Analytical methods development for bisphenols and p-alkoxy alkyl benzoates.

General Introduction and literature survey.

Section A.

Typical analytical methods developments for Bisphenols.

Section B.

Typical analytical methods development for p-alkoxy alkyl benzoates
Introduction

Bisphenol is an important raw material for polymer industries. The bisphenol containing cardo groups are very useful in synthesizing polymer with very specific property such as enhanced thermal stability together with excellent solubility due to the backbone structure [1] during Bisphenol synthesis side products are created which, if not removed, can result in bisphenol having an unacceptable purity for use as a monomer for producing polycarbonates. The side products or impurities include both inorganic and organic species. The impurities can hinder polymerization resulting in low molecular weight. Polycarbonates that exhibit undesirable physical properties, such as increased brittleness. Furthermore, the impurities in monomer can undesirably produce discoloration in the polycarbonates, thereby affecting the transparency of the products [2]. While referring literature of bisphenol synthesis, it was found that iron is an agent that changes the color of bisphenol and affect other properties of end use product [3]. Similarly, p-alkoxy alkyl benzoates are an important family in the catalyst system for the preparation of polypropylene. They are used as inside electron donor in conjunction with a solid particulate catalyst precursor. Triethylaluminium as co-catalyst and an outside electron donor. Primary purpose of p-alkoxy alkyl benzoate in the catalyst system is to function as the selectivity control agent. Keeping in mind the importance of bisphenol and p-alkoxy alkyl benzoates characterization as a view of polymer catalyst and additive or raw material. We have developed a simple, safe, economical and time-efficient analytical methods like iron estimation [4-10], purity by HPLC [11,12], purity by Gas chromatography [16,17], moisture measurement [18-20], residual analysis of phenol and substituted phenol [21], inorganic species, and
loss on drying, acidity and color [22-26], residual phenol and iron estimation method were confirmed by linearity study [27].

Section A

Typical analytical method development for bisphenol.

1) Determination of Color number (APHA) in Bisphenol by Visual comparison.

Principle:

Color is determined by visual comparison of the sample with known concentration of colored solutions.

Reagents:

(1) Potassium Chloroplatinate (AR grade).

(2) Cobaltous Chloride hexahydrate (AR grade).

(3) Hydrochloric Acid (AR grade).

(4) Methanol (AR grade).

Standard preparation:

0.1245 gm of potassium chloroplatinate and 0.1 gm cobalt chloride was accurately weighed and dissolved in 10 mL water and transferred in to 100 mL flask. 10 mL hydrochloric acid was added in flask and sonicated the flask and final volume was made up to 100 mL with distilled water to get APHA No. 500 stock solution.

Prepared standards having colors of 10, 20, 30, 40 and 40 units by diluting 1.0, 2.0, 3.0, 4.0 mL stock color standard with reagent water to 50 mL in volumetric flask and mixed well.
Sample preparation

2.5 gm of sample was accurately weighed and dissolved in 25 mL methanol in a volumetric flask and sonicated properly to get clear solution and stoppard the flask.

Procedure:

Transferred 25 mL of the sample to a matched 50 mL Nessler tube and compared the color of the sample with the equal volume of color of the series of platinum-cobalt standards in matching Nessler tubes. View vertically down through the tubes against a white background and noted as the color of the number of the APHA standard that most nearly matches the sample.

Determination of Color Table 5.1

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound name</th>
<th>Color (APHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane</td>
<td>15-20</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)4-methyl cyclohexane</td>
<td>20-25</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>20-25</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)4-methylcyclohexane</td>
<td>20-25</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>15-20</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>40-50</td>
</tr>
</tbody>
</table>

2) Loss on Drying.

A dry clean empty glass-stoppard shallow weighing bottle was accurately weighed and put about 2.0 gm sample in the bottle and again
accurately weighed. Distribute the sample as evenly as practicable and loaded bottle for drying in vacuum oven.

Dried the sample at 75 °C for 2 hr under vacuum (750 mm of Hg) in a vacuum oven. Upon opening drying oven, closed the bottle promptly and allowed it to come to room temperature in desiccators before weighing.

**Calculation:**

\[
\frac{(W_2 - W_3) \times 100}{W_1}
\]

\(\%\) Loss on drying = \(\frac{(W_2 - W_3) \times 100}{W_1}\)

Where,

- \(W_1\) = wt. in gm of empty weighing bottle
- \(W_2\) = wt. in gm of weighing bottle + sample (before drying)
- \(W_3\) = wt. in gm of weighing bottle + sample (after drying)
Table 5.2

Determination of loss on drying in Bisphenols

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Compound name</th>
<th>Weight of sample (gm)</th>
<th>Weight loss (gm)</th>
<th>% LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxy phenyl)cyclohexane</td>
<td>2.0</td>
<td>0.0012</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)-4-methylcyclohexane</td>
<td>2.0</td>
<td>0.0011</td>
<td>0.055</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>2.0</td>
<td>0.0013</td>
<td>0.065</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane</td>
<td>2.0</td>
<td>0.0012</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>2.0</td>
<td>0.0013</td>
<td>0.065</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>2.0</td>
<td>0.0008</td>
<td>0.040</td>
</tr>
<tr>
<td>7</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>2.0</td>
<td>0.0014</td>
<td>0.07</td>
</tr>
</tbody>
</table>
3) Determination of Iron:

**Principle:** This method is based on a coupled two-step redox and complexation reaction. In the first step, iron present in Bisphenol in higher oxidation state Fe(III) is converted into Fe(II) ion by reduction with hydroxylamine hydrochloride. Subsequently, Fe(II) is complexed with Ferrozine reagent to form the dark magenta color, highly stable complex which absorbs light at 565 nm. The intense color allows trace analysis of iron present in bisphenols.

