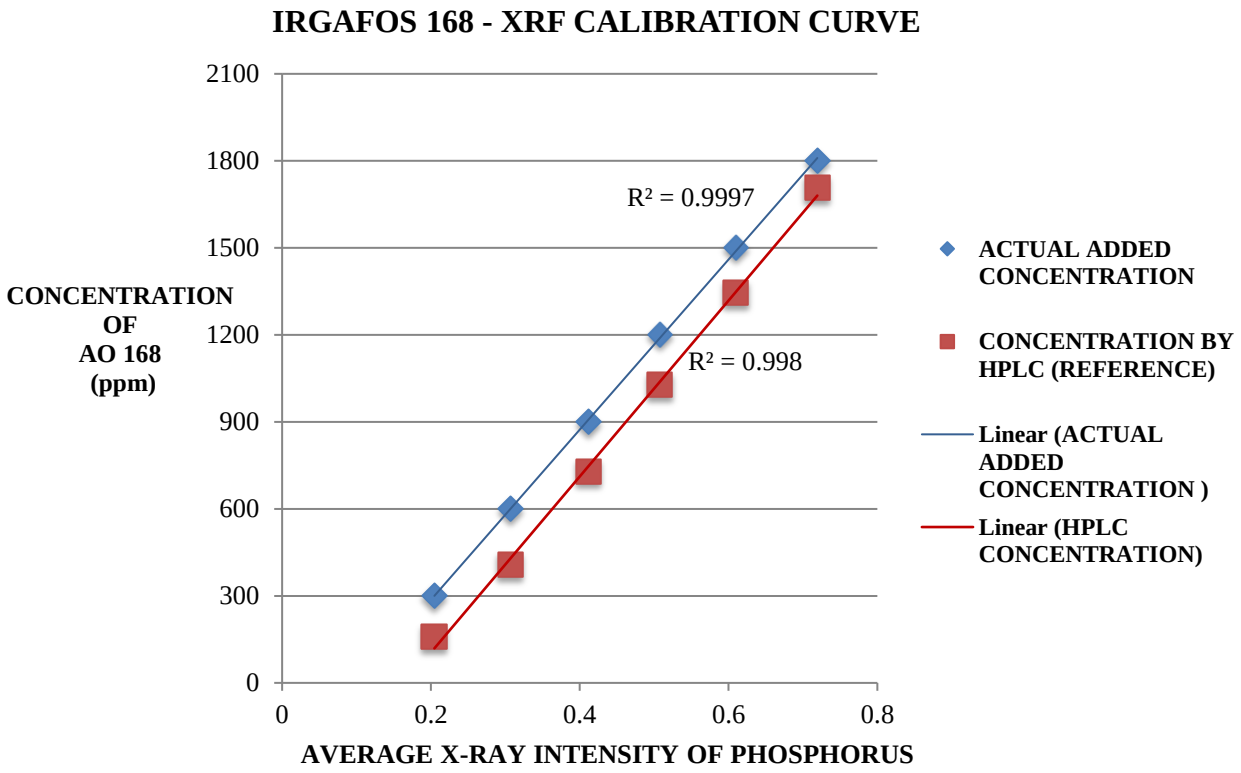
Hence; λ = 6.155 A

Thus, corresponding to the characteristic wavelength 'λ', the averaged x-ray intensity (3 samples each) of Phosphorus 'P' present in secondary anti-oxidant Irgafos 168, when used in presence of CaSt is shown below:

Table 4.3: Average x-ray intensity of Phosphorus (kcps)

S.NO	ACTUAL AO 168 CONCENTRATION (ppm)	AO 168 CONCENTRATION BY HPLC ANALYSIS (ppm)	AVERAGE X-RAY INTENSITY OF PHOSPHORUS (kcps)
F1	300	158	0.2046
F2	600	405	0.3068
F3	900	728	0.4125
F4	1200	1027	0.5082
F5	1500	1343	0.6101
F6	1800	1706	0.7193

Calibration curve between x-ray intensity & corresponding HPLC reference concentration has been plotted further:



Graph 4.3: XRF Calibration Curve- *HPLC concentration of AO 168 v/s Average x-ray intensity of Phosphorus*

