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Determination of formaldehyde by ion exclusion and ion exchange separation with amperometric detection

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DETERMINATION OF FORMALDEHYDE BY ION EXCLUSION
AND ION EXCHANGE SEPARATION WITH
AMPEROMETRIC DETECTION

by
Yilin Shi

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

in

Chemistry

Department of Chemistry
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May, 1995
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ABSTRACT

A method has been developed for determination of formaldehyde in air sample extracts by ion exclusion and ion exchange separation followed by amperometric detection. Optimum eluant compositions and separation columns for the best separation have been determined, as well as the optimum working electrode, electrolytes, and applied potentials for the best detection. An internal standardization was used to correct for detector drift. An interference study was performed for organic acids, other aldehydes, and alcohols. Using impingers containing aqueous bisulfite solution for collection, a side by side comparison study with the 2,4-DNPH method (also using impingers) was conducted. The detection limit of the method is 1 ng (in solution). The method has been used to determine formaldehyde concentrations in air on the UNLV campus. The method is also potentially applicable to biological and food sample analysis.
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ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. Brian J. Johnson for his guidance and support during the course of this study and in the preparation of this manuscript.

The author would like to thank Dr. Spencer Steinberg, Dr. Vern Hodge, and Dr. Moses Karakouzian for their valuable help, assistance and advice.

The author would also like to thank the Department of Chemistry, University of Nevada, Las Vegas.
Chapter 1

Introduction

Formaldehyde is one of the most important compounds in the atmospheric environment because of its ubiquitous occurrence, its unique chemistry, and its adverse health effects. Formaldehyde is released into the atmosphere through a variety of natural and anthropogenic sources. In the clean atmosphere, formaldehyde is generated indirectly through the interaction of various reactive species (O₃, OH radicals) with hydrocarbons (1). The major anthropogenic sources (both direct and indirect) of formaldehyde in polluted air are incompletely combusted automobile fuels and industrial emissions (2). The content of hydrocarbons in emissions from automobiles is controlled by law in the United States because of subsequent reactions that form the compounds of photochemical smogs, including formaldehyde. Formaldehyde can be released indoors, as well as outdoors, from formaldehyde-containing products, such as particle board, insulation materials, plywood, etc (3). In fact, indoor concentrations of formaldehyde are often higher than outdoor concentrations (4).

Many studies have shown that formaldehyde has adverse health effects on both humans and animals. Eye irritation and respiratory tract irritation are common results to
human exposure to formaldehyde (5,6). High formaldehyde concentrations can apparently cause cancer in laboratory animals (e.g., rats and mice), although potential carcinogenicity of formaldehyde to humans has not been clearly demonstrated (7).

1.1 Focus of Study

Due to the importance of formaldehyde in the environment, the focus of this study was on the development of a new method which had advantages over previous methods in several areas (section 1.3.), especially in using less toxic reagents, for the formaldehyde determination.

1.2. Sources of Formaldehyde

1.2.1. Industrial Production

Formaldehyde is one of the top 50 chemical products in U.S. About 7.61 billion pounds of formaldehyde (37% aq. solution) were produced in 1993 (8). Also, it is a large-volume chemical used in a wide variety of building materials as well as in other industrial products, such as cosmetics, textiles, etc..

1.2.2. Importance in Background Atmospheric Chemistry

There are different mechanisms of formaldehyde generation in different atmospheric environments. Of the hydrocarbons found in the clean troposphere, methane (CH₄) has the highest concentration at 1.6 ppmv (9). It thus provides the major natural source of formaldehyde in the clean troposphere through methane oxidation chain reactions
first suggested by Levy (10):

\[
\text{HO} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3 \quad (1.1)
\]

\[
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \quad (1.2)
\]

\[
\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (1.3)
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad (1.4)
\]

The accumulation of formaldehyde in the atmosphere is suppressed by natural removal processes. The major removal processes of formaldehyde are photolysis and reaction with intermediates present in the atmosphere - HO, NO₃, etc.

The following reaction sequence occurs (11,12):

\[
\text{HCHO} + h\nu \rightarrow \text{HCHO}^* \quad (1.5)
\]

\[
\text{HCHO}^* \rightarrow \text{H}_2 + \text{CO} \quad (1.6a)
\]

\[
\text{HCHO}^* \rightarrow \text{H} + \text{HCO} \quad (1.6b)
\]

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (1.7)
\]

\[
\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad (1.8)
\]

In case of the reaction of formaldehyde with HO and NO₃ radicals, the reactions are as follows (13,14):
\[ HO + HCHO \rightarrow H_2O + HCO \]  \hspace{1cm} (1.9)

\[ NO_3 + HCHO \rightarrow HONO_2 + HCO \]  \hspace{1cm} (1.10)

\[ HCO + O_2 \rightarrow HO_2 + CO \]  \hspace{1cm} (1.8)

Based upon the above reactions for formaldehyde removal, the HO_2 radical is a major product (the sum of reactions 5-8 is HCHO + 2O_2 + hv \rightarrow 2HO_2 + CO), which results in an overall increase in the chemical reactivity of the atmosphere (15).

1.2.3. Importance in Polluted Air Chemistry

While hydroxyl attack on methane is the predominant source of formaldehyde in the clean troposphere, the major sources of formaldehyde in the polluted troposphere are the reactions of anthropogenic and natural nonmethane (i.e. alkane, alkene, and aromatic) hydrocarbons with HO radicals and ozone (16). The reaction pathways for these non-methane hydrocarbons (NMHC's) are much more complex than for methane and have been less studied. Complex mixtures of intermediates may be formed but formaldehyde is still a major species.

1.3. Methods for Formaldehyde Determination

Many analytical methods for formaldehyde determination have been developed due to its large-volume production, importance to the atmospheric chemistry, and its possible exposure-related health effects. Each developed method has been found to have some
disadvantages; for example, high blank values, use of toxic reagents, or instability of chromophore formed. They will be addressed in detail in the following sections. Most methods are classified into two major categories: spectrophotometric methods and chromatographic methods.

1.3.1. Spectrophotometric Methods

The chromotropic acid method was one of the first analytical methods for formaldehyde analysis. Ever since Eegriwe described the use of chromotropic acid for the detection of formaldehyde (17), many studies have been done on the modification of this method. Basically, chromotropic acid and concentrated sulfuric acid are added sequentially to a formaldehyde sample collected in distilled water. Formaldehyde reacts with chromotropic acid to form a deep purple chromophore which is detected at 580 nm. The major problem with this method is the interferences from a number of substances, such as phenol, ethanol, nitrite, nitrate, etc. (18,19).

