Polarographic determination of Formaldehyde, Acetaldehyde and Propionaldehyde by external standard addition and internal standard addition method

Gupta Swaroopa Rani N

Department of Chemistry, Brijlal Biyani Science College Amravati, Maharashtra, India
Email: swargupta@yahoo.com

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ABSTRACT

Formaldehyde is widely used in the manufacture of many resins, polymers, and construction materials. It is also used as a preservative, disinfectant, and biocide. Formaldehyde is one of the volatile organic compounds that are widely used in household materials, which is associated with many health risk factors. Acetaldehyde is a Group 1 carcinogen. Propionaldehyde is used in the manufacture of plastics, in the synthesis of rubber chemicals, and as a disinfectant and preservative.

Present paper deals with Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by external standard addition and internal standard addition method. In alkaline medium it is possible to have well defined and separated waves relative to the reduction of formaldehyde, acetaldehyde and propionaldehyde. The determination of these aldehydes are carried out effectively in presence of $3.8 \times 10^{-6}$ % methyl red and $5.94 \times 10^{-7}$ % bromocresol green as maxima suppressor and 0.025 N lithium hydroxide and 0.0025 N lithium chloride as supporting electrolyte at pH 12 by external standard addition and internal standard addition method. Polarograms of all systems were recorded on Toshniwal manual polarograph using Dropping Mercury Electrode as cathode and Saturated Calomel Electrode as anode. The results of estimation of formaldehyde, acetaldehyde and propionaldehyde in synthetic solution by external standard addition and internal standard addition methods are found to be accurate and precise with low values of standard deviation.

Keywords: Formaldehyde, Acetaldehyde, Propionaldehyde, Methyl red, Bromocresol green, Lithium hydroxide, Lithium chloride, Polarographic External standard addition and Internal standard addition method.
INTRODUCTION

Formaldehyde is widely used in the manufacture of many resins, polymers, and construction materials. It is also used as a preservative, disinfectant, and biocide. Formaldehyde is one of the volatile organic compounds that are widely used in household materials, which is associated with many health risk factors. The thermal or chemical decomposition of such materials, however, occurs surprisingly readily from urea-formaldehyde foam insulation, particle board and formaldehyde-based resins [1]. Formaldehyde is a probable human carcinogen, allergenic, and an intense irritant of eyes and mucous membranes and is therefore highly problematic as an indoor pollutant [1-3]. The ability to detect formaldehyde at very low concentrations is critical: the World Health Organization has set a standard for safe exposure of 80 ppb averaged over 30 minutes [2]; for comparison, OSHA has set the permissible exposure level (PEL) to 750 ppb and the immediately dangerous to life or health (IDLH) level at 20 ppm [3]. While there are numerous methods for detecting and measuring gaseous formaldehyde, there remains a need for an inexpensive, sensitive and rapid analytical technology. Past analytical approaches include relatively expensive instrumentation [4] (e.g., electrochemical, gas chromatography, optical, chemiluminescence, etc), but also inexpensive colorimetric methods, which see some field use [5]. A number of colorimetric or fluorometric methods for the detection of formaldehyde have been proposed [5], e.g., hydrazones, triazoles, pararosaniline, etc. These prior methods are generally relatively slow (typically >30 min), often cumbersome and multistep, and frequently lack sensitivity. Thus, there remains a pressing need for the development of a rapid, sensitive and highly convenient formaldehyde detection method.

Many methods based on spectrophotometric, fluorometric, piezoresistive, amperometric or conductive measurements have been proposed for detecting the concentration of formaldehyde in air. However, conventional formaldehyde measurement systems are bulky and expensive and require the services of highly-trained operators. Accordingly, the emergence of sophisticated technologies in recent years has prompted the development of many microscale gaseous formaldehyde detection systems. Besides their compact size, such devices have many other advantages over their macroscale counterparts, including a real-time response, a more straightforward operation, lower power consumption, and the potential for low-cost batch production.