Reaction.

\[
2\text{HONH}_2\text{HCl} + \text{Fe}^{3+} \rightleftharpoons 4\text{H} + 2\text{H}_2\text{O} + \text{N}_2 + 2\text{Fe}^{2+} + 2\text{Cl}^- 
\]

**Formation of [Fe (FZ)$_3$]$^{2+}$ complex [Fig.5.1]**

![Diagram of [Fe (FZ)$_3$]$^{2+}$ complex](image)

**Instrumentation:**

Shimadzu double beam UV-Vis spectrophotometer -1601 with matched quartz cell.
Reagents:

(1) Concentrated hydrochloric acid (A.R. grade).
(2) Distilled water. (Double distilled)
(3) Hydroxylamine hydrochloride (Aldrich)
(5) Sodium acetate trihydrate (A.R. grade)
(6) Ferrozine (Sigma)
(7) Ferric ammonium sulphate. (A.R.grade)

Reagents Preparation:

(1) Hydroxylamine hydrochloride (25 %w/v)  
25.0 gm of hydroxylamine hydrochloride was accurately weighed and dissolved in 100 mL of distilled water.

(2) Sodium acetate trihydrate (1N)  
Prepared by dissolving 136.0 gm sodium acetate trihydrate in 500 mL distilled water.

(3) (Ferrozine 0.1%)  
1.0 gm of Ferrozine was accurately weighed and dissolved in distilled water and diluted to 1000 mL distilled water.

Standard Preparation:

0.8634 gm of ferric ammonium sulphate was accurately weighed and dissolved in water with addition of 2-3 drops of hydrochloric acid and dilute to 100 mL of water to get 1000 ppm stock solution. This stock solution was further diluted with same solvent to get working standard solution of 100 ppm.

Procedure for calibration curve:

Aliquots of standard solution (100 ppm) 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 1.5, 2.0 mL transferred in to a series of 100 mL volumetric flask. 2 mL
concentrated hydrochloric acid was added to each flask. 5 mL hydroxylamine hydrochloride solution was added to all flasks. Then 50 mL sodium acetate solution was added to each flask and finally 2 mL Ferrozine solution was added to all flasks and let set for 30 minute and final volume was made up to 100 mL with distilled water.

The absorbance was measured at 565 nm against corresponding reagent blanks. The amount of Fe$^{2+}$ in sample was estimated from corresponding calibration graph.

**Calibration curve:**

Calibration curve line for determination of Fe (II) in the form of complex with Ferrozine.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Std. concentration of Fe (ppm)</th>
<th>Absorbance ($\lambda_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.19</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.23</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.27</td>
</tr>
<tr>
<td>7</td>
<td>0.70</td>
<td>0.32</td>
</tr>
<tr>
<td>8</td>
<td>1.00</td>
<td>0.46</td>
</tr>
<tr>
<td>9</td>
<td>1.50</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Correlation coefficient $= r^2 = 0.99976.$

Acceptance criteria $= \text{should not be less than } 0.999.$
Table 5.4
Calculation table for determination of r² value.

<table>
<thead>
<tr>
<th>X value</th>
<th>Y value</th>
<th>X-X</th>
<th>Y-Y</th>
<th>(X-X) (Y-Y)</th>
<th>(X-X)²</th>
<th>(Y-Y)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>-0.63</td>
<td>-0.2855</td>
<td>0.179865</td>
<td>0.3969</td>
<td>0.08151</td>
</tr>
<tr>
<td>0.2</td>
<td>0.09</td>
<td>-0.53</td>
<td>-0.2455</td>
<td>0.130115</td>
<td>0.2809</td>
<td>0.06027</td>
</tr>
<tr>
<td>0.3</td>
<td>0.14</td>
<td>-0.43</td>
<td>-0.1955</td>
<td>0.084065</td>
<td>0.1849</td>
<td>0.03822</td>
</tr>
<tr>
<td>0.4</td>
<td>0.19</td>
<td>-0.33</td>
<td>-0.1455</td>
<td>0.048015</td>
<td>0.1089</td>
<td>0.02117</td>
</tr>
<tr>
<td>0.5</td>
<td>0.23</td>
<td>-0.23</td>
<td>-0.1055</td>
<td>0.024265</td>
<td>0.0529</td>
<td>0.01113</td>
</tr>
<tr>
<td>0.6</td>
<td>0.27</td>
<td>-0.13</td>
<td>-0.0655</td>
<td>0.008515</td>
<td>0.0169</td>
<td>0.00429</td>
</tr>
<tr>
<td>0.7</td>
<td>0.32</td>
<td>-0.03</td>
<td>-0.0155</td>
<td>0.000465</td>
<td>0.0009</td>
<td>0.00024</td>
</tr>
<tr>
<td>1.0</td>
<td>0.46</td>
<td>0.27</td>
<td>0.1245</td>
<td>0.033615</td>
<td>0.0729</td>
<td>0.0155</td>
</tr>
<tr>
<td>1.5</td>
<td>0.68</td>
<td>0.77</td>
<td>0.3455</td>
<td>0.265265</td>
<td>0.5929</td>
<td>0.11868</td>
</tr>
<tr>
<td>2.0</td>
<td>0.92</td>
<td>1.27</td>
<td>0.5845</td>
<td>0.742315</td>
<td>1.6129</td>
<td>0.34164</td>
</tr>
</tbody>
</table>

\[
X = 0.73 \quad \quad Y = 0.3355 \quad \quad 1.5165 \quad 3.321 \quad 0.692653
\]