Other spectrophotometric methods include the pararosaniline method and the 3-methyl-2-benzothiazolone hydrazone (MBTH) method. Both methods are similar to the chromotropic acid method. Reagents (sodium tetrachloromercurate/pararosaniline and FeCl₃-NH₂SO₃H, respectively) are added into formaldehyde samples collected in sodium sulfite solution or MBTH solution to form colored chromophores which are measured at 560 nm and 628 nm, respectively. A major drawback of the pararosaniline method is the use of the toxic sodium tetrachloromercurate salt. For the MBTH method, it is subject to the instability of the color chromophore and positive interferences from other aldehydes.
1.3.2. Chromatographic Methods

In this category, the 2,4-dinitrophenylhydrazine (2,4-DNPH) method is one of the most often used methods. With the 2,4-DNPH procedure, formaldehyde reacts with 2,4-DNPH to form 2,4-dinitrophenylhydrazone which is determined by HPLC with UV detection. Major drawbacks of this method are the use of toxic 2,4-DNPH reagent and the interference from ozone in air (20).

The 2-(benzylamino)ethanol-coated sorbent tube method is a gas chromatographic method. The major disadvantage of the method is the lack of sensitivity and high blank values found in unexposed tubes (21).

At least two methods based on ion chromatography have been developed. In the first method, formaldehyde is collected on tubes containing impregnated charcoal, then desorbed and converted to formic acid by hydrogen peroxide (22). The HCOO\(^-\) is determined by ion chromatography. Concerns about this method include quantitative recovery of formaldehyde from the charcoal, and formation of artifact HCOOH (i.e., not due to formaldehyde).

In the second method, formaldehyde is desorbed with bisulfite solution from molecular sieves. The additive product hydroxymethanesulfonate (HOCH\(_2\)SO\(_3\)\(^-\)) is determined by ion chromatography. This method suffers from the loss of formaldehyde by oxidation before the desorption step (23).

As was discussed above, no one optimum method for the determination of formaldehyde exists. The objective of the current study was to develop a new method which would overcome disadvantages of previous methods.
2.1. Chemical Properties of Formaldehyde and Hydroxymethanesulfonate

The carbonyl group (C=O), the functional group in aldehydes, is highly polarized due to the large difference in electronegativity between carbon and oxygen. It is because of the polarity of this functional group that the carbonyl carbon is susceptible to attack by nucleophiles, such as H\textsubscript{2}O (eq. 2.1) and bisulfite (eq. 2.2).

\[
\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2 \quad (2.1)
\]

\[
\text{HCHO} + \text{HSO}_3^- \rightleftharpoons \text{HOCH}_2\text{SO}_3^- \quad (2.2)
\]

The product HOCH\textsubscript{2}SO\textsubscript{3}\textsuperscript{-} in eq. 2.2 is called hydroxymethanesulfonate (HMSA). HMSA has been found to be resistant to oxidation by several oxidants, such as iodine (24), ozone (25), and H\textsubscript{2}O\textsubscript{2} (26). The equilibrium constant $K_{eq}$ of eq. 2.2 has been measured by several authors. The values are $8.5 \times 10^6$ at pH 4 and 20°C by Dong and Dasgupta (27), $3.64 \times 10^6$ at pH 5.6 and 25°C by Deister et. al. (28), and $6.67 \times 10^6$ at pH 5 and 25°C by Kok et. al. (26). These values show a high degree of formation and a high stability of...
HMSA in intermediate pH solutions. However, HMSA behaves in a different way in strong base, where it breaks down to free formaldehyde and sulfite ion (eq. 2.3).

\[
\text{HOCH}_2\text{SO}_3^- + \text{OH}^- \rightarrow \text{HCHO} + \text{SO}_3^{2-} + \text{H}_2\text{O}
\]  

(2.3)

The time required for the dissociation of HMSA was computed to be (five half-lives, 25°C) 40s and 4.0s at pH 9 and 10, respectively based on the data obtained by Sorenson et. al. (29).

The above properties of HMSA were exploited in this study for formaldehyde collection and separation (this will be addressed in a later section).

2.2. Separation Mechanisms

As will be discussed later, the collected form of formaldehyde in this study is the formaldehyde-bisulfite complex -- HOCH\textsubscript{2}SO\textsubscript{3}\textsuperscript{-}. This target compound was separated from other species through two steps: ion exclusion separation and ion exchange separation.

2.2.1. Ion Exchange Resins

Ion exchange reactions have been known for many years. Natural ion exchangers such as zeolite clays, long known to have ion exchange characteristics (30), have not found widespread applications. It was not until synthetic resins were produced that ion exchange technology became commercially important. The synthesis of modern ion exchange resins, which features high efficiencies and capacities, was pioneered by Adams et. al. (31).

There are several types of ion exchange resins used in current ion separation processes,
including pellicular, gel, and macroporous. No matter which type the resin is, basically they are all styrene-divinylbenzene (S-DVB) copolymer based. The differences between each type of exchanger are in structures, percentage of divinylbenzene content, etc.

Macroporous resins have high divinylbenzene content (15-50%), which results in extreme rigidity, compared with gel-type resins (usually 2-15%) (32). Because of easier deformation and compression due to lower divinylbenzene content, gel-type resins are usually used in suppressor columns, while macroporous resins are used in separation columns (as are pellicular resins). Among the most prominent characteristics of pellicular resins are their unique structure, which was developed by Dow Chemical and Dionex (32). This unique structure leads to high efficiencies and low back pressures for ionic separation.

In order to achieve ionic separation, ionic exchange sites have to be introduced into each type of resin. The two most commonly used types of active groups, which are bound to the S-DVB substrate, are sulfonate (-SO$_3^-$) for cation exchange processes and quaternary ammonium [-N$^+$($R$)$_3$] for anion exchange processes. Other active groups used in different resins are summarized in Table 2.1.
Table 2.1. Active Groups used in Ion-exchange Resins

<table>
<thead>
<tr>
<th>Classification</th>
<th>Active Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-Exchange Resins</td>
<td></td>
</tr>
<tr>
<td>Weak Acid</td>
<td>Carboxylic Acid</td>
</tr>
<tr>
<td>Weak Acid</td>
<td>Phosphoric Acid</td>
</tr>
<tr>
<td>Anion-Exchange Resins</td>
<td></td>
</tr>
<tr>
<td>Weak Base</td>
<td>Secondary Amine</td>
</tr>
<tr>
<td>Weak Base</td>
<td>Tertiary Amine</td>
</tr>
</tbody>
</table>

2.2.2. Ion Exclusion

Ion exclusion is a separation mechanism observed when using ion exchange resins; it can be utilized as a separation technique for nonionic or weakly ionic materials. Although ion exchange resins are used in this technique, true ion-exchange interactions do not occur. Retention occurs via partition or adsorption, but analytes with the same sign of charge (e.g. positive or negative) as the ion exchanger are repelled and thus excluded. Therefore, anions are separated on cation exchangers, and cations are separated on anion exchangers.