Results of a study of certain methods like iodimetric, alkali-peroxide and neutral sulfite for determination of formaldehyde in the presence of some of the organic substances that may be present in a formalin solution has been presented [6]. The results of a study of certain methods like fixed alkali, iodimetric, peroxide, neutral sulfite and oxidation with permanganate or dichromate in an acid solution and weighing the carbon dioxide produced for the determination of formaldehyde in paraformaldehyde has been presented [7]. A rapid and simple technique was developed for detecting formaldehyde with very small amount of sample by using heated PDMS (polydimethylsiloxane) microfluidic chip, which has four reaction reservoirs and one substrate reservoir [8]. The current status of indoor-related formaldehyde research is also summarized [9]. A colorimetric detection method using amine-functionalized polymer films doped with a pH indicator has been developed for the rapid, sensitive, and quantitative detection of gaseous formaldehyde at concentrations well below the immediately dangerous to life or health (IDLH) limit [10]. A strategy for analyzing formaldehyde in beer, wine, spirits, and unrecorded alcohol was developed, and 508 samples from worldwide origin were analyzed [11]. Testing for formaldehyde is by blood and/or urine by gas chromatography-mass spectrometry. Other methods include infrared detection, gas detector tubes, etc., of which HPLC is the most sensitive [12]. A headspace gas chromatographic method (HS-GC) for the determination of residual formaldehyde in formaldehyde related polymer latexes has been reported [13]. High level overview of the formaldehyde gas sensing field has been provided by some workers and then they described some of the more significant real-time sensors presented in the literature over the past 10 years or so [14]. In the last two decades of the 20th century, a number of analytical methods for the determination of formaldehyde have been reported. These methods include spectrophotometry [15], gas chromatography (GC) [16], high-performance liquid chromatography [17], ion chromatography [18] and polarography [19]. Since these methods required expensive and bulky instrumentation with high power demand and well-trained operators, clearly, these procedures are unable to provide formaldehyde exposure information on a real-time basis. To simplify the measurement of ambient

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formaldehyde, Hopkins et al. [20] proposed a GC-pulsed Helium Ionization Detector (pPHID) apparatus aiming at formaldehyde detection and designed to operate at relatively high frequencies (>10 h−1). Over the past decade, emerging measurement technologies have contributed significantly to the miniaturization of measurement apparatus. As a result of advances in measurement technology, sensing instrumentation capable of accessing information at a real-time level is now available [21-47]. In 1996, Vianello et al. [22] proposed a potentiometric formaldehyde detection system based on an aldehyde dehydrogenase ion-selective field effect transistor.

Acetaldehyde is one of the most important aldehydes, occurring widely in nature and being produced on a large scale in industry. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants. It is also produced by the partial oxidation of ethanol by the liver enzyme alcohol dehydrogenase and may be a contributing factor to hangovers from alcohol consumption. Pathways of exposure include air, water, land, or groundwater, as well as drink and smoke [48]. Consumption of disulfiram inhibits acetaldehyde dehydrogenase, the enzyme responsible for the metabolism of acetaldehyde, thereby causing it to build up in the body. The International Agency for Research on Cancer (IARC) has listed acetaldehyde as a Group 1 carcinogen [49].

A spectrophotometric method for the determination of acetaldehyde in aqueous solution is described [50]. A technique based on photoacoustic spectroscopy and utilizing pulsed laser excitation has been developed for quantitatively detecting acetaldehyde in purified air at total pressures of 1 atm [51]. A gas chromatography with flame ionization detection method (GC–FID) with direct injection, using a capillary column, was validated to determine ethanol, acetaldehyde, methanol, and acetone in different human matrices, such as whole blood, vitreous humour, and urine, with clinical and forensic interest [52]. Acetaldehyde (ethanal) is a genotoxic carcinogen, which may occur naturally or as an added flavour in foods. An efficient method has been developed to analyze the compound in a wide variety of food matrices. The analysis is conducted using headspace (HS) gas chromatography (GC) with flame ionization detector [53].

Propionaldehyde is used in the manufacture of plastics, in the synthesis of rubber chemicals, and as a disinfectant and preservative. Limited information is available on the health effects of propionaldehyde. No information is available on the acute (short-term), chronic (long-term), reproductive, developmental or carcinogenic effects of propionaldehyde in humans. Animal studies have reported that exposure to high levels of propionaldehyde, via inhalation, results in anesthesia and liver damage, and intraperitoneal exposure results in increased blood pressure. EPA has not classified propionaldehyde for carcinogenicity.