Numerator for r = 1.5165
Denominator for r = 1.516674
r value = 0.99988
r² value = 0.99976

Sample preparation:

5.0 gm of 1,1-bis(3-methyl-4-hydroxyphenyl)cyclohexane was accurately weighed into quartz crucible and added 2-3 drops of concentrated sulphuric acid. Placed the quartz crucible in muffle furnace and increased temperature slowly up to 800 °C and kept for 6 hr to convert the sample into ash. After cooling the muffle furnace 1ml conc. HCl was
added carefully in crucible and transferred into 100 mL volumetric flask, then added 5 mL hydroxylamine hydrochloride solution and 20 mL sodium acetate solution. Finally 5 mL ferrozine solution was added and let set for 30 minute final volume was made up to 100mL with distilled water. The absorbance was measured at 565 nm.

**Table 5.5**

<table>
<thead>
<tr>
<th>sr. no.</th>
<th>Description</th>
<th>Absorbance ($\lambda_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sample</td>
<td>0.0162</td>
</tr>
<tr>
<td>2</td>
<td>Blank</td>
<td>0.005</td>
</tr>
</tbody>
</table>

\[
\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1}
\]
\[
= \frac{0.46 - 0.23}{1.0 - 0.5}
\]
\[
= 0.46
\]
\[
= \frac{(\text{Sample absorbance} - \text{Blank absorbance}) \times 100}{\text{Slope of std. Fe curve} \times \text{Weight of sample}}
\]
\[
= \frac{(0.0162 - 0.005) \times 100}{0.46 \times 5}
\]
\[
\text{Fe (ppm)} = 0.4869
\]

Similarly, some representative compounds of the series shown in the Table 5.4. was analyzed by using above analytical method.
### Table 5.6

**Results of trace amount of iron present in Bisphenols**

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Compound name</th>
<th>Weight of sample (gm)</th>
<th>Absorbance of blank solution</th>
<th>Absorbance of sample solution</th>
<th>Iron in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl) cyclohexane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0162</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)4-methylcyclohexane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0186</td>
<td>0.59</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0201</td>
<td>0.65</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)4-methylcyclohexane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0301</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0200</td>
<td>0.65</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0311</td>
<td>1.13</td>
</tr>
<tr>
<td>7</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>5.0</td>
<td>0.005</td>
<td>0.0296</td>
<td>1.06</td>
</tr>
</tbody>
</table>

4) **Chloride Content:**

**Principle:**

A known concentration of silver nitrate solution was added to the sample and unconsumed silver nitrate solution was back titrated against standard ammonium thiocyanate solution. Silver nitrate consumed gives a measure of chloride present in sample
Ag⁺ + Cl⁻ → AgCl

Ag⁺ + SCN⁻ → AgSCN

3 NH₄SCN + NH₄₂Fe (SO₄)₂ → Fe (SCN)₃ + 2 (NH₄)₂SO₄

Fe (SCN)₃ + 3NH₄SCN → (NH₄)₃[Fe (SCN)₆]

Reagent preparation:

(1) Silver nitrate (A R Grade, 0.1N) 17 gm of silver nitrate was accurately weighed and dissolved in distilled water and diluted to 1000 mL distilled.

(2) Ferric alum indicator (A R Grade, 40% solution) 40 gm of ferric sulphate was accurately weighed and dissolved in 15 mL of concentrated nitric acid and transferred in to 100 mL volumetric flask. 50 mL distilled water was added and swirled properly and final volume was made up to 100 mL with distilled water.

(3) Nitric acid (A R Grade, 1:1 v/v) 50 mL concentrated nitric acid was measured accurately and mixed with 50 mL distilled water.

(4) Ammonium thiocyanate (A R Grade, 0.1N) 8.5 gm of ammonium thiocyanate was accurately weighed and dissolved in 1000 mL distilled water.

Standardization of 0.1N Ammonium thiocyanate: 0.3 gm of silver nitrate was accurately weighed and transferred in 250 mL conical flask containing 25 mL distilled water and flask was sonicated for few minutes to get dissolved completely. 5 mL dilute nitric acid solution and 1 mL ferric alum indicator was added and titrated with 0.1N ammonium thiocyanate solution till color changes to faint brown color indicated end point of titration and recorded burette reading.
Normality of ammonium thiocyanate

Weight of silver nitrate
--------------------------------
Burette reading x0.16987

\[
\frac{0.3946 \times 1000}{23.0 \times 169.87} = 0.1010 \text{ N}
\]

Procedure:

0.2 gm of bisphenol was accurately weighed in to conical flask and added 25 mL distilled water. 3 mL diluted nitric acid solution and 10 mL silver nitrate solution was added to the conical flask and titrated with standard ammonium thiocyanate solution using ferric alum as indicator and recorded burette reading. Similarly carried out blank titration without taking sample.

Calculation:

\[
\frac{(B-V) \times N \times 3.546}{M}
\]

Chloride content (Cl\(^-\)) =

where

B = Volume in mL of standard ammonium thiocyanate solution required for blank titration.

V = Volume in mL of standard ammonium thiocyanate solution required for titration of sample.

N = Normality of standard ammonium thiocyanate solution.