To illustrate the manner in which an ion exclusion separation works, consider an analyte mixture of chloride (Cl\(^{-}\)), and formic (HCOOH) and acetic (CH\(_3\)COOH) acids eluted with dilute sulfuric acid. As the chloride, HCOOH and CH\(_3\)COOH pass through the resin, the repulsive forces between the chloride and the fixed sulfonate group (\(-\text{SO}_3\) of the resin prevent chloride from entering the pores of the resin. Therefore, the Cl\(^{-}\) elutes
with the void volume. Meanwhile, formic and acetic acids can enter the pores and partition between the mobile phase and the stationary phase (i.e. the resin). They are retained on the resin to different degrees mainly based upon the degree of ionization, which influences the degree of exclusion. Because \( K_a \) is a measure of the degree of ionization, weak acids tend to elute in the order of their \( pK_a \). Therefore, formic acid emerges ahead of acetic acid (\( pK_a \) for HCOOH = 3.74; \( pK_a \) for CH₃COOH = 4.75; ref. 33).

The ion exclusion process is usually used for the separation of organic acids, sugars, alcohols and organic bases (34). It is also applicable to the group separation of ionic species from nonionic species. The latter application was used to advantage in this study. The target compound hydroxymethanesulfonate (an ionic species), is not retained on the resin. This complex is excluded and eluted with the void volume. During this separation process, the HOCH₂SO₃⁻ is separated from all other nonionic (or weakly ionic) species which are retained on the cation exchange resin.

2.2.3. Ion Exchange Separation

Ion exchange techniques require an ionic species in the eluant (as do ion exclusion techniques). The ionic species in the eluant acts as the "pusher" of the analyte species. Eluants, such as CO₃²⁻/HCO₃⁻ mixtures or OH⁻, are usually used in anion exchange processes, while acidic eluants, such as HCl or H₂SO₄, are commonly used in cation exchange processes. When analyte species and eluant pass down the column, they compete with each other for the ion exchange sites. The analyte species migrate differentially down the column and separate from one another.
The order of elution for various ions is controlled by the exchange affinities of ions to ion exchange resins. The ratio of valence/non-hydrated ionic radius ($Z/r$) has been successfully used as a measure of the exchange affinities. The ratio of $Z/r$ along with exchange constants ($K_{ex}$) for some common anions and cations are listed in Table 2.2.

Table 2.2. Exchange Constants of Common Anions and Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>$Z/r^{(a)}$</th>
<th>$K_{ex}^{(b)}$</th>
<th>Anion</th>
<th>$Z/r^{(a)}$</th>
<th>$K_{ex}^{(c)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>0.75</td>
<td>1.0</td>
<td>I$^-$</td>
<td>0.46</td>
<td>8.7</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.0</td>
<td>0.67</td>
<td>Br$^-$</td>
<td>0.51</td>
<td>2.8</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1.3</td>
<td>0.40</td>
<td>Cl$^-$</td>
<td>0.55</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F$^-$</td>
<td>0.74</td>
<td>0.09</td>
</tr>
</tbody>
</table>

(a) GoldSchmidt (35), (b) Kressman and Kitchener (36,37), (c) Wheaton and Bauman (38)

It can be seen that the exchange affinity (the order of elution) of an ion varies inversely as the ratio of $Z/r$. Although Table 2.2. only shows the trend of exchange affinities for different ions with the same valence, it can also apply to the ions with different valence. Normally, the exchange affinity increases with increasing valence of the exchanging ion, for example, Na$^+$ < Ca$^{2+}$ < Al$^{3+}$ (39), and Cl$^-$ < SO$_4^{2-}$. 
2.3. Amperometric Detection

The conductivity detector is typically used in ion chromatography because all ionic species are conductive. There are some disadvantages and limitations for conductivity detection. First, it requires a difference in conductance between the eluant (which itself contains ionic species) and analyte ions. Therefore, the eluant usually needs to be converted to a weakly conductive form to be made less conductive than the analyte ions. In this case, a suppressor membrane or post-column reactor needs to be used. Second, it does not give a response to nonionic species, such as formaldehyde.

Besides conductivity detection, other detection methods developed for ion chromatography include amperometric detection, UV/vis absorbance, refractive index, and fluorescence. Among these detection methods, amperometric detection has received considerable interest after its first introduction by Hughes et. al. (40) in 1981. Basically, amperometric detection is only applicable to electroactive species, which means the species must be either oxidizable or reducible on the surface of an electrode. Determination of formaldehyde by amperometric detection after ion exclusion separation was reported by Roclin (41) in 1985. In his method, an aqueous sulfuric acid and potassium sulfate solution was used as the eluant and a platinum electrode was used as the working electrode. The major problem of his method was a low detection limit for formaldehyde (approximately 1ppm in solution) and poor separation between formaldehyde and alcohols.

Due to the low sensitivity of Roclin’s method to formaldehyde detection, the part of the objective of the current study was to develop a new approach to achieving a high sensitivity to formaldehyde by amperometric detection.
2.4. Proposed Work

A new method of determination of formaldehyde, which is characteristic of high selectivity and sensitivity to formaldehyde, is to be developed. Figure 2.1 shows the proposed experimental layout.

Air samples are collected in aqueous bisulfite solution using an impinger. Because of the great stability of hydroxymethanesulfonate at intermediate pH values, the formaldehyde is preserved in this form (e.g., stabilized against oxidation). Furthermore, the sensitivity of detection is improved versus non-complexed formaldehyde, due to the shorter retention time.