Spectrophotometric analysis of propionaldehyde in presence of several other aldehydes was done which may be used for its determination in solutions and in air [54]. The polarographic behavior of aldehyde, namely formaldehyde, acetaldehyde and propionaldehyde were studied in the pH range 1-12 [55-58].

Present paper deals with Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by external standard addition and internal standard addition method. In alkaline medium, it is possible to have well defined and separated waves relative to the reduction of formaldehyde, acetaldehyde and propionaldehyde. The determination of these aldehydes are carried out effectively in presence of 3.8 x 10−6 % methyl red and 5.94 x 10−7 % bromocresol green as maxima suppressor and 0.025 N lithium hydroxide and 0.0025 N lithium chloride as supporting electrolyte at pH 12 by external standard addition and internal standard addition method. Polarograms of all systems were recorded on Toshniwal maul polargraph using Dropping Mercury Electrode as cathode and Saturated Calomel Electrode as anode.

**METHODOLOGY**

All chemicals were of A.R. grade. Propionaldehyde solution was purified before use. It was washed several times with 5 % sodium carbonate in order to remove propionic acid and then with distilled water and was dried with anhydrous Calcium chloride and distilled. Lithium chloride was prepared using A.R. grade chemicals. 21.2426 g of lithium carbonate was dissolved in 50 ml of hydrochloric acid. After complete dissolution, it was cooled, the solid lithium chloride was crystallized out, which was separated and dried.
Systems were prepared containing an aliquot of formaldehyde solution, 1 ml of mixture containing $1.9 \times 10^{-4}$ % methyl red and $2.97 \times 10^{-5}$ % bromocresol green, 25 ml of mixture of 0.05 N lithium hydroxide and 0.005 N lithium chloride and the pH was adjusted to pH 12. The volume of each system was made upto 50 ml with pH water. So the resultant concentration of maxima suppressor becomes $3.8 \times 10^{-6}$ % methyl red and $5.94 \times 10^{-7}$ % bromocresol green; the resultant concentration of supporting electrolyte becomes of 0.025 N lithium hydroxide and 0.0025 N lithium chloride. After passing nitrogen gas, the polarograms of all systems were recorded on Toshniwal maular polarograph using Dropping Mercury Electrode as cathode and Saturated Calomel Electrode as anode between 0 mV and -2400 mV. Saturated KCl salt bridge was used to connect them. The mercury drop rate was maintained at around 20 drops per minute. Further experiments of formaldehyde, acetaldehyde and propionaldehyde were carried out in presence of same quantities of maxima suppressor and supporting electrolyte.

Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by external standard addition method The polarogram of the unknown solution was recorded, and then a known volume of a standard solution of the formaldehyde, acetaldehyde and propionaldehyde were added and the polarograms repeated. From the increase in the diffusion current, the original concentration of formaldehyde, acetaldehyde and propionaldehyde present in respective samples were computed.

Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by internal standard addition method
In internal standard addition method wave heights of two solutions were measured; Solution 1 containing an aliquot of the unknown solution, and Solution 2 containing the same quantity of unknown solution plus a measured amount of a standard solution of the formaldehyde, acetaldehyde and propionaldehyde. The quantities of formaldehyde, acetaldehyde and propionaldehyde in each of these solutions was then determined from their recorded diffusion currents and standard calibration curve.

OBSERVATIONS
Cathodic waves for determination of formaldehyde, acetaldehyde and propionaldehyde by external standard addition method are represented in Figure 1, 2 and 3 while that by internal standard addition method are shown in Figure 4(A), 5(A) and 6(A). Figure 4(B), 5(B) and 6(B) shows graphic representation of the internal standard addition method of evaluation for formaldehyde, acetaldehyde and propionaldehyde respectively.