M = Mass in grams of the sample taken for the test.
### Table 5.7

Trace amount of chloride present in Bisphenols

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Compound name</th>
<th>Weight of sample</th>
<th>Normality of 0.1N NH₄SCN</th>
<th>Burette reading mL</th>
<th>% Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl) cyclohexane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)4-methylcyclohexane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)4-methylcyclohexane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>7</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>0.2</td>
<td>0.1010</td>
<td>0.0</td>
<td>Nil</td>
</tr>
</tbody>
</table>

5) Alkalinity:

**Principle**

The sodium bicarbonate reacts with hydrochloric acid to form NaCl and water. The excess HCl changes bromophenol blue orange color from yellow to orange.
Reagents preparation:

(1) 35 % Hydrochloric acid (A R Grade 0.1 N) 8.9 ml 35 % hydrochloric acid was diluted with 1000 ml distilled water to get 0.1N solution.

(2) Methyl orange indicator.

Standardization of 0.1 N Hydrochloride: Sodium carbonate was dried in hot air oven at 260 °C. 0.220 gm of dried sodium carbonate was weighed accurately in 250 mL conical flask containing 50 mL distilled water and sonicated for 5 minutes to dissolve completely. Added 2-3 drops of methyl orange indicator and titrated with 0.1N hydrochloric acid solution till color changes from yellow to orange and calculated normality of 0.1N hydrochloric acid solution using following formula.

\[
\text{Weight of Sodium carbonate} \\
\text{Normality of HCl} = \frac{\text{Burette reading} \times 0.053}{0.220} \\
N = \frac{0.220}{35.7 \times 0.053} = 0.11620
\]

Procedure:

0.2 gm of bisphenol was accurately weighed in to conical flask and added 25 mL A R Grade methanol to dissolve completely and titrated with standard 0.1N Hydrochloric acid solution using methyl orange indicator as indicator till color changes from yellow to pink and recorded burette reading.

\[
\% \text{ of NaHCO}_3 = \frac{\text{B.R} \times \text{normality of HCl} \times 8.45}{\text{Weight of Bisphenol taken}}
\]
Table 5.8

Trace amount of alkalinity as NaHCO$_3$ present in Bisphenols

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Compound name</th>
<th>Weight of sample (gm)</th>
<th>Normality of 0.1N HCl</th>
<th>Burette reading mL</th>
<th>Alkalinity as NaHCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl) cyclohexane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)-4-methylcyclohexane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
<tr>
<td>7</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>0.2</td>
<td>0.1162</td>
<td>0.0</td>
<td>Nil</td>
</tr>
</tbody>
</table>
6) Determination of trace amount of Phenol and substituted phenol present in Bisphenols by HPLC.

Principle:
This method is based on High performance liquid chromatography using UV detector for detection of trace amount of phenol and substituted phenol present in bisphenol. Measurements are made using UV detector at 230 nm and electronic area integration.

Experimental:

Instrumentation:
Quantitative HPLC was performed on Agilent 1100 prominence isocratic, Agilent EZ Chrom Elite software, Column Kromosil C\textsubscript{18} (250x 4.6 mm ID, particle size 5 micron).

Reagents:

(1) Water (HPLC Grade).

(2) Acetonitrile (HPLC Grade)

(3) Phenol (AR Grade)

(4) o-cresol (AR Grade)

Instrumentation and Chromatographic condition:
The content of the mobile phase was acetonitrile and water was prepared in the ratio of 70:30 v/v. The contents of the mobile phase were filtered before use through 0.45 micron membrane filter, degassed by ultrasonication for 15 min and pumped from the respective solvent reservoirs to the column at the flow rate of 0.8 mL/min which yielded a column back pressure 138-141 bar. The run time was set for 20 min and
the column temperature was maintained at 30°C. The volume of injection loop was 10µL. Prior to the injection of sample solution, the column was equilibrated for at least 0.5 h with mobile phase flowing through the system. The elements were monitored at 230 nm and data were acquired, stored and analyzed with EZChrom Elite software (Agilent)

**Standard preparation:**

**Phenol:**

0.05 gm of phenol was accurately weighed in to a 100 mL volumetric flask and made up to the mark by mobile phase to get 500 ppm stock solution of phenol. Aliquots of standard solution 1, 2, 3, 4, 5 mL transferred in to 100 mL volumetric flask and diluted with same solvent to get 5, 10, 15, 20 and 25 ppm solution of phenol.

**o-cresol:**

0.05 gm of o-cresol was accurately weighed in 100 mL volumetric flask and made up to the mark by mobile phase to get 500 ppm stock solution. Same procedure was repeated as above to get 5, 10, 15, 20 and 25 ppm solution of o-cresol.

**Linearity determination of standard phenol and o-cresol solution.**

Injected 10µL of 5, 10, 15, 20 and 25 ppm of phenol solution 2 times in to the column. The mean value of peak area for two such determinations was calculated and plotted linearity graph of phenol. Same procedure was repeated as above for o-cresol solution.
Table 5.9
Linearity of standard phenol

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Parameter</th>
<th>Concentration of phenol in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>Sample size (µL)</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Retention</td>
<td>3.527</td>
</tr>
<tr>
<td>3</td>
<td>Peak Area of 1st injection</td>
<td>47587</td>
</tr>
<tr>
<td>4</td>
<td>Peak area of 2nd injection</td>
<td>47674</td>
</tr>
<tr>
<td>5</td>
<td>Mean area of Phenol peak</td>
<td>47630</td>
</tr>
</tbody>
</table>