The collected sample in the impinger is injected onto the system (Figure 2.1) directly without any pretreatment. An acidic eluant, which is pumped into the system by pump #1, is used for the first separation process: ion exclusion. Hydroxymethanesulfonate, the collected form of formaldehyde, is separated from all other nonionic or weakly ionic species after ion exclusion separation due to its ionic properties. A mixing tee is placed immediately after the ion exclusion column, where the effluent from the ion exclusion column is mixed with a basic solution which is delivered by a second pump and has a higher concentration than the acidic eluant. Because of the mixing of the eluants creates a strongly basic solution, hydroxymethanesulfonate readily breaks down to formaldehyde and sulfite prior to the second separation process: ion exchange. After the ion exchange process, the formaldehyde (from HMSA) is separated from all ionic components. A pulsed amperometric detection is placed after the ion exchange column for formaldehyde detection.
Columns and eluants for separation and conditions for detection that were developed are addressed in chapters 3 and 4.
Figure 2.1 System Schematic

- Readout Device
- PAD
- Ion Exchange
- Mixing Tee
- Ion Exclusion
- Pump #2
- Pump #1
- Acidic eluant
- Basic eluant

Injector
Separation of sample components is the primary goal in any chromatographic method. A frequent problem in any type of chromatography is the need to increase the resolution (or quality of separation) between two or more peaks. This is described mathematically by equation 3.1:

\[
R = \frac{1}{4}(\alpha - 1)\left(\frac{k'}{k' + 1}\right)\sqrt{N}
\]  

(3.1)

where \(\alpha\) is the selectivity or separation factor, \(k'\) is the partition ratio, \(N\) is the column efficiency, and \(R\) is the resolution. \(R\) can be calculated experimentally by:

\[
R = \frac{2(t_{r1} - t_{r2})}{w_1 + w_2}
\]  

(3.2)

where \(t_{r1}\) is the retention time of the first component, \(t_{r2}\) is the retention time of the second component, \(w_1\) is the width of the first peak at the base, and \(w_2\) is the width of the second peak at the base.
From eq. 3.1, one method of achieving better separation is either to increase N by lengthening the column or to use a column with greater efficiency per unit length. This is defined as height equivalent to a theoretical plate, H:

\[ H = \frac{L}{N} \]  

(3.3)

where \( L \) is the column length. For a column with constant \( H \), separation is increased with increasing length of the column. Also, separation can be improved by selecting different columns with different selectivities to the species of interest; this affects \( \alpha \) in eq. 3.1.

A second effective method of increasing separation is to change eluants. As a general rule, changes in eluant concentration or in eluting ion type can alter separation by affecting \( \alpha \) (eq. 3.1). Ion chromatographic separations are based upon competition between sample ions and eluting ions for the active sites of the resin. To compete effectively, sample ions and eluting ions should have similar affinities to the resin. Therefore, various eluants (either in concentration or in composition) should be considered for separations of various sample ions. For example, weakly ionized sodium tetraborate (\( \text{Na}_2\text{B}_4\text{O}_7 \)) eluant is used instead of carbonate/bicarbonate (\( \text{CO}_3^{2-}/\text{HCO}_3^- \)) eluant to obtain better separation between acetate and formate, which are weakly retained on most ion-exchange columns.

Time is an aspect of chromatography that also needs to be considered during the optimization of separation. In general, a shorter analysis time is strongly preferred. There are several ways to shorten the analysis time:

1. use of columns with shorter length (affects N)
2. increasing flow rate of eluant (affects \( k' \))
3. use of eluants with higher ionic strength (affects $\alpha$)

However, separation and analysis time are two parameters which are in direct conflict with each other in chromatography. For example, use of a longer column for better separation causes a longer analysis time. Use of a stronger eluant for shorter analysis time may result in poorer separation of certain species on a specific column. In general, shorter analysis time is desirable only if adequate separation can be obtained.

In this study, we were interested in the separation between formaldehyde and other components present in samples, such as bisulfite ion ($\text{HSO}_3^-$) and sugars such as ribose (used as an internal standard; section 4.2.3.), as well as analysis time. As mentioned in chapter 2, formaldehyde was converted to hydroxymethanesulfonate and separated through two processes: ion exclusion and ion exchange. However, at the beginning of our work, these two steps were investigated separately and then they were combined at the final stage. This chapter describes the process of method development that led to the optimal operating parameters for formaldehyde separation.

### 3.1. Columns

Changes in length or type of column can alter the separation as well as the analysis time. To investigate these various effects, four kinds of columns were investigated in this study. They were anion exchange columns AS4A and AG10 from Dionex and cation exchange columns AS1 from Dionex and Rezex RFQ from Phenomenex. Table 3.1. summarizes some parameters of these columns.
Table 3.1 Parameters of Columns Used

<table>
<thead>
<tr>
<th></th>
<th>Dionex AS4A</th>
<th>Dionex AG10</th>
<th>Dionex AS1</th>
<th>Phenomenex Rezex RFQ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>matrix</strong></td>
<td>Polystyrene</td>
<td>Polystyrene</td>
<td>Divinylbenzene</td>
<td>Hydrogen</td>
</tr>
<tr>
<td><strong>ionic form</strong></td>
<td>Depends on eluants</td>
<td></td>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td><strong>standard dimension</strong></td>
<td>4 x 250 mm</td>
<td>4 x 50 mm</td>
<td>9 x 250 mm</td>
<td>7.8 x 100 mm</td>
</tr>
<tr>
<td><strong>pH range</strong></td>
<td>0 - 14</td>
<td>0 - 14</td>
<td>1 - 3</td>
<td>1 - 3</td>
</tr>
<tr>
<td><strong>designed application</strong></td>
<td>anions and organic acids</td>
<td>anions and organic acids</td>
<td>organic acids</td>
<td>organic acids and carbohydrates</td>
</tr>
</tbody>
</table>

All the columns listed in Table 3.1 are analytical columns except the AG10 which is a guard column for the AS10 analytical column. A guard column is normally placed prior to an analytical column to prevent contaminants in samples or eluants from eluting onto the analytical column. Usually, the guard column has the same column packing as the analytical column. Therefore, a guard column can be used as an analytical column with lower column capacity (due to its shorter length). The AG10 guard column was used as an analytical column because it has a greater ionic capacity than the AS4A column and it provides faster elution of formaldehyde than the AS4A column due to the shorter length. The detailed experimental data will be presented in the following sections.
3.2. Experimental

All chromatography was performed on a Dionex Qic ion chromatographic system with either an external pulsed amperometric detector (PAD) or conductivity detector. Samples were injected into system through a sample loop of 100ul volume. For routine work, formaldehyde standard solutions were prepared from 37.3% (w/v) formaldehyde in water and used directly. For more precise work, formaldehyde was standardized via the sulfite titration method (42 and Appendix A). The concentration of formalin used in this study was 37.8% (w/v) by standardization. Only 0.5% difference existed between labeled value (37.3%) and standardized value. Therefore, the value of 37.3% (w/v) was used for all studies with no correction. Hydroxymethanesulfonate standard solutions were made by mixing known amounts of formaldehyde with excess sodium bisulfite and diluting to a standard volume. The deionized water used for preparation of eluants and standard solutions had a specific resistance of at least 18 megohm-cm (Barnstead). All eluants were degassed with helium (He) before use. All chemicals used were analytical grade (or above). They are listed by manufacturer in Appendix B.

