Chapter-IV

Indirect Spectrophotometric Determination Of Formaldehyde
Indirect Spectrophotometric Determination of Formaldehyde with Sulphur Dioxide in Air Samples using p-Amino benzene Sulphonic Acid

SUMMARY :-

An indirect determination of formaldehyde in air samples is described. The method is based on colour reaction of formaldehyde, p-amino benzene sulphonic acid and sulphur dioxide in hydrochloric acid medium. The absorbance of pinkish-red coloured dye formed is measured at 510 nm. The colour system obeys Beer’s law in the range of 1.8 to 9.6 µg of formaldehyde per 25 ml (0.072 – 0.38 ppm). Optimum conditions for colored development, and possible interferences, have been studied. The method is simple, sensitive and cost effective and have been used for the determination of formaldehyde in varies environmental samples.

Part of Paper is Published in “Asian Journal of Research in chemistry” ISSN 0974-4169.
4.1: Introduction:-

Formaldehyde was declared a Priority Existing Chemical on 5 March 2002 in response to occupational and public health concerns. \(^{(1)}\)

Formaldehyde (HCHO or CH\(_2\)O) is also known as methanal, methylene oxide, oxymethylene, methylaldehyde, oxomethane, and formic aldehyde. At room temperature, it is a colourless gas with a pungent, irritating odour. It is highly reactive, highly flammable, and can form explosive mixtures in air. It decomposes at temperature above 150 °C. Formaldehyde is readily soluble in water, alcohols, and other polar solvents. In aqueous solutions, formaldehyde hydrates and polymerizes and can exist as methylene glycol, polyoxymethylene, and hemiformals. \(^{(2-3)}\)

**Formalin**, solution of formaldehyde in water, is formerly used as disinfectants and for preservation of biological specimens. In view of its widespread use, toxicity and volatility, exposure to formaldehyde is a significant consideration for human health. On 10 June 2011, the US National Toxicology Program has described formaldehyde as "known to be a human carcinogen". \(^{(4-8)}\) Formaldehyde is produced industrially by the catalytic oxidation of methanol. \(^{(9-11)}\)

**Industrial Uses :-** Formaldehyde is a common building block for the synthesis of more complex compounds and materials like urea formaldehyde resin, melamine resin, phenol formaldehyde resin, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate. The textile industry uses formaldehyde-based resins as finishers to make fabrics crease-resistant. Formaldehyde-based materials are key to the manufacture of automobiles, and used to make components for the transmission, electrical system, engine block, door panels, axles and brake shoes. Including indirect employment, over 4 million work in
the formaldehyde industry across approximately 11,900 plants in the U.S. and Canada. (12-13)

**Commercial Uses:** Formaldehyde is also a precursor to polyfunctional alcohols which is used to make paints and explosives. It is used in low concentrations in photography and extensively in the woodworking and cabinet-making industries. Urea-formaldehyde is used in the glues that are applicable in plastic laminate bond part. An aqueous solution of formaldehyde can be useful as a disinfectant as it kills most viruses, bacteria and fungi. [14-16] Formaldehyde is used to inactivate bacterial products for toxoid vaccines. [17]

Some topical creams, cosmetics and personal hygiene products also contain derivatives of formaldehyde as the active ingredients. For example, nail hardeners may contain concentrations equal to or less than 5% and oral care products may contain concentrations equal to or less than 0.1%. (18-23)

**4.2 Environmental Occurrence:**

Formaldehyde occurs naturally in the environment and is the product of many natural processes as released during biomass combustion, such as forest and brush fires. In 2005, annual world production of formaldehyde was estimated to be 23 million tones (50 billion pounds). (24) Occurrence in homes are generally due to new pressed wood products, but level is between 0.1-0.3 ppm. (25). Formaldehyde is the most abundant carbonyl compound in the atmosphere, is generated as an intermediate product in the oxidation of nonmethane hydrocarbons. Sources contributing to elevated formaldehyde indoors are primarily related to building products and furnishings. Formaldehyde is only one compound of concern that is emitted from these materials. (26-27): 61% of the children’s bath products
like Baby Shampoo, Bubble Bath, Milk & Honey Baby Wash and Huggies Naturally Refreshing Cucumber & Baby Wash, tested for this report contained formaldehyde. (28)