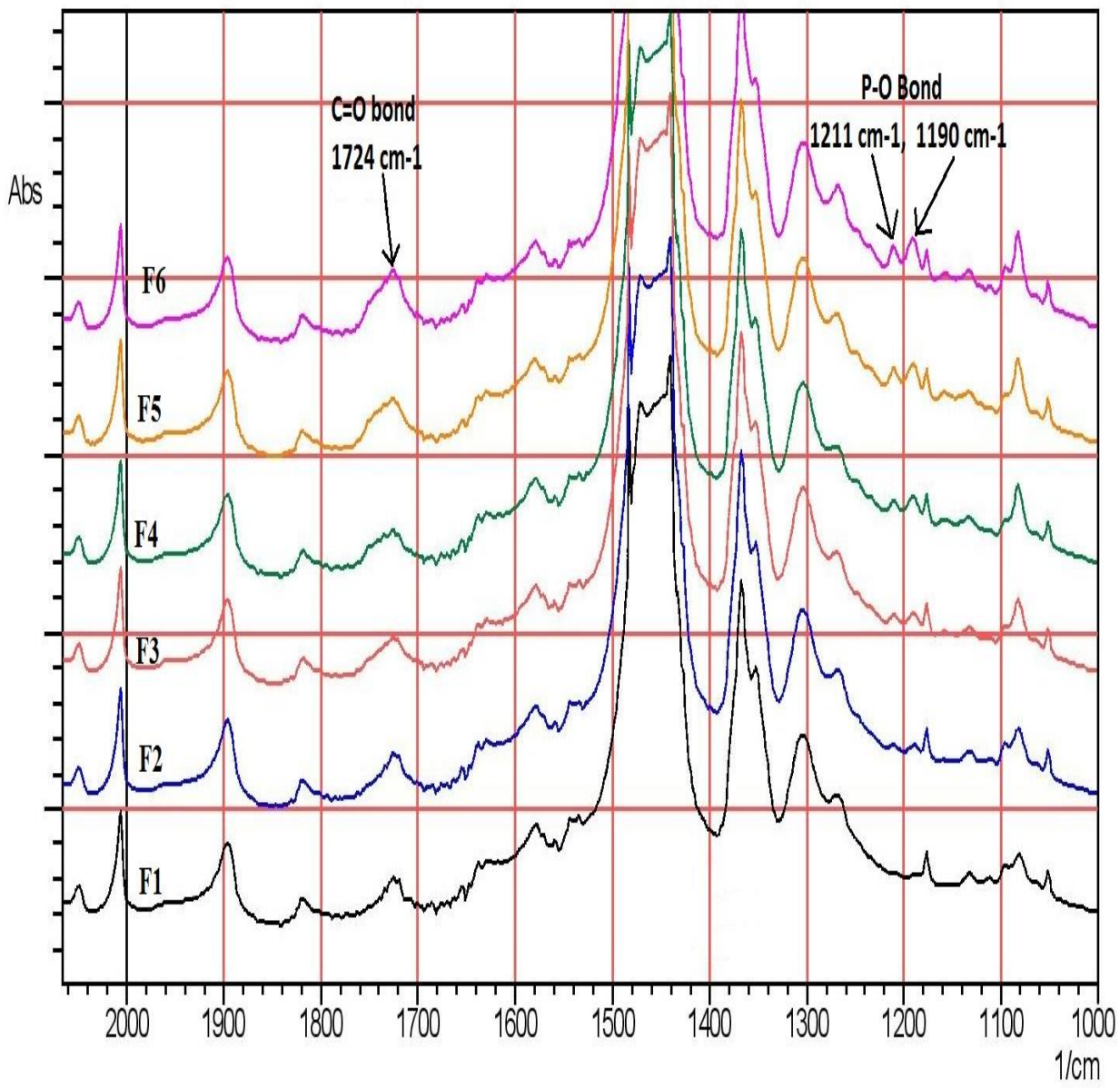
The above plot shows the relationship between concentration of Irgafos 168 in HDPE and its peak intensity corresponding to phosphorus element (P) as detected by XRF spectroscopy. Linear regression analysis has been performed using HPLC concentration values as reference. A Regression coefficient value (R^2) of ***"0.998"*** was obtained, which shows that the plot is almost linear.

Also, the difference between concentration values predicted by using "Actual concentration v/s Intensity" calibration curve; and those using "HPLC concentration v/s Intensity" as calibration model, is visibly clear. It is well known from the stabilization mechanism that Irgafos 168 gets consumed to protect polymer from degradation. The XRF will show total phosphorus content added into polymer, whereas, HPLC will show only the Irgafos 168 and its oxidized form. Hence, the calibration plot between "HPLC concentration" & "x-ray intensity" is more reliable and unambiguous.