Correlation coefficient = $R^2 = 0.9995$

Acceptance criteria = should not be less than 0.999

![Linearity graph of phenol](image-url)
### Table 5.10

**Linearity of standard o-cresol**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Parameter</th>
<th>Concentration of o-cresol in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Sample size µL</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Retention</td>
<td>4.007</td>
</tr>
<tr>
<td>5</td>
<td>Peak Area of 1\textsuperscript{st} injection</td>
<td>53986</td>
</tr>
<tr>
<td>6</td>
<td>Peak area of 2\textsuperscript{nd} injection</td>
<td>53845</td>
</tr>
<tr>
<td></td>
<td>Mean area of o-cresol peak</td>
<td>53915</td>
</tr>
</tbody>
</table>

**Correlation coefficient = 1**

**Linearity graph of o-cresol**

![Linearity graph of o-cresol](image-url)
Sample preparation:

0.02 gm bisphenol (test sample) was accurately weighed and transferred to a 100 mL volumetric flask containing 50 mL of mobile phase. The contents of the flask were sonicated for 15 min to dissolve bisphenol and made final volume up to the mark with mobile phase. Injected 10 µL sample in to the system and recorded area of corresponding phenols and quantified the amount of phenols in the sample using following formula.

\[
\text{R.F.} = \frac{\text{weight of standard phenols} \times \text{purity of standard phenols}}{100 \times 100 \times \text{area of standard phenols}}
\]

\[
\% \text{ phenol} = \frac{\text{Area of phenol in test sample} \times \text{R.F.} \times 100}{\text{Weight of sample}}
\]

Phenol in ppm = % phenol x 10,000
Table 5.11

Traces amount of residual phenol and o-cresol present in Bisphenols

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Compound name</th>
<th>Weight of sample (gm)</th>
<th>Area of phenol present in sample</th>
<th>Area of o-cresol present in sample</th>
<th>Phenol/o-cresol in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane</td>
<td>0.0202</td>
<td>-</td>
<td>50.00</td>
<td>22.97</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)4-methylcyclohexane</td>
<td>0.0206</td>
<td>-</td>
<td>42.00</td>
<td>18.9</td>
</tr>
<tr>
<td>3</td>
<td>1,1-bis(4-hydroxyphenyl)4-methylcyclohexane</td>
<td>0.0203</td>
<td>38.00</td>
<td>-</td>
<td>19.65</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>0.0200</td>
<td>28.00</td>
<td>-</td>
<td>14.7</td>
</tr>
<tr>
<td>5</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>0.0200</td>
<td>48.00</td>
<td>-</td>
<td>25.2</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>0.0200</td>
<td>32.00</td>
<td>-</td>
<td>16.8</td>
</tr>
</tbody>
</table>
7) Insoluble matter:

Principle:

The material is dissolved in acetone and insoluble content is filtered, dried it.

Apparatus and reagent:

1) Crucible
2) Measuring cylinder (capacity 100 mL)
3) Beaker 250 mL
4) Glass rod.
5) Flirtation flask
6) Acetone A R Grade

Procedure:

2 gm of sample was accurately weighed and transferred in to 250 mL beaker. Added 50 mL acetone and sonicated for few minutes to get clear solution. Weighed accurately clean dry sintered glass crucible and recorded empty weight of crucible. The clear solution was filtered through sintered glass crucible and dried the crucible in hot air oven at 110 0C for 1 hr. After drying removed crucible from oven and kept in desicicator for cooling and recorded weight of crucible.

\[ \text{Insoluble matter} = \frac{B-A \times 100}{\text{Weight of sample}} \]

Where,

B = Weight of crucible after drying.

A = Empty weight of crucible.
Table 5.12

Trace amount of insoluble matter present in Bisphenols

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>Compound name</th>
<th>Insoluble matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl) cyclohexane</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td>1,1-bis(3-methyl-4-hydroxyphenyl)4-methylcyclohexane</td>
<td>Nil</td>
</tr>
<tr>
<td>3</td>
<td>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane</td>
<td>Nil</td>
</tr>
<tr>
<td>4</td>
<td>1,1-bis(4-hydroxyphenyl)4-methylcyclohexane</td>
<td>Nil</td>
</tr>
<tr>
<td>5</td>
<td>1,1-bis(4-hydroxyphenyl)cyclohexane</td>
<td>Nil</td>
</tr>
<tr>
<td>6</td>
<td>1,1,1-tris(4-hydroxyphenyl)ethane</td>
<td>Nil</td>
</tr>
<tr>
<td>7</td>
<td>1,1,1-tris(4-hydroxyphenyl)methane</td>
<td>Nil</td>
</tr>
</tbody>
</table>
8) Determination of Bisphenol purity by HPLC method:

**Principle**

Bisphenol and other impurities are separated on reverse phase column using mixture of acetonitrile and water as mobile phase. The bisphenol peak and other eluted impurities peak area are distributed into 100%.

**Experimental:**

**Instrumentation:**

Quantitative HPLC was performed on Agilent 1100 prominence Gradient, Agilent EZ Chrom Elite software, Column Kromosil C\textsubscript{18} 250x 4.6 mm;5 micron.

**Reagents:**

(1) Water (HPLC Grade).

(2) Acetonitrile (HPLC Grade).

(3) Acetic acid (AR Grade)

(4) Bisphenol sample

**Chromatographic condition:**

The content of the mobile phase was 0.1 % containing acetonitrile and 0.1 % Acetic acid containing water were prepared into the ratio of 65:35. The contents of the mobile phase were filtered before use through 0.45 micron membrane filter and degassed by ultrasonication for 15 min and pumped from the respective solvent reservoirs to the column at the flow rate of 1 mL/min which yielded a column back pressure 138-141 bar. The run time was set for 45 min and the column temperature was maintained at 30 °c. The volume of injection loop was 10 micro lit. Prior
to the injection of sample, the column was equilibrated for at least 0.5 h with mobile phase flowing through the system. The elements were monitored at 280 nm and data were acquired, stored and analyzed with EZChrom Elite software (Agilent).