**In Air**

Formaldehyde emitted to air through both direct emissions as vapour and emission from fuel combustion. In air it primarily reacts with photochemically generated hydroxyl radicals in the troposphere or undergoes direct photolysis. Minor processes include reactions with nitrate radicals, hydroperoxyl radicals, hydrogen peroxide, ozone, and chlorine. Small amounts of formaldehyde may also transfer into rain, fog, and clouds or be removed by dry deposition. (29-31)

![Emission of Formaldehyde in Air](image)

**In Water**

Formaldehyde is highly water soluble. Concentrations as high as 95% formaldehyde in water are obtainable. However, at low concentrations, formaldehyde is readily biodegradable. In water, formaldehyde is hydrated and found largely in the form of methylene glycol and its oligomers. In a study in Taiwan, formaldehyde
concentrations in bottled and packaged drinking-water were all below the detection limit of 129 μg/litre. \(^{(33-40)}\)

**In Soil and sediments:-**

Limited data are available about the fate of formaldehyde in soil and sediment. Formaldehyde is formed in the early stages of decomposition of plant residues in soils and is degraded by soil bacteria such that accumulation in soil does not occur.\(^{(41-42)}\) Formaldehyde is susceptible to degradation by various soil microorganisms.\(^{(43-44)}\)

**4.3 Toxic Effect:-**

Many research study report on the contact and exposure in formaldehyde, shows skin, eye and respiratory irritation, vomited streaks of blood, ulceration of the esophagus, gastric necrosis. Research reports are agreed that formaldehyde exposure may cause decrease in vital capacity of lung, and cancer in respiratory system. In addition, inhaled formaldehyde has been shown to cause behavioral and memory disorders in mammals and has been classified as ‘probably neurotoxic. Formaldehyde has been described as one of the chemical mediators to cause apoptosis, which is programmed cell death in humans. On the basis of studies in which humans and experimental animals were exposed to formaldehyde by inhalation, IARC (2004) has classified formaldehyde in Group 1 (carcinogenic to humans).

Further studies of groups who have been occupationally exposed to formaldehyde by inhalation have largely supported this position but provide more evidence that formaldehyde may possibly pose a carcinogenic risk of lung or sino-nasal cancer, and possibly lymphoid leukemia, in occupationally exposed groups, however, all of the authors urged caution in interpreting their data. \(^{(45-53)}\)
Table-1. Effect and symptoms of Formaldehyde. (54)

<table>
<thead>
<tr>
<th>Concentration in Air</th>
<th>Symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-5 ppm</td>
<td>Eye irritation, tears, skin irritation, respiratory tract irritation</td>
</tr>
<tr>
<td>5-20 ppm</td>
<td>Burning of eyes and respiratory tract, tears, difficulty in breathing/coughing</td>
</tr>
<tr>
<td>20-100 ppm</td>
<td>Chest tightening, pain, irregular heartbeat, severe lung irritation, pulmonary edema, <em>Death in severe cases.</em></td>
</tr>
</tbody>
</table>

As formaldehyde is most common toxicant present in environment. Because of its widespread use and adverse health effects, interest in improved analytical methodology for the determination of formaldehyde is high. Various methods have been developed for the determination of formaldehyde including Gas Chromatography, HPLC, voltammetry, chemiluminescence, and fluorimetry. Spectrophotometric analytical methods and spectrophotometric catalytic kinetic methods become important means in trace analysis of formaldehyde with the application of various reagents. (55-78)

The aim of the present investigation is to overcome the existing inadequacies, like instability of colour and interference of co-pollutants and provide reliable, accurate and cost effective procedure in determining formaldehyde. In the prescribed method formaldehyde reacts with p-amino benzene sulphonic acid and SO₂ resulting in the formation of a pinkish-red colour dye. The pink coloured dye formed in this reaction shows maximum absorbance at 510 nm.
4.4: Experimental

**Apparatus:** A Systronics UV-VIS spectrophotometric (model 104) with matched silica cells was used for all spectral measurements. Systronic pH meter (model 331) was used for pH measurements. A Remi C-854/4 clinical centrifuge force of 1850 g with fixed swing out rotors was used for centrifugation. A calibrated rotameter was used for measurement of the air flow-rates.

**Reagent:** All reagents used were of Anal R grade or of the best available quality. Double distilled demineralized water was used throughout. 