3.2.1. Ion Exchange Separation Studies

A: AS4A Column

The initial separation studies were performed on the AS4A column. The normal eluant used on the AS4A column is 1.8 x 10^{-3} M Na_2CO_3/1.7 x 10^{-3} M NaHCO_3 for Cl^-, Br^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} separation. Because species that represented possible interferences (e.g. organic acids) are weakly retained on the AS4A column using this
eluant, eluants with different selectivity were tried. An aqueous potassium hydrogen phthalate (KHP)/potassium sodium phthalate (KNaP) eluant was used first. Fifty ppm solutions of HCHO, HCOOH, SO$_3^{2-}$, C$_2$O$_4^{2-}$ and HOCH$_2$SO$_3$ (50ppm or 25ppm HSO$_3^{-}$ in excess HCHO) were made and then run under different chromatographic conditions using pulsed amperometric detection with a platinum working electrode. The applied potentials were: $E_1 = +0.40V$, $E_2 = +1.25V$, $E_3 = -0.10V$ (section 4.1.). Experimental data are summarized in Table 3.2.

Table 3.2 Experimental Data of Separation on the AS4A with KHP/KNaP Eluant

<table>
<thead>
<tr>
<th>concentration</th>
<th>flow rate (mL/min)</th>
<th>analytes</th>
<th>retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.0 \times 10^{-4}$ M KHP</td>
<td>2.0</td>
<td>HCHO</td>
<td>0.6</td>
</tr>
<tr>
<td>$8.0 \times 10^{-4}$ M KNaP</td>
<td></td>
<td>HCOOH</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br$^-$</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$O$_4^{2-}$</td>
<td>0.9</td>
</tr>
<tr>
<td>$4.0 \times 10^{-4}$ M KHP</td>
<td>1.1</td>
<td>HCHO</td>
<td>1.0</td>
</tr>
<tr>
<td>$4.0 \times 10^{-4}$ M KNaP</td>
<td></td>
<td>HCOOH</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br$^-$</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$O$_4^{2-}$</td>
<td>1.1</td>
</tr>
<tr>
<td>$3.5 \times 10^{-4}$ M KHP</td>
<td>1.1</td>
<td>HCHO</td>
<td>1.0</td>
</tr>
<tr>
<td>$3.5 \times 10^{-4}$ M KNaP</td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>6.6</td>
</tr>
</tbody>
</table>
All three HOCH$_2$SO$_3^-$ runs showed two peaks with the same retention times as formaldehyde and sulfite. This indicates that HOCH$_2$SO$_3^-$ breaks down to formaldehyde and sulfite, otherwise the sulfite peak should disappear since HOCH$_2$SO$_3^-$ is not readily oxidized for detection. Also based on the data in table 3.2, retention times of analytes increased with the decreasing of eluant flow rates and eluant concentrations, but the formaldehyde/formic acid pair was essentially not separated. A new eluant was considered at this stage. A mixture of boric acid (B(OH)$_3$) and sodium chloride (NaCl) was the second eluant studied. Table 3.3 summarizes experimental data on this eluant. The same working electrode and applied potentials were used as for KHP/KNaP eluant. Figure 3.1 shows the chromatogram of HOCH$_2$SO$_3^-$ (50ppm HSO$_3^-$ in excess HCHO) with 1.0 x $10^{-3}$ M B(OH)$_3$/1.0 x $10^{-4}$ M NaCl eluant and 1.5 mL/min of flow rate. Two peaks with the same retention times as formaldehyde and sulfite were noted in the chromatogram, also indicating break down of the hydroxymethanesulfonate. Another phenomenon accompanying the use of this eluant (evident from Figure 3.1) was the occurrence of peak tailing, which is undesirable from a separation standpoint.
Table 3.3 Experimental Data on the AS4A with B(OH)$_3$/NaCl Eluant

<table>
<thead>
<tr>
<th>concentration</th>
<th>flow rate (mL/min)</th>
<th>analytes</th>
<th>retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.5 \times 10^{-3}$ M B(OH)$_3$</td>
<td>1.1</td>
<td>HCHO</td>
<td>1.0</td>
</tr>
<tr>
<td>$0.05 \times 10^{-3}$ M NaCl</td>
<td></td>
<td>HCOOH</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br$^-$</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$O$_4^{2-}$</td>
<td>3.4</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$ M B(OH)$_3$</td>
<td>1.5</td>
<td>HCHO</td>
<td>0.88</td>
</tr>
<tr>
<td>$0.1 \times 10^{-3}$ M NaCl</td>
<td></td>
<td>HCOOH</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br$^-$</td>
<td>2.3</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$ M B(OH)$_3$</td>
<td>0.8</td>
<td>HCHO</td>
<td>1.9</td>
</tr>
<tr>
<td>$0.1 \times 10^{-3}$ M NaCl</td>
<td></td>
<td>HCOOH</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_3^{2-}$</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br$^-$</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure 3.1 Chromatogram of 50ppm HSO₃⁻ with excess HCHO
Column: AS4A,
Eluants: 1.0 x 10⁻³ M B(OH)₃/0.1 x 10⁻³ M NaCl,
Flow rate: 1.5 mL/min.
Peaks: #1, HCHO; #2, bisulfite.
B: AG10 Column

In the final version of the combined system (later sections), the AS4A column was replaced with the AG10 column since the AG10 column has advantages over the AS4A column in having higher ionic capacity and smaller column dead volume. Experimental data listed in Tables 3.4 and 3.5 show these advantages of the AG10 column. The pulsed amperometric detector with silver electrode was used for the experiments in Table 3.4, while the conductivity detector was employed for the experiments in Table 3.5. Note that since formaldehyde is unretained on the ion-exchange column, its retention time reflects the column dead volume.

Table 3.4. Retention Times of Formaldehyde on the AS4A and AG10 Columns

<table>
<thead>
<tr>
<th>column</th>
<th>eluant</th>
<th>flow rate (mL/min)</th>
<th>retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS4A</td>
<td>1.0 x10^-3 M NaOH</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>AG10</td>
<td>1.0 x10^-3 M NaOH</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The higher ionic capacity of the AG10 column allows higher ionic strength eluants to be used, which are advantageous in electrochemical detection. However, replacement of some of hydroxide with the stronger eluant carbonate allowed more moderate eluant concentrations to be used, which was an advantage experimentally. In anticipation of utilizing the AG10 column in combination with an ion exclusion separation and amperometric detection, a mixed eluant was also tried. It was found that HSO₃⁻ could be
eluted in 8.7 minutes after injection by using an eluant of 3 mM NaOH, 2 mM Na₂CO₃, and 1 mM NaNO₃ (added as HNO₃) with the same flow rate of 0.6 mL/min (i.e., similar to the results for 50 mM NaOH).