![Figure 1](http://www.irjse.in)

**Figure 1.** Polarographic determination of Formaldehyde by external standard addition method.

![Figure 2](http://www.irjse.in)

**Figure 2.** Polarographic determination of Acetaldehyde by external standard addition method.
Figure 3. Polarographic determination of Propanaldehyde by external standard addition method.
Figure 4 (A). Polarographic determination of Formaldehyde by internal standard addition method.
Figure 4 (B). Plot of diffusion current as a function of amount of Formaldehyde added to unknown sample.
Figure 5 (A). Polarographic determination of Acetaldehyde by internal standard addition method.
Figure 5 (B). Plot of diffusion current as a function of amount of Acetaldehyde added to unknown sample.
RESULTS AND DISCUSSION

Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by external standard addition method

External standard addition method can be applied for estimation of formaldehyde and acetaldehyde within experimental error of less than 3 % and standard deviation 0.4 to 3 (Table 1). In case of propionaldehyde excess recovery is obtained due to less increase in the diffusion current for repeated polarograms of unknown solution with a known volume of its standard solution. In the vicinity of the mercury drop the equilibrium is perturbed during the electrolysis of unknown solution in which the reducible form of aldehyde is consumed. Therefore, the wave height is limited for electrolysis of unknown solution second time along with added standard solution. Thus, with increase in concentration the anion wave only due to added depolarizer is observed on the polarographic curves and very slightly due to previous one. A correction is applied in the standard addition equation by introducing ratio (K) of the proportionality constants, for $i_a$ and concentration. For present case $K = 1.32$ is considered and error is minimized. Thus this factor must be considered in order to make any necessary correction for determination of propionaldehyde by external standard addition method.

Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde by internal standard addition method

Internal standard addition method can be applied satisfactorily for determination of formaldehyde and acetaldehyde at Dropping Mercury Electrode under same experimental condition as that for external standard addition method with low values of standard deviation as may be seen from Table 2. Propionaldehyde analysis again needs correction in K value. Present experimental error in propionaldehyde determination is corrected by assuming $K = 0.88$. 

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Table 1. Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde in synthetic sample by external standard addition method.

### External Standard Addition method - Formaldehyde

<table>
<thead>
<tr>
<th>Unknown sample taken, ml</th>
<th>0.39 M Formaldehyde added to unknown sample, ml</th>
<th>id, µA</th>
<th>Amount of Formaldehyde in unknown sample (Cx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cx, M</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>75</td>
<td>0.0148</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>86</td>
<td>0.0162</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
<td>105</td>
<td>0.0163</td>
</tr>
</tbody>
</table>

### External Standard Addition method - Acetaldehyde

<table>
<thead>
<tr>
<th>Unknown sample taken, ml</th>
<th>0.49 M Acetaldehyde added to unknown sample, ml</th>
<th>id, µA</th>
<th>Amount of Acetaldehyde in unknown sample (Cx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cx, M</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>19</td>
<td>0.0097</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>30</td>
<td>0.0101</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>32</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

### External Standard Addition method - Propionaldehyde

<table>
<thead>
<tr>
<th>Unknown sample taken, ml</th>
<th>0.028 M Propionaldehyde added to unknown sample, ml</th>
<th>id, µA</th>
<th>Amount of Propionaldehyde in unknown sample (Cx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cx, M</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3.5</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

### External Standard Addition method - Propionaldehyde - K = 1.32

<table>
<thead>
<tr>
<th>Unknown sample taken, ml</th>
<th>0.028 M Propionaldehyde added to unknown sample, ml</th>
<th>id, µA</th>
<th>Amount of Propionaldehyde in unknown sample (Cx)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cx*, M</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3.5</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

\[
C_x, M = \frac{id_1 \cdot v \cdot C_s}{v(id_1-id_2)+id_2 \cdot v}, \quad C_x^*, M = \frac{id_1 \cdot v \cdot C_s}{v(id_2-K \cdot id_1)+id_2 \cdot K \cdot v}, \quad K = \frac{id_1 \cdot (V \cdot C_x + v \cdot C_s)}{id_2 \cdot C_x^* \cdot (V+v)}
\]

\[
C_{x, mg} (\text{Formaldehyde}) = C_x, M \cdot 30.026 \cdot (V+v)
\]

\[
C_{x, mg} (\text{Acetaldehyde}) = C_x, M \cdot 45.03128 \cdot (V+v)
\]

\[
C_{x, mg} (\text{Propionaldehyde}) = C_x, M \cdot 58.08 \cdot (V+v)
\]
Table 2. Polarographic determination of formaldehyde, acetaldehyde and propionaldehyde in synthetic sample by internal standard addition method.