The calibration curve can thus be used for accurate determination of additives in unknown compounded samples.

4.4 FOURIER TRANSFORM INFRARED SPECTRA

Following is an overlay spectral plot (absorbance v/s wavenumber) for all the six formulations:



F1- AO1010 (264ppm), AO168 (158 ppm), CaSt (2000 ppm)
F2- AO1010 (522ppm), AO168 (405 ppm), CaSt (2000 ppm)
F3- AO1010 (789ppm), AO168 (728 ppm), CaSt (2000 ppm)
F4- AO1010 (1108ppm), AO168 (1027 ppm), CaSt (2000 ppm)
F5- AO1010 (1357ppm), AO168 (1343 ppm), CaSt (2000 ppm)
F6- AO1010 (1662ppm), AO168 (1706 ppm), CaSt (2000 ppm)

Fig 4.4: FTIR overlay spectra of compounded HDPE

The spectral plot clearly depicts the concerned peaks for carbonyl (C=O) at 1724 cm^{-1} corresponding to Irganox 1010 and for phosphite (P-O) at 1211 & 1190 cm^{-1} corresponding to Irgafos 168. The peak intensity can be seen to increase as the concentration of additives in the compounded polyethylene resin increases; thus, clearly depicting the direct proportionality between component concentration and absorbance intensity.

Concentration values for Irganox 1010 & Irgafos 168 as first predicted by ***"Absorbance Ratio"*** method have been tabulated below:

*Table 4.4: FTIR predicted concentration of anti-oxidants by **'Absorbance Ratio'** method*

S.NO	AO 1010 CONCENTRATION (ppm)			AO 168 CONCENTRATION (ppm)		
	HPLC*	Predicted**	% Diff	HPLC*	Predicted**	% Diff
F1	264	290	***-10***	158	103	***35***
F2	522	669	***-28***	405	421	***- 4***
F3	789	767	***3***	728	759	***- 4***
F4	1108	889	***20***	1027	889	***- 5***
F5	1357	1545	***-14***	1343	1076	***7***
F6	1662	1542	***7***	1706	1434	***8***

** = From HPLC analysis (ppm)*

*** = From IR-Absorbance Ratio method (ppm)*

Extremely high disparity is obtained between the HPLC concentration values and those determined by Absorbance Ratio method in FTIR analysis. This renders the method as unfavorable, and thus it has not been used further for developing a calibration model.

Therefore, to obtain a better model by limiting the discrepancy in predicted v/s reference values, PLS regression analysis had been performed. PLS model results are tabulated further:

*Table 4.5: FTIR predicted concentration of anti-oxidants by **'PLS'** analysis*

S.NO	AO 1010 CONCENTRATION (ppm)			AO 168 CONCENTRATION (ppm)		
	HPLC*	Predicted**	% Diff	HPLC*	Predicted**	% Diff
1	264	277	***-5.2***	158	164	***-3.7***
2	522	493	***5.6***	405	398	***1.7***
3	789	776	***1.6***	728	739	***-1.5***
4	1108	1111	***-0.3***	1027	1044	***-1.6***
5	1357	1395	***-2.8***	1343	1355	***-0.9***
6	1662	1634	***1.7***	1706	1684	***1.3***

** = From HPLC analysis (ppm)*

*** = From IR-PLS analysis (ppm)*

There is a very moderate difference in the additive concentration values from HPLC analysis & those from PLS model, and thus can be regarded as adequately close to each other. When compared with the predicted concentration values from Absorbance Ratio method, the PLS predicted values are in far better agreement with the reference HPLC values for both the additives.