**Sample preparation:**

0.02 gm bisphenol was accurately weighed and transferred to a 25 mL volumetric flask containing 15 mL of Acetonitrile. The contents of the flask were sonicated for 15 min to dissolve bisphenol and final volume made up to 25 mL with Acetonitrile. Injected 10 microlitre samples in to the system and set the run time up to 45 min. Quantitative purity was obtained by area percentage.
Fig. 5.2 HPLC Chromatogram of 1,1-bis (3-methyl-4-hydroxy pehenyl) cyclohexane
Fig. 5.3 HPLC Chromatogram of 1,1-bis (3-methyl-4-hydroxy pheynyl)4-methyl cyclohexane
Section B

Typical analytical method development of p-alkoxy alkyl benzoate:-

1) Determination of moisture content (By Karl Fischer Apparatus)

Principle

The method is based on the reaction of water with iodine and sulphur dioxide in pyridine solution. The pyridine serves to prevent loss of sulphur dioxide from the reagent by uniting with it to form an additive compound and also facilitate completion of the reaction with water by combining with the reaction products. The reaction are expressed in the following equation,

\[ \text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 + 3\text{C}_5\text{H}_5\text{N} = 2\text{C}_5\text{H}_5\text{N.HI} + \text{C}_5\text{H}_5\text{NSO}_3 \]

\[ \text{C}_5\text{H}_5\text{NSO}_3 + \text{CH}_3\text{OH} = \text{C}_5\text{H}_5\text{N.HSO}_4\text{CH}_3 \]

Apparatus:

Karl Fischer Titrator.

Reagents:

1) Methanol – AR grade
2) Karl Fischer reagent

Standardization of Karl Fischer reagent (Water equivalent)

1) Placed 25 mL of methanol in titration vessel of Karl Fischer titrator.
2) Neutralized methanol with Karl Fischer reagent till the end point is reached.
3) Weighed accurately the weighing bottle with dropper filled with distilled water (W1 gm). Added one drop of distilled water in the reaction vessel and reweighed bottle (W2 gm).

4) Stirred and titrated against Karl Fischer reagent till the end point is reached.

5) Noted the volume of Karl Fischer reagent.

Calculations:

\[
\text{Weight of water taken} = \frac{\text{Water equivalent,}}{\text{Volume of Karl Fischer reagent in ML}} \times 1000
\]

\[
= \frac{0.0404}{4.009} \times 1000 = 6.17
\]

Sample analysis:

Placed 25 mL of methanol in titration vessel of Karl Fischer titrator. Neutralized methanol with Karl Fischer reagent till the end point is reached.

1) Immediately added accurately 2 gm. sample in titration vessel and titrated with the Karl Fischer reagent till the end point is reached as above.

2) Noted the volume of Karl Fischer reagent consumed.

Calculations:

\[
\text{Moisture, % by mass} = \frac{V1 \times \text{W.E.} \times 100}{W \times 1000}
\]
Where,

\[ V_1 = \text{Volume in mL of Karl Fischer Reagent consumed for sample titration.} \]

\[ \text{W.E} = \text{Water equivalent of Karl Fischer reagent, mg/mL} \]
\[ W = \text{Weight of sample in gm.} \]

**Table 5.13**

**Moisture content of p-alkoxy alkyl Benzoates.**

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Compound name</th>
<th>Wt of sample taken</th>
<th>Burette reading mL</th>
<th>Moisture content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-isoproxy ethyl benzoate</td>
<td>2.0</td>
<td>0.113</td>
<td>0.033</td>
</tr>
<tr>
<td>2</td>
<td>p-propoxy methyl benzoate</td>
<td>2.0</td>
<td>0.141</td>
<td>0.043</td>
</tr>
<tr>
<td>3</td>
<td>p-pentoxy methyl benzoate</td>
<td>2.0</td>
<td>0.127</td>
<td>0.039</td>
</tr>
<tr>
<td>4</td>
<td>p-butoxy butyl benzoate</td>
<td>2.0</td>
<td>0.137</td>
<td>0.042</td>
</tr>
<tr>
<td>5</td>
<td>p-pentoxy butyl benzoate</td>
<td>2.0</td>
<td>0.107</td>
<td>0.033</td>
</tr>
<tr>
<td>6</td>
<td>p-propoxy propyl benzoate</td>
<td>2.0</td>
<td>0.126</td>
<td>0.038</td>
</tr>
<tr>
<td>7</td>
<td>p-pentoxy propyl benzoate</td>
<td>2.0</td>
<td>0.121</td>
<td>0.037</td>
</tr>
<tr>
<td>8</td>
<td>p-propoxy isobutyl benzoate</td>
<td>2.0</td>
<td>0.117</td>
<td>0.036</td>
</tr>
<tr>
<td>9</td>
<td>p-pentoxy isobutyl benzoate</td>
<td>2.0</td>
<td>0.150</td>
<td>0.046</td>
</tr>
<tr>
<td>10</td>
<td>p-ethoxy ethyl benzoate</td>
<td>2.0</td>
<td>0.139</td>
<td>0.042</td>
</tr>
</tbody>
</table>
Determination of acidity as p-hydroxy benzoic acid in p-alkoxy alkyl benzoates.