A: **Standard Formaldehyde Solution:** One ml of 37-40% formaldehyde solution (Big Chemicals) diluted to 100 ml and further, 0.005M hydrochloric acid was added to give a 6 µg/ml working formaldehyde standard.

B: **Sulphite Solution:** 0.005M Prepared by dissolving anhydrous sodium sulphite in water.

C: **p-Aminobenzenesulphonic acid (E. Merck, Germany):** 0.05% (m/v) solution of the reagent was prepared by dissolving 500 mg of the p-aminobenzenesulphonic acid in 100 ml of ethanol. (79)

D: **Hydrochloric Acid solution:** - 0.005M-1.5 M Hydrochloric acid solutions were prepared by dilution of concentrate HCl solution.

4.5: Procedure:-

Two midget impingers, each containing 10ml of 0.005M hydrochloric acid, were connected in series and then to a rotameter and a vacuum pump. Air was drawn through the system at ca. 1.5 to 1 min (79). Then the solutions were quantitatively transferred to a 25 ml calibrated tube and 1 ml each of the p-aminoazobenzene sulphonic acid and sulphite solution was added. The solution was thoroughly mixed and kept for 20-
25 min. The acidity was then adjusted between 0.4 and 1.2M with hydrochloric acid and the solution was made up to the mark with double distilled water. The absorbance of the pink dye was measured at 510 nm against distilled water and the amount of formaldehyde was computed from a calibration graph prepared in a similar manner after correction for the absorbance of a reagents blank measured at the same wavelength.

4.6: Result and Discussion:-

Proposed Reaction Mechanism in the formation of Dye (Colour Reaction):-

\[
\begin{align*}
\text{p-amino benzene} & \quad \text{Formaldehyde} \quad \text{Intermediate compound} \quad \text{sulphonic Acid} \\
\text{H-O-S} & \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{C-O-H} \\
\text{H-O-S} & \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{C-O} \\
\text{H-O-S} & \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{C-O-S} \\
\end{align*}
\]

The pink coloured dye formed in the proposed reaction shows maximum absorbance at 510 nm. The dye is formed after the reaction of formaldehyde with p-amino benzene sulphonic acid followed by reaction

Absorption Spectra:-

The pink coloured dye formed in the proposed reaction shows maximum absorbance at 510 nm. The dye is formed after the reaction of formaldehyde with p-amino benzene sulphonic acid followed by reaction
of sulphur-dioxide in acidic medium. The absorption spectra are shown in figure-2. The reagent blank shows negligible absorbance at this wavelength. (Figure-2).

![Absorption Spectra](image)

**Figure-2.** Absorption Spectra of formaldehyde with p-amino benzene sulphonic Acid.

![Calibration curve](image)

**Figure-3.** Calibration curve of Absorption Spectra of formaldehyde with p-amino-benzene sulphonic acid.
Effect of Temperature and Time:-

Under optimum condition, the time necessary for the full colour development was found to be 20 min, and the absorbance remains constant up to 90 minutes. The determination was carried out at room temp. 30 to 35°C. (Figur-4 & 5).

Figure-4. Effect of Temperature on Absorbance.

Figure-5. Effect of Time on Absorbance.
Effect of Acidity:-

The effect of acidity, before and after addition of sulphite solution, was studied. The acidity range of 0.02M to 0.1M hydrochloric acid was necessary before the addition of sulphite solution and 0.4M HCl was for full colour development after the addition of sulphide solution. It was also found that the absorbance was constant by increasing hydrochloric acid concentration up to 1.2M. (Figure-6).

![Figure-6. Effect of Acidity (Concentration of HCl) on Absorbance.](image)
Effect of the Concentration of Reagents:-

A: - Effect of the concentration of p-Amino benzene sulphonic Acid Solution: It was observed that a minimum 1 ml. of p-aminobenzene sulphonic acid solution was required for full colour development. By increasing the quantity of p-aminobenzene sulphonic acid, the absorbance of both the reagent blank and the sample solutions increased. (Figure-7).

![Figure-7.Effect of Concentration of Reagent (PABSA) on Absorbance.](image)

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B: - Effect of the concentration of Sodium Sulphite Solution:-

The constant and maximum absorbance was found at the addition of 1ml. of 0.005M sodium sulphite solution. (Figure-8).