The significant statistical performance parameters for PLS are reported below:

Table 4.6: Statistical performance output parameters for PLS model

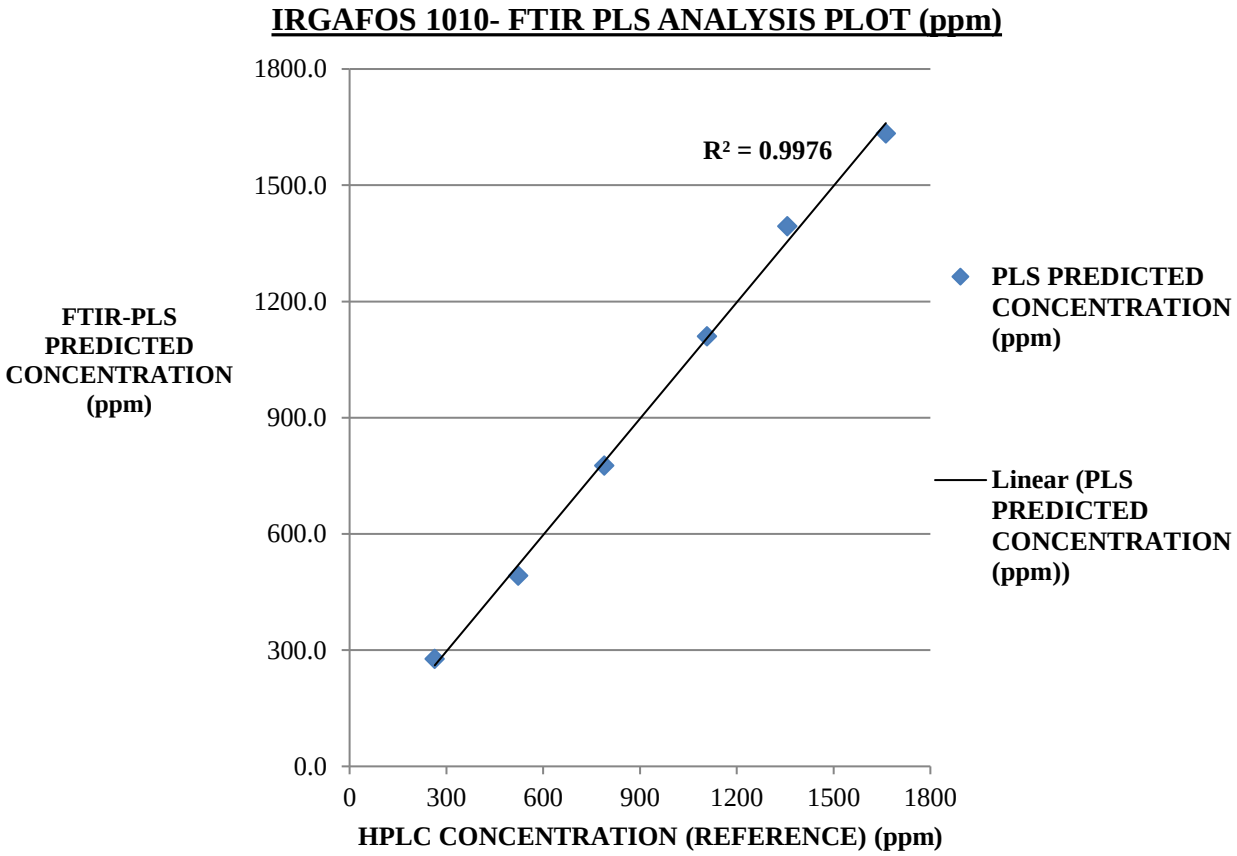
PARAMETER	IRGANOX 1010	IRGAFOS 168
Correlation coefficient	0.997	0.999
MSEP	0.00647	0.0011
SEP	0.08044	0.03318