Table 3.5 Capacity Study on the AG10 Column

<table>
<thead>
<tr>
<th>analyte</th>
<th>eluant</th>
<th>flow rate (mL/min)</th>
<th>retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10ppm Cl⁻</td>
<td>50 x10⁻³ M NaOH</td>
<td>0.6</td>
<td>4.0</td>
</tr>
<tr>
<td>10ppm HSO₃⁻</td>
<td>5 x10⁻³ M NaOH</td>
<td>0.6</td>
<td>6.8</td>
</tr>
<tr>
<td>10ppm SO₄²⁻</td>
<td>5 x10⁻³ M NaOH</td>
<td>0.6</td>
<td>10.1</td>
</tr>
<tr>
<td>10ppm NO₃⁻</td>
<td>5 x10⁻³ M NaOH</td>
<td>0.6</td>
<td>14.5</td>
</tr>
</tbody>
</table>

C: Summary of Ion Exchange Separation

Formaldehyde could be separated from formic acid by using the B(OH)₃/NaCl eluant instead of the KHP/KNaP eluant. But peak tailing was severe using the B(OH)₃/NaCl eluant. Although the problem of peak tailing was improved by using eluants with higher concentration or increasing eluant flow rate, it could not be totally solved. In general, the requirements of detection and separation made it difficult to conceive of eluants that would perform well using this separation mode alone. Therefore, studies of ion exclusion separation were conducted. The AS1 cation exchange column from Dionex was the first column studied using this separation mode.
3.2.2. Ion Exclusion Studies: AS1 Column

The AS1 column is a sulphonated polystyrene/divinylbenzene based cation exchange resin used for ion exclusion separation of anions and organic acids. An acidic eluant is required for the AS1 column. Fifty ppm solutions of HCHO, HCOOH, and HOCH$_2$SO$_3^-$ (50ppm HCHO in 200ppm HSO$_3^-$) were made and injected onto the AS1 column with 1.0x$10^{-3}$ M HCl as eluant and 0.8 mL/min of flow rate. Since HOCH$_2$SO$_3^-$ is unretained on the AS1 column, it elutes out at the void volume. The retention times of HCHO, HCOOH, and HOCH$_2$SO$_3^-$ were 12.8 min, 13.1 min, and 6.6 min, respectively.

Simple chromotropic acid tests were performed on fractions collected at the void volume for HCHO, SO$_3^{2-}$, and HCHO/SO$_3^{2-}$ mixture runs. One mL of 2% (w/v) chromotropic acid and 8 mL of concentrated sulfuric acid were added to each collection (1 mL volumes). The 50ppm HCHO in 200ppm HSO$_3^-$ was the only sample of the three to produce a strong violet color indicative of formaldehyde. The other two appeared similar to a blank.

The retention times and the chromotropic acid test results verified two things. First, the product hydroxymethanesulfonate from SO$_3^{2-}$ and HCHO can be separated from weakly ionic species like HCOOH through the ion exclusion process. Second, the further separation for HCHO (retrieved from HMSA in a base) and other ionic species could be achieved thereafter on an ion exchange column.
3.2.3. Studies on combined system: ion exclusion plus ion exchange

A: AS1 and AS4A System

To design a separation system that incorporates both ion exclusion and ion exchange, two major points must be considered. First, the two columns require different types of eluants. An acidic eluant must be used for the AS1 column, while either an acidic or a basic eluant can be employed for the AS4A column. Second, considering that hydroxymethanesulfonate needs a basic environment (also for the detection requirement, chapter 4) to break down to free formaldehyde and sulfite ion, a basic eluant, which is pumped into the system by the second pump (see Figure 2.1), is required for the AS4A column. Therefore, HNO₃ was used as the acidic eluant for the AS1 column and NaOH as the basic eluant for the AS4A column. Also, the basic eluant was at a higher concentration than the acidic eluant to convert the mobile phase from acidic to basic after the ion exclusion step and prior to the ion exchange step and detection. Table 3.6. summarizes experimental data of separation on the AS1 and AS4A combined system using the pulsed amperometric detector with a silver working electrode. Chromatograms of HCHO, and HOCH₂SO₃ are shown in Figure 3.2. Chromatograms of other species (e.g., CH₃OH, C₂H₅OH, and C₂O₄²⁻) are discussed in section 5.2.
Figure 3.2 A: Chromatogram of 1.0 ppm HCHO
B: Chromatogram of 1.0 ppm HCHO in 400 ppm HSO₃⁻
Columns: AS1 and AS4A.
Eluants: 1.0 x 10⁻³ M HNO₃ and 6.0 x 10⁻³ M NaOH.
Peak: #1, HCHO.
Table 3.6. Experimental Data on AS1 and AS4A Combined System

<table>
<thead>
<tr>
<th>eluant</th>
<th>flow rate (mL/min)</th>
<th>analyte</th>
<th>retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-3}$ M HNO$_3$</td>
<td>1.5</td>
<td>50ppm HCHO</td>
<td>14.8</td>
</tr>
<tr>
<td>$6.0 \times 10^{-3}$ M NaOH</td>
<td></td>
<td>50ppm HCOOH</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50ppm HCHO</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(from HMSA)</td>
<td></td>
</tr>
</tbody>
</table>

The shift of HCHO peak (Figure 3.2) indicates that the complex HOCH$_2$SO$_3^-$ itself broke down to free HCHO and SO$_3^-$ in a basic environment, and HCHO eluted at the void volume. Data in Table 3.6 proves that free HCHO from HOCH$_2$SO$_3^-$ can be separated from other components after two separation processes.

B: AS1 and AG10 Combined System

Most of the combined system characterization studies were done using the AS1 and AG10 columns rather than the AS1 and AS4A system due to the advantages of the AG10 column over the AS4A column addressed above.

Analyses of 50ppm HCHO, 50ppm HSO$_3^-$, and 5.0ppm HCHO in 200ppm HSO$_3^-$ were performed on the AG10 column solely using pulsed amperometric detection with silver electrode. The eluant was a mixture of $1.0 \times 10^{-3}$ M HNO$_3$, $2.0 \times 10^{-3}$ M Na$_2$CO$_3$, and $3.0 \times 10^{-3}$ M NaOH and the flow rate was 0.6 mL/min. Two peaks appeared in the 5.0ppm HCHO/200ppm HSO$_3^-$ run. Retention times of HCHO and HSO$_3^-$ were 1.0 min
and 8.7 min, respectively. Retention times of two peaks in the 5.0ppm HCHO/200ppm HSO₃⁻ run were 1.0 min and 8.7 min, respectively. Comparing these retention times, we can conclude that HOCH₂SO₃⁻ in a basic eluant breaks to HCHO and SO₃²⁻, and HCHO can be separated from ionic species like SO₃²⁻. Moreover, HCHO can be separated from nonionic species with addition of the AS1 or RFQ column to the AG10 column.