Principle:

Reagents preparation:

(1) sodium hydroxide pellet: (A R Grade 0.1 N) 4.0 gm dissolved in 100 mL water and sonicated for few minutes to get clear solution and finally it was diluted up to 1000 mL distilled water to get 0.1N solution.

(2) Phenolphthalein indicator.

Standardization of 0.1N Sodium hydroxide: Potassium hydrogen phthalate was dried in hot air oven at 200 °C. 0.6738 gm of dried Potassium hydrogen phthalate was weighed accurately in 250 mL conical flask containing 50 mL distilled water and sonicated for 5 minute to dissolve completely. Added 2-3 drops of Phenolphthalein indicator and titrated with 0.1N Sodium hydroxide till color changes from colorless to light pink. Calculated normality of 0.1N Sodium hydroxide solutions using following formula.

\[
\text{Normality of } \text{NaOH} = \frac{\text{Weight of potassium hydrogen phthalate}}{\text{Burette reading x 204.22}} \times 1000
\]

\[
\frac{0.6738 \times 1000}{33.65 \times 204.22} = 0.09805 \text{ N}
\]

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Procedure:

2.0 gm of p-propoxy methyl benzoate was accurately weighed in to conical flask containing previously neutralized 25 mL A R Grade methanol and titrated with standard 0.1N Sodium hydroxide solution using methyl orange indicator till color changes from pink to yellow.

\[
\text{\% Acidity} = \frac{\text{B.R} \times \text{normality of NaOH} \times 13.8}{\text{Weight of sample taken}}
\]

Table 5.14

Acidity of p- alkoxy alkyl benzoates

<table>
<thead>
<tr>
<th>Sr no.</th>
<th>compound</th>
<th>Weight of sample (gm)</th>
<th>Burette reading (mL)</th>
<th>Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-propoxy methyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td>p-pentoxy methyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>3</td>
<td>p-ethoxy ethyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>4</td>
<td>p-isopropoxy ethyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>5</td>
<td>p-propoxy propyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>6</td>
<td>p-pentoxy propyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>7</td>
<td>p-butoxy butyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>8</td>
<td>p-pentoxy butyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>9</td>
<td>p-propoxy isobutyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
<tr>
<td>10</td>
<td>p-pentoxy isobutyl benzoate</td>
<td>2.0</td>
<td>0.0 ml</td>
<td>Nil</td>
</tr>
</tbody>
</table>
3) Determination of p-alkoxy alkyl benzoate purity by Gas chromatography Method:

**Principle:**
Gas chromatography principle is based on volatization of organic sample in injection port and separation in specified tubular column by carrier gas stream. The components are separated and detected by high sensitive detector. The results are measured and computed by suitable electronic media.

**Instrumentation:**
Quantitative Gas chromatography was performed on Shimadzu 14B

**Reagents:**
(1) Methanol: AR Grade.

**Gas chromatographic condition:**
Gas chromatography analyses were carried out on a Shimadzu 14B Gas chromatography and a BP-1 (non polar 100 %dimethyl polysiloxane) capillary column (30m x 0.32mm; 1micron film thickness). The oven temperature was held at 50°C for 2.5 min then programmed at 9.5 °C/min up to 220 °C and set the run time up to 60 min. Other operating conditions were as follows: carrier gas nitrogen, with a flow rate of 2 ml/min; injector temperature 240°C, detector temperature 290 °C split ratio 1:10. Injected 0.5 microlitre sample in to the system injector port and started run time. Quantitative purity was obtained from FID area percentage.
Code E1

**GC Parameters:**
- Instrument: Shimadzu GC-14B
- Recording date & time: 14.01.11, 12:04
- Column: BP-1, 30m*0.32mmID, 3μm
- Column Temp.: 100°C-3min-20°C/min-240°C-50min
- Injector Temp.: 250°C
- Detector Temp.: 260°C
- Split /Purge: 40ml/min. / 3ml/min.
- Inlet N2 Pressure: 50kpa
- Sensitivity: 10×1
- Injection Volume: 0.2μl

**Chromatogram:**

![Chromatogram Image]

**Result:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (Min.)</th>
<th>Area mV*min.</th>
<th>Rel.Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.80</td>
<td>6057</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>16.32</td>
<td>3667</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>17.98</td>
<td>9286300</td>
<td>99.90</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>9296024</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 5.4 GC Chromatogram of p-ethoxy ethyl benzoate
Code E3

GC Parameters:
Instrument: Shimadzu GC-14B
Recording date & time: 14.01.11, 16:14
Column: BP-1, 30m*0.32mmID, 3μm,
Column Temp.: 100°C-3min-20°C/min-240°C-50min
Injector Temp.: 250°C
Detector Temp: 260°C
Split/Purge: 40ml/min / 3ml/min.
Inlet N2 Pressure: 50kpa
Sensitivity: 10*1
Injection Volume: 0.2μl

Chromatogram:

Result:

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (Min.)</th>
<th>Area mV*min.</th>
<th>Rel.Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.90</td>
<td>7702</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>18.85</td>
<td>7056321</td>
<td>99.78</td>
</tr>
<tr>
<td>3</td>
<td>19.59</td>
<td>7929</td>
<td>0.11</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>7071952</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 5.5 GC Chromatogram of p-isoproxy ethyl benzoate
Results and discussion

Analytical chemistry deals with methods for determining chemical composition of sample of matter. Analytical chemistry plays an important role in the resolution of a chemical compound into its proximate or ultimate parts, determination of its elements or of the foreign substance it may contain. Analytical chemistry encompasses two branches Qualitative and Quantitative. A qualitative method is the information about identification of atomic or molecular species or functional group in the sample. A quantitative method provides numerical information as to the relative amount of one or more of these components. Most manufacturing industries rely upon both qualitative and quantitative analysis to ensure that the raw material used meets certain specifications and also to check the quality of the final product.