![Graph showing the effect of concentration of sodium sulphite solution on absorbance.](image)

Figure-8. Effect of Concentration of Sodium Sulphite Solution on Absorbance.
C: - Effect of the concentration of Formaldehyde Solution:

It was found that the constant and maximum absorbance was obtained with a 6 µg/ml working formaldehyde standard solution. (Figure-9).

Figure -9:- Effect of Concentration of Formaldehyde solution on Absorbance.
Analytical Data: The adherence to Beer’s Law was studied by measuring the absorbance value of the solutions for various formaldehyde concentrations. A linear curve was obtained by plotting the absorbance against the concentration of formaldehyde, and thus obeying Beer’s Law in the range of 1.8-9.6 µg formaldehyde per 25 ml of the final solution. The apparent molar absorptivity and Sandell’s sensitivity were found to be $1.5 \times 10^3$ lmol$^{-1}$ cm$^{-1}$ and 0.002µg cm$^{-2}$, respectively. The reproducibility of the method was checked by seven replicate measurements, each containing 5 µg of formaldehyde per 25 ml of final solution over a period of seven days. The standard deviation and R.S.D. were found to be $\pm 0.002$ and 1.8%, respectively.

Effect of foreign species: To assess the validity of the method, the effect of foreign species commonly found with formaldehyde was studied. The tolerance limits for different foreign species are shown in Table 2. Several common organic species, viz, other aldehydes and hydrocarbons, do not interfere with the present method. The interference from nitrogen dioxide is removed by the addition of 1 ml of 5% potassium hydroxide solution, and that of sulphite can be removed by passing the air sample through a tube containing lead acetate solution. (Table-2).
Table 2. Interference and tolerance limits* of other species in the determination of 4 µg of formaldehyde.

<table>
<thead>
<tr>
<th>Inorganic Species (ppm)</th>
<th>Tolerance Limit</th>
<th>Organic Species</th>
<th>Tolerance Limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>15</td>
<td>Ethanol</td>
<td>20</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>10</td>
<td>Benzaldehyde</td>
<td>2.5</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>12</td>
<td>Ethylamine</td>
<td>2.5</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>3.0</td>
<td>Isobutyl methyl ketone</td>
<td>2.0</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>0.5</td>
<td>Formic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.6</td>
<td>Nitrobenzene</td>
<td>0.5</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.5</td>
<td>Acetic acid</td>
<td>0.25</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.6</td>
<td>Acetone</td>
<td>0.25</td>
</tr>
<tr>
<td>NO²⁺ **</td>
<td>0.5</td>
<td>Benzene</td>
<td>0.25</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.2</td>
<td>Urea</td>
<td>0.25</td>
</tr>
<tr>
<td>VO₃⁻</td>
<td>0.2</td>
<td>Toluene</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aniline</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetaldehyde</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Amount (mg) which cause a 2% error

** Masked up to this level by 1 ml of 5 % potassium hydroxide.

4.7: Applications:-

The method has been successfully applied for analyzing formaldehyde in air and automobile exhaust.

A. In Air:- The samples were introduced to the sampling train through a sintered funnel to avoid the entrance of particulate matters. The Wilson’s procedure \(^{80}\) was used to investigate the collection efficiency of the absorbing solution \(^{81}\). Purified air was passed
through an evaporation chamber preheated to 60-70°C. Known amounts of formaldehyde were added from a micro burette and then allowed to evaporate in the chamber. The formaldehyde present in the air stream was collected in the absorbing solution, achieving 95% collection efficiency in the first impinger with a flow rate of 1.5l/min. and 5% in the second. (Table-3).

**Table 3: Analysis of Formaldehyde in the Air and Automobile Exhaust:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampling time Min.</th>
<th>Volume sampled (liter)</th>
<th>Formaldehyde found (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>60</td>
<td>90</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>90</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>180</td>
<td>67.0</td>
</tr>
<tr>
<td>Automobile exhaust (scooter)</td>
<td>2</td>
<td>3</td>
<td>44.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.5</td>
<td>78.0</td>
</tr>
</tbody>
</table>

* Flow rate = 1.5 lit./min.