MSEP = Mean squared error of prediction

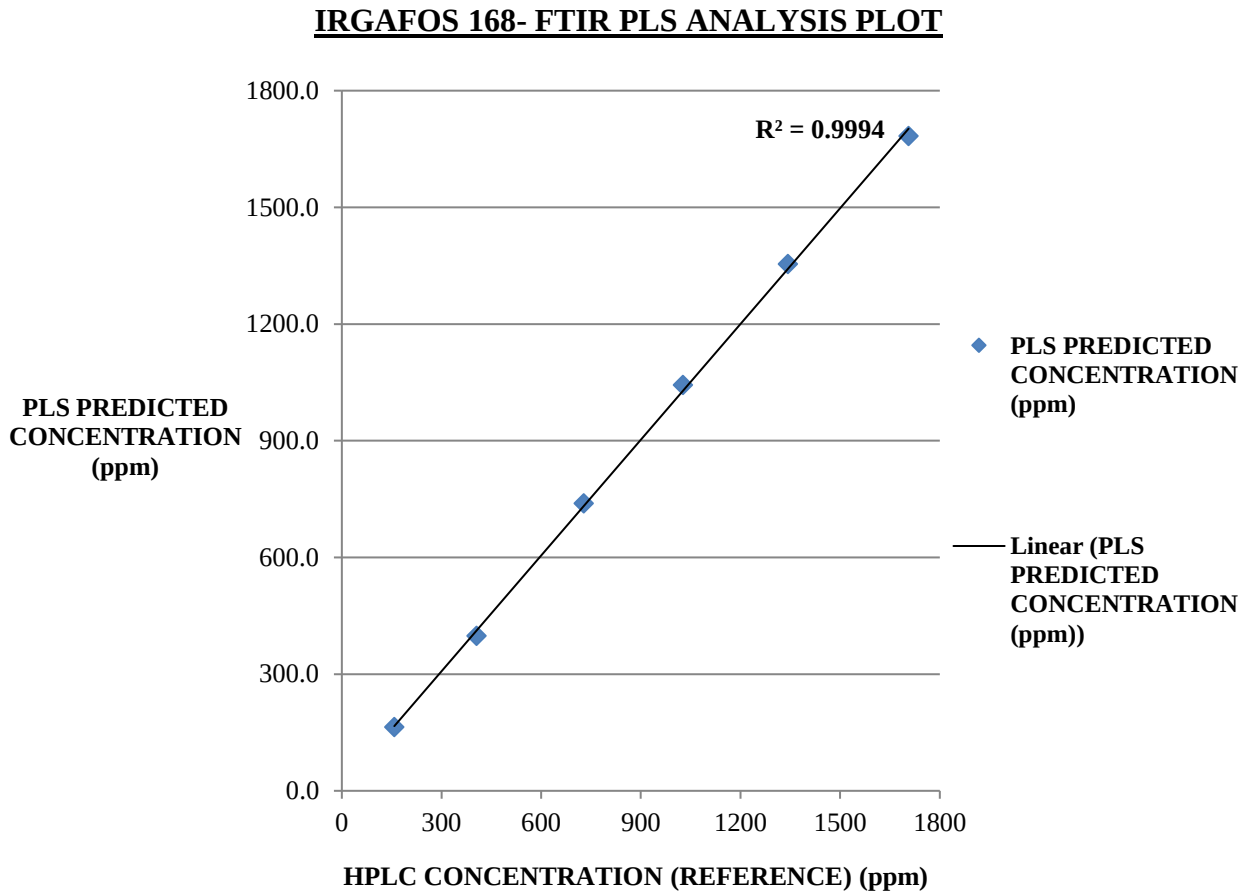
SEP = Standard error of prediction

Very fine values for performance parameters have been obtained after requisite optimization of the PLS model; values of the correlation coefficient being exceedingly close to one. Particularly low values for both the error functions (MSEP & SEP) have been attained, as is preferred.

Curves between FTIR-PLS predicted concentration & HPLC concentration (reference) values have been plotted for both the additives:



Graph 4.4: FTIR PLS Analysis Plot- *HPLC Reference concentration v/s FTIR-PLS predicted concentration of AO 1010.*



Graph 4.5: FTIR PLS Analysis Plot- HPLC Reference concentration v/s FTIR-PLS predicted concentration of AO 168

The predicted curves are almost linear as desired, with regression coefficients approaching unity. These curves can prove convenient means of determining additive concentration in unknown samples without the need for extraction & chromatographic procedures.

The general under estimation of anti-oxidants can be accounted for by the following aspects:

- Possible thermal degradation of anti-oxidants during compounding because of their sensitivity to elevated temperature, thus forming undefined oxidized products.
- Potential loss of additives during analysis, especially during the course of extraction procedures. This renders some part of additives as undetectable.

The following table shows the concentration values of Irgafos 168 as determined by HPLC, FTIR & XRF analytical techniques:

*Table 4.7: Concentration of **Irgafos 168** determined by HPLC, FTIR &XRF analysis*

S.No	THEORETICAL ADDED CONC. (ppm)	HPLC CONC. (ppm)	FTIR CONC. (ppm)	XRF CONC. (ppm)
F1	300	158	164	134
F2	600	405	398	443
F3	900	728	739	765
F4	1200	1027	1044	1045
F5	1500	1343	1355	1352
F6	1800	1706	1684	1672

As seen from the table the concentration of AO 168 as determined by HPLC, FTIR and XRF are in close agreement to each other. In view of this, concentration of Irgafos 168 can be quickly determined via IR spectroscopy or XRF.