Herein, we report the simple, reproducible, highly efficient analytical methods for p-alkoxy alkyl benzoates and Bisphenols as a view of polymer catalyst and additives.

1) Color

Color is an indication of quality and uniformity of compound. Several methods for color determination have been reported, we have chosen potassium chloroplatinate and it is well established in the present study for bisphenol. The color values of some representative compounds are included in Table 5.1

2) Loss on drying

This method is important to know the solvent, water and volatile matter present in the compound. After optimizing test condition and parameter,
we next examined the loss on drying of synthesized compound and the results are summarized in Table 5.2.

3) Determination of Iron

The iron in higher oxidation state Fe+3 is converted to Fe+2 ion by reduction with hydroxylamine hydrochloride is then complexed with Ferrozine to produce a chromophore detectable at 565 nm by UV-Vis spectroscopy. The intense color allows trace analysis to be done on these ions in solution using high absorption measurement. The ferrous ion becomes highly absorbing to visible light when it forms a complex with organic chelator Ferrozine. This is very stable complex, is dark purple and can be spectrophotometrically detected even at very low amount of iron present in Bisphenols. The ashing method proposed in this work proves quite adequate. Linearity and range of this method were confirmed by linearity study. This method shown linear response in the applied concentration range and correlation coefficient was within limit. This method helps for exact quantification of trace amount of iron present in the Bisphenol. Some synthesized compounds were analyzed by this developed method and results are summarized in the Table 5.6.

4) Chloride content

This method gives information of inorganic species present in the compound. Synthesized compound tested chloride and it was observed free from chloride. The result is included in Table 5.7.

5) Alkalinity

Alkalinity test also gives information of free alkalinity or salt as a impurity in the compound. Synthesized compound tested for alkalinity
and observed compound are free from salt and alkali. The results are included in Table 5.8.

6) **Quantification trace amount of phenol present in compound by HPLC**

Herein, we developed the HPLC method for quantification of phenol and substituted phenol. This method is based on High performance liquid chromatography using UV detector at 230 nm for detection of trace amount of phenol and substituted phenol. Quantitative HPLC was performed on Agilent 1100 prominence isocratic, Repeatability and accuracy of the method was confirmed by injecting 10 micro lit sample twicely of each concentration and found to be 99% repeatability in Area. Linearity and range of this method was confirmed by linearity study, phenol and o-cresol shown linear response in the applied concentration range and correlation coefficient was within limit. This method helps for exact quantification of trace amount of phenol present in bisphenol. Some compound was analyzed by this method and it was observed phenolic component in the range of 15-25 ppm. The results are included in Table 5.11.

7) **Insoluble matter**

Insoluble matter gives the information of foreign particle present in the bisphenol compound. Bisphenol is highly soluble in acetone and it is easy to filter and drying. Some representative compounds of this series analyzed and it was observed all compound are free from suspended particle. The results are summarized in Table 5.12

8) **Determination of bisphenol purity by HPLC**

Bisphenol and other impurities are separated on reserve phase. Using mixture of acetonitrile and water as mobile phase. The bisphenol peak
and other eluted impurities peak area distributed in to 100% Quantitative HPLC was performed on Agilent 1100 prominence gradient. This method is simple highly efficient and accurate. By using this method synthesized compounds of this series are analyzed for purity. The representative HPLC chromatograms of two compounds are shown in Fig.5.2 and 5.3.

9) Determination of moisture contain in p-alkoxy alkylbenzote.

From the literature review it has been observed moisture content seems to be a crucial parameter in polypropylene synthesis. The method of moisture determination is developed by Karl fisher. The synthesized compound of this series was analyzed and it was observed, moisture content is in range of 0.03-0.05%. Accuracy and reproducible of this method was confirmed. Some representative compound of this series is analyzed and results are included in Table 5.13.

10) Acidity

This method was developed to determine the acidity of present in compound. The synthesized compound of this series was analyzed developed method and confirmed pure compound is free from –OH and -COOH The result of this series is included in Table 5.14.

11) Determination of p-alkoxy alkyl benzoates purity by Gas Chromatography.

Gas chromatography principle is based on volatilization of organic compound in injection port and separation in specified tubular column by carrier gas stream. Quantitative Gas chromatography was performed on Shimadzu 14B using BP-1 non polar 100% dimethylpolysiloxane for
Separation of all impurities. The representative HPLC chromatograms of two compounds are shown in Fig.5.4 and 5.5.

**Conclusion**

In summary, we have developed simple, safe, reproducible and highly efficient analytical methods for p-alkoxy alkyl benzoates and bisphenols characterization.

1) Accuracy and precision were confirmed, linearity and range of these methods were confirmed by linearity study. These methods shown linear response in the applied concentration ranges and correlation coefficient was within limit.

2) High performance liquid chromatography and Gas chromatography were found to be simple, accurate, precise, economical and less time consuming for determination of purity.

3) Qualitative and Quantitative analytical methods are important to ensure that, the used raw material meets certain specification and also to check the Quality of the final product and most manufacturing industries rely upon qualitative and quantitative analysis.

4) These methods are simple, sensistive, safe, accurate and reproducible

5) We believe that these analytical methods will help for industrial purpose for the analysis of p-alkoxy alkyl benzoates and bisphenols as a view of polymer catalyst and additive.
References:


List of Publications