**B. In Automobile Exhaust:** - Automobile exhaust (scooter) was sampled from the inner part of the muffler. No comparative analysis was made. The results are presented in Table 4.
Table 4: Analysis of Formaldehyde in Scooter Exhaust:

<table>
<thead>
<tr>
<th>Vol. of sample taken</th>
<th>HCHO found in µg</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I\textsuperscript{st} set impinger</td>
<td>II\textsuperscript{nd} set impinger</td>
</tr>
<tr>
<td>4.5</td>
<td>68.5</td>
<td>66.5</td>
</tr>
<tr>
<td>4.5</td>
<td>64.2</td>
<td>62.4</td>
</tr>
<tr>
<td>4.5</td>
<td>70.0</td>
<td>71.5</td>
</tr>
<tr>
<td>4.5</td>
<td>67.4</td>
<td>70.0</td>
</tr>
<tr>
<td>4.5</td>
<td>71.0</td>
<td>72.5</td>
</tr>
<tr>
<td>4.5</td>
<td>62.0</td>
<td>63.0</td>
</tr>
<tr>
<td>4.5</td>
<td>65.0</td>
<td>66.0</td>
</tr>
<tr>
<td>Mean</td>
<td>67.62</td>
<td>67.62</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>± 3.54</td>
<td>± 3.54</td>
</tr>
<tr>
<td>Relative standard deviation</td>
<td>± 5.23</td>
<td>± 5.23</td>
</tr>
</tbody>
</table>

C. In Water: - In order to evaluate the applicability of the proposed method, water samples were analyzed to determine formaldehyde contents. The results are presented in Table 2. Good recoveries with precise results show good reproducibility and accuracy of the method. (Table 5).

Table 5. Determination of formaldehyde in water samples.

<table>
<thead>
<tr>
<th>Samples **</th>
<th>Formaldehyde Added mg/lit.</th>
<th>Formaldehyde Found mg/lit. *</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore Water-1</td>
<td>2.0</td>
<td>1.9</td>
<td>95</td>
</tr>
<tr>
<td>Bore Water-2</td>
<td>4.0</td>
<td>3.8</td>
<td>95</td>
</tr>
<tr>
<td>Bore Water-3</td>
<td>5.0</td>
<td>4.7</td>
<td>94</td>
</tr>
</tbody>
</table>

* Mean of five replicate analyses.
**Water sample 250 mL, after treatment 1 mL aliquot was analysed.**

**CONCLUSIONS:** - The proposed method for determining Formaldehyde is facile, rapid, sensitive, and has a good analytical range without the need for extraction or heating. The method offers the advantages of high colour stability compared to the other reported method. This method is satisfactorily applied to the determination of Formaldehyde in air automobile exhaust and water samples. The results obtained were in good agreement with the reported method. All the non-target species do not interfere with the present method. (Table - 6)

**Table 6. Comparison of some Spectrophotometric methods for the determination of Formaldehyde in air samples.**

<table>
<thead>
<tr>
<th>SN</th>
<th>Reagents</th>
<th>( \lambda_{\text{max}}, \text{nm} )</th>
<th>( \varepsilon ) ( 1 \text{ mole}^{-1} \text{cm}^{-1} )</th>
<th>Colour stability</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Schiff’s reagent(^{(82)})</td>
<td>550*</td>
<td>3.5 x 10(^3)</td>
<td>30 min</td>
<td>SO(_2), NO(_2), Alcohol, Phenol</td>
</tr>
<tr>
<td>2.</td>
<td>Chromotropic acid(^{(83,84)})</td>
<td>278</td>
<td>1.57 x 10(^4)</td>
<td>24 hr</td>
<td>SO(_2), NO(_2), NO(_3) hydrocarbons</td>
</tr>
<tr>
<td>3.</td>
<td>Phenlhydrazine(^{(85)})</td>
<td>520</td>
<td>6.50 x 10(^4)</td>
<td>15 min</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>Oxaldihydrazone (\text{Cu(11)})^{(86)}</td>
<td>620</td>
<td>7.7 x 10(^4)</td>
<td>150 min</td>
<td>Sulphur compounds</td>
</tr>
<tr>
<td>5.</td>
<td>p-Aminozobenzene(^{(87)})</td>
<td>505</td>
<td>4.5 x 10(^4)</td>
<td>90 min</td>
<td>Phenolic, and sulphur compounds</td>
</tr>
<tr>
<td>6.</td>
<td>p-Aminobenzene sulphonic-acid (present method)</td>
<td>510*</td>
<td>1.5x10(^3)</td>
<td>60 min</td>
<td>See table - 1</td>
</tr>
</tbody>
</table>

* Beer’s law not obeyed
First impinger (100°C with two impingers in series)

References:

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