CHAPTER 5

SUMMARY & CONCLUSION

A method based on FTIR and XRF has been developed to quantify the content of anti-oxidants, viz. Irganox 1010 & Irgafos 168 in polyolefins. The method based on FTIR can be used for simultaneous estimation of Irganox 1010 & Irgafos 168, whereas, XRF based method can be used for Irgafos 168 estimation.

Microwave assisted solvent extraction technique was used to extract anti-oxidants from HDPE, which proved to be a very fast procedure for successful extraction while consuming less solvent. Followed by extraction, HPLC analysis was performed which helped to accurately determine the concentration of the respective anti-oxidants. It was observed that in the absence of CaSt (acid scavenger), comparatively large amounts of anti-oxidants were consumed. Thus, further analysis was confined to formulations containing CaSt & HPLC determined concentration as reference amounts.

Successive to the HPLC analysis, XRF and FTIR spectroscopic analysis had been carried out for compounded HDPE. FTIR was used for quantifying both Irganox 1010 and Irgafos 168, using absorption intensities of ester carbonyl and phosphate bond respectively. Partial least squares regression analysis was employed to predict the values of concentration from FTIR spectral data. It was found that PLS provided far better prediction results compared to absorbance ratio method. Curves were then generated between HPLC concentration values as reference and PLS predicted concentration values. Exceedingly good values for regression coefficients were obtained for both the anti-oxidants. Also, equally commendable values resulted for PLS statistical error output parameters.

XRF analysis quantified only Irgafos 168 by means of x-ray intensities of phosphorus element. XRF analysis of each sample took less than 1 min. Subsequently, calibration curve was plotted between HPLC concentration values as reference and x-ray intensity of elemental phosphorus. Regression coefficient value very close to unity was obtained, thus confirming the linearity of the calibration curve.

Consequently, these calibration curves can now be employed to quantify both the anti-oxidants for the concerned grade of HDPE in unknown samples by direct FTIR & XRF spectroscopic analysis. Thus, it prevents the quality control personnel from spending time on tedious extraction and chromatographic procedures and makes the whole process hassle free, prompt and consistent.

CHAPTER 6

FUTURE PROSPECTS

Proceeding ahead in the realm of polymer additive analysis, lot of encouraging research can be done. A particular problem in additive analysis concerns accuracy and traceability. Hence, latest evolving statistical modeling and error analysis methods can be employed for concentration prediction. Some future needs are more reliable quantification, reference materials and simplification of data management. Also, there are still many quantitative analytical methods waiting to be developed, such as GC– SMB–MS, PTV–HTGC–ToFMS, PHWE-LC-GC etc. It will be essential for the future of polymer/additive analysis that progress is made towards accepted techniques and broad use. Today, the number of additives used in the polyolefin industry is far higher than those addressed in the present research, and so, optimized methods are still required. Thus, calibration models can be developed for a host of other important polymer additives like Irganox 1076, Irganox 1330, Irganox MD 1024, P-EPQ, Ultranox 626 and much more.

ABBREVIATIONS

AOs	–	Anti-oxidants
ASE	–	Assisted solvent extraction
CE	–	Capillary electrophoresis
FTIR	–	Fourier transform infrared spectroscopy
GC	–	Gas chromatography
HALS	–	Hindered amine light stabilizer
HDPE	–	High density polyethylene
HPLC	–	High pressure liquid chromatography
HT–GC	–	High temperature gas chromatography
kcps	–	Kilo counts per second
LC	–	Liquid chromatography
MAE	–	Microwave assisted extraction
MS	–	Mass spectroscopy
MSEP	–	Mean squared error of prediction
NMR	–	Nuclear magnetic resonance
PHWE	–	Pressurized hot water extraction
PLS	–	Partial least squares
POs	–	Polyolefins
PTV	–	Programmed temperature vaporizing
PVC	–	Polyvinyl chloride
SEP	–	Standard error of prediction
SFE	–	Supercritical fluid extraction
SMB	–	Supersonic molecular beam

T_g	–	Glass transition temperature
ToF-MS	–	Time of flight-mass spectrometry
UV	–	Ultraviolet
XRD	–	X-ray diffraction
XRF	–	X-ray fluorescence

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