Because the separation between formaldehyde and sulfite was more than adequate and retention times would only increase with addition of the ion exclusion column, the ionic strength of the eluant was increased to decrease the retention time of the sulfite. Figure 3.3 shows the chromatogram of 0.5ppm HCHO in 300ppm HSO₃⁻ using a mixture of 17 x 10⁻³ M NaOH and 5.0 x 10⁻³ M Na₂CO₃ as an eluant for the AG10 column and 1.0 x 10⁻³ M HNO₃ for the AS1 column. Base line separation between formaldehyde and sulfite was easily achieved with retention times of 3.2 min and 8.2 min for formaldehyde and sulfite, respectively. Also, peak tailing problem was solved.
Figure 3.3 Chromatogram of 0.5ppm HCHO in 300ppm HSO₃⁻.
Columns: AS1 and AG10,
Eluants: 1.0 x 10⁻³ M HNO₃, 17 x 10⁻³ M NaOH, and 5.0 x 10⁻³ M Na₂CO₃,
Peaks: #1, HCHO; #2, sulfite.
**C: Rezex RFQ and AG10 System**

When using a routine chromatographic method, shorter analysis times are naturally better if reasonable separation between species of interest can be obtained. Therefore, the Rezex RFQ column, an ion exclusion column with smaller capacity than the AS1 column, was coupled to the AG10 ion exchange column. The retention times of formaldehyde (3.0 min) and sulfite (5.6 min) from the injection of 0.1 ppm HCHO in 100 ppm HSO₃⁻ were reduced considerably compared with their retention times on the AS1 and AG10 system using the same eluant.

Although at this point separation parameters appeared adequate, detection consideration (section 4.2.4.) dictated further changes in eluant composition. Reproducibility of detector response was better when sodium carbonate was absent from the eluant (section 4.2.4.). Also, 1.0 x 10⁻³ M H₂SO₄ was used as eluant instead of 1.0 x 10⁻³ M HNO₃ because HNO₃ created a negative peak about 10 min after injection, which lengthened analysis time. Therefore, a study of the appropriate concentration of H₂SO₄ needed to obtain the best separation between formaldehyde and sulfite in a reasonable analysis time was undertaken. Subtle changes in concentration of H₂SO₄ caused dramatic changes in both HSO₃⁻ retention, with regard to both time and peak shape. Table 5.7 lists retention time of HSO₃⁻ for the corresponding H₂SO₄ concentration used and total analysis time needed for HSO₃⁻ elution. The peak shape became narrower with increasing concentration, however, when the concentration of H₂SO₄ eluant was more than 1.5 x 10⁻³ M, a second peak appeared after the HCHO peak (Figure 3.4). This phenomenon appears to be due to the formation of disulfite on the column (43) due to the reaction:
\[ 2\text{HSO}_3^- \rightarrow \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O} \] (3.4)

Table 3.7. Relationship between Retention Time of \( \text{HSO}_3^- \) and Concentration of \( \text{H}_2\text{SO}_4 \)

<table>
<thead>
<tr>
<th>( \text{H}_2\text{SO}_4 ) conc. (x10^3 M)</th>
<th>retention time of ( \text{HSO}_3^- ) (min)</th>
<th>total analysis time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>15.0</td>
<td>22.5</td>
</tr>
<tr>
<td>1.0</td>
<td>12.5</td>
<td>17.5</td>
</tr>
<tr>
<td>1.5</td>
<td>10.8</td>
<td>14.4</td>
</tr>
<tr>
<td>2.5</td>
<td>9.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

The 1.0 x 10^3 M \( \text{H}_2\text{SO}_4 \) eluant was selected to avoid the double peaks. To further correct for instrumental drift, an internal standard was desired (section 4.2.4.). Ribose, xylose, and glucose were selected as candidates for an internal standard. Retention times of ribose, xylose, and glucose using 1.0 x 10^3 M \( \text{H}_2\text{SO}_4 \) (eluant #1 delivered by pump #1, Figure 2.1) and 20 x 10^3 M \( \text{NaOH} \) (eluant #2 delivered by pump #2) as eluants were 5.1 min, 4.2 min, and 4.1 min, respectively. Comparing these retention times with the 3.0 min required for formaldehyde, ribose is the best selection for an internal standard.

A solution containing 0.1ppm \( \text{HCHO} \) in 400ppm \( \text{HSO}_3^- \) with an internal standard of 4.0 ppm ribose was run on the Rezex RFQ and AG10 combined system using eluants of 1.25 x 10^3 M \( \text{H}_2\text{SO}_4 \) (#1) and 20 x 10^3 M \( \text{NaOH} \) (#2). The total flow rate (i.e., after the basic eluant was added) was 1.6 mL/min. The chromatogram is shown in Figure 3.5. Base line separation among following components \( \text{HCHO}, \text{ribose}, \text{and HSO}_3^- \) was
achieved. Also, the analysis time of about 13 minutes is reasonable. Therefore, the optimal operating parameters for separation are:

1. Columns: Rezex RFQ column for ion exclusion process, AG10 column for ion exchange process.
2. Eluants: $1.25 \times 10^{-3}$ M $\text{H}_2\text{SO}_4$ for Rezex RFQ column, $20 \times 10^{-3}$ M $\text{NaOH}$ for AG10 column.
3. Flow rates: 1.0 mL/min of 1.25 mM $\text{H}_2\text{SO}_4$, 0.6 mL/min of 20 mM $\text{NaOH}$. 
Figure 3.4 Chromatogram of 0.1ppm HCHO in 400ppm HSO₃⁻. Columns: Rezex RFQ and AG10, Eluants: 1.5 x 10⁻³ M H₂SO₄ and 20 x 10⁻³ M NaOH. Peaks: #1, HCHO; #2, disulfite; #3, sulfite.

Figure 3.5 Chromatogram of 0.1ppm HCHO in 400ppm HSO₃⁻ with 4.0ppm ribose as internal standard. Columns: Rezex RFQ and AG10, Eluants: 1.25 x 10⁻³ M H₂SO₄ and 20 x 10⁻³ M NaOH. Flow rate: 1.6 mL/min. Peaks: #1, HCHO; #2, ribose; #3, sulfite.
Chapter 4

Detection

The original IC concept is to separate ions with ion exchange resins and use conductivity as the basis for detection. Also, due to the conductivities of all the ions, conductivity detection is the most commonly used method in ion chromatography. However, there is one limitation for conductivity detection: nonionic species like formaldehyde are not detectable on the conductivity detector. To remove this limitation, an amperometric detection can be employed instead. This detection is only applied to species that can be oxidized or reduced at the working electrode surface. This chapter describes amperometric detection, and also describes experiments performed in finding optimal detection parameters for formaldehyde.