<table>
<thead>
<tr>
<th>Internal Standard Addition method - Formaldehyde</th>
<th>Amount of Formaldehyde Taken, mg</th>
<th>Amount of Formaldehyde Found in unknown sample, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown Sample (Cx)</td>
<td>Standard Sample (Cs)</td>
</tr>
<tr>
<td>17.52</td>
<td>0</td>
<td>41</td>
</tr>
<tr>
<td>17.52</td>
<td>17.52</td>
<td>84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal Standard Addition method - Acetaldehyde</th>
<th>Amount of Acetaldehyde Taken, mg</th>
<th>Amount of Acetaldehyde Found in unknown sample, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown Sample (Cx)</td>
<td>Standard Sample (Cs)</td>
</tr>
<tr>
<td>22.24</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>22.24</td>
<td>44.48</td>
<td>36</td>
</tr>
<tr>
<td>22.24</td>
<td>66.72</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal Standard Addition method - Propionaldehyde</th>
<th>Amount of Propionaldehyde Taken, mg</th>
<th>Amount of Propionaldehyde Found in unknown sample, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown Sample (Cx)</td>
<td>Standard Sample (Cs)</td>
</tr>
<tr>
<td>6.456</td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>6.456</td>
<td>3.228</td>
<td>5.1</td>
</tr>
<tr>
<td>6.456</td>
<td>6.456</td>
<td>6.3</td>
</tr>
<tr>
<td>6.456</td>
<td>9.684</td>
<td>8.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal Standard Addition method - Propionaldehyde</th>
<th>Amount of Propionaldehyde Taken, mg</th>
<th>Amount of Propionaldehyde Found in unknown sample, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown Sample (Cx)</td>
<td>Standard Sample (Cs)</td>
</tr>
<tr>
<td>6.456</td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>6.456</td>
<td>3.228</td>
<td>5.1</td>
</tr>
<tr>
<td>6.456</td>
<td>6.456</td>
<td>6.3</td>
</tr>
<tr>
<td>6.456</td>
<td>9.684</td>
<td>8.4</td>
</tr>
</tbody>
</table>

\[ C_x = \frac{id_1 \cdot C_s}{id_2 - id_1} \]

CONCLUSION

In alkaline medium it is possible to have well defined and separated waves relative to the reduction of formaldehyde, acetaldehyde and propionaldehyde. The determination of formaldehyde, acetaldehyde and propionaldehyde can be carried out effectively in presence of 3.8 x 10⁻⁶ % methyl red and 5.94 x 10⁻⁷ % bromocresol green as maxima suppressor and 0.025 N lithium hydroxide and 0.0025 N lithium chloride as supporting electrolyte at pH 12 by external as well as internal standard addition method.

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The results of estimation of formaldehyde, acetaldehyde and propionaldehyde in synthetic solution by external standard addition and internal standard addition methods are found to be accurate and precise with low values of standard deviation.

External standard addition method can be applied for estimation of formaldehyde and acetaldehyde within experimental error of less than 3 % and standard deviation 0.4 to 3. In case of propionaldehyde excess recovery is obtained due to less increase in the diffusion current for repeated polarograms of unknown solution with a known volume of its standard solution. Propionaldehyde analysis again needs correction in K value.

Internal standard addition method can be applied satisfactorily for determination of formaldehyde and acetaldehyde at Dropping Mercury Electrode under experimental condition as that for external standard addition method with low values of standard deviation. Propionaldehyde analysis again needs correction in K value.

Conflicts of interest: The authors stated that no conflicts of interest.

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48. Chemicals in the environment: acetaldehyde (CAS NO. 75-07-0)

49. List of IARC Group 1 carcinogens


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