4.1. Pulsed Amperometric Detection

Amperometric methods of liquid chromatographic detection have been receiving increasing interest in the past decade (44). There are two types of amperometric detections: single potential amperometric detection and pulsed amperometric detection. In the single potential amperometric method, a single potential is applied to the working electrode, and
the resulting current is continuously monitored. Pulsed amperometric detection is a newer method, where a repeating sequence of three potentials are used. The analytes are oxidized or reduced on the working electrode at the first potential (E1) which is held constant during analysis, and the current is measured. After the measurement of current, the potential is stepped to a more positive or negative value (E2), and an oxidic or reductive layer is formed on the working electrode surface. Then, the third potential (E3) of negative or positive value is applied to reducing or oxidizing the formed oxidic or reductive layer to produce the bare metal. Both E2 and E3 should be set close to the positive or negative potential limit. Pulsed amperometric detection has an advantage over single amperometric detection in detecting chemical species whose oxidation or reduction products would coat on and poison the working electrode which results in the degradation of the working electrode, because the electrode is automatically cleaned by the alternating positive and negative pulsing. The current measured in an amperometric method is proportional to the concentration of the analyte.

4.2. Experimental

A number of parameters affect quality of detection in amperometry; among them are the type of working electrode, the type of electrolyte, and the values of E1 (primary oxidation or reduction potential). In the following sections, all of these factors will be discussed in detail through experimental data for the formaldehyde detection that was a major interest in this study.
4.2.1. Working Electrode Materials

Four kinds of electrode materials have been most widely used in amperometric detectors: platinum (Pt), silver (Ag), glassy carbon, and gold (Au). Both platinum and silver electrodes were used in this study. Comparative studies on these two electrodes were conducted using various types of electrolytes (section 4.2.2.).

The detector used in this study is the Dionex PAD pulsed amperometric detector, which can be used in either a pulsed or single potential mode. The PAD has a flow-through cell design with three electrodes: the working electrode, the reference electrode, and the counter electrode. Electrolytes flow across the surface of the working electrode. Electroactive species are oxidized or reduced on the surface of the working electrode. The reference electrode is used to control the potential of the working electrode while the counter electrode carries the current. The reference electrode used in this study was the silver wire electrode, e.g., Ag⁺/Ag (s).
### 4.2.2. Electrolytes

Different electrolytes were studied on both platinum and silver electrodes for formaldehyde detection. Two types of electrolytes were investigated: acidic electrolytes and basic electrolytes. Table 4.1. summarizes the electrolytes and electrodes used for experiments of detection. Chromatograms and discussions will be presented in the following sections.

<table>
<thead>
<tr>
<th>type of electrolytes</th>
<th>working electrodes</th>
<th>electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>acidic</td>
<td>Pt</td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HNO₃ / Cu(NO₃)₂</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HNO₃ / Cu(NO₃)₂</td>
</tr>
<tr>
<td>basic</td>
<td>Pt</td>
<td>KHP / KNaP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaOH</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>NaOH</td>
</tr>
</tbody>
</table>

**A: Acidic Electrolytes with Platinum Working Electrode**

A solution of 50ppm HCHO was run using two different acidic electrolytes of a) $1.0 \times 10^3 \text{ M HCl}$ and b) mixture of $1.0 \times 10^3 \text{ M HNO}_3$ and $0.01 \times 10^3 \text{ M Cu(NO}_3)_2$. The three applied potentials were: E₁ = +0.40V, E₂ = +1.25V, and E₃ = -0.10V. Sensitivities to formaldehyde from electrolytes a and b were 0.33 nA/ppm and 16 nA/ppm, respectively. It is obvious that the detector had much better response to formaldehyde...
when using the mixture of \(1.0 \times 10^{-3} \text{ M HNO}_3\) and \(0.01 \times 10^{-3} \text{ M Cu(NO}_3\)\)_2 as electrolyte. This suggested that formaldehyde was more easily oxidized on the active copper layer, which was formed from the reduction of copper ion (\(\text{Cu}^{2+}\)) present in the electrolyte, than the inert platinum surface. While this approach appeared promising, better sensitivity was later found with a different electrode/electrolyte combination (subsection D below), therefore no further study was pursued.

**B: Acidic Electrolytes with Silver working Electrode**

The \(1.0 \text{ mM HNO}_3\) and \(0.05 \text{ mM Cu(NO}_3\)\)_2 electrolyte was also applied to the silver working electrode for formaldehyde detection. The effect of copper ion on formaldehyde detection that was observed on the platinum electrode was not seen when using the silver electrode; formaldehyde was essentially undetected on the silver electrode when this acidic electrolyte was used.

**C: Basic Electrolytes with Platinum Working Electrode**

To continue the study for suitable working electrode/electrolyte combinations, two basic electrolytes were applied to the detection study on both platinum and silver electrodes.

Fifty ppm of standard formaldehyde was run with a mixture of \(4.0 \times 10^{-4} \text{ mM KHP}\) and \(4 \times 10^{-4} \text{ M KNaP}\) as electrolyte. Three applied potentials were set to the same values as for acidic electrolytes. Sensitivities to formaldehyde from this electrolyte was 0.87 nA/ppm, which was not particularly high.
Sodium hydroxide (NaOH) was another basic electrolyte used for formaldehyde detection study. Sensitivity to formaldehyde from this electrolyte was 0.34 nA/ppm. Again, the result was not satisfactory.

**D: Basic Electrolytes with Silver Working Electrode**

Fifty ppm of standard formaldehyde was run on the silver electrode with 1.0 x 10^{-3} M NaOH as electrolyte. The values of the three applied potentials were +0.10V, +0.09V, and -1.15V for E1, E2, and E3; the sensitivity to formaldehyde was 60 nA/ppm. This sensitivity, the highest obtained in this study, clearly suggests that the combination of sodium hydroxide electrolyte with the silver electrode is the best choice for formaldehyde detection. Furthermore, as previously mentioned in chapter 3 that sodium hydroxide is an optimal eluant for formaldehyde retrieving from HMSA and separation. Therefore, sodium hydroxide integrates the separation method with the detection method.

**4.2.3. Potentials used**

In amperometric detection, one important factor that affects the detection of electroactive species is the three applied potentials (E1, E2, and E3). Of these three potentials, E1 is the most important because the current is measured at this potential. The optimal value of E1 is usually determined by making a series of injections of the same amount of solute while varying E1, and then by evaluating the peak heights as a function of these potentials. Each electrode has a potential limit region in a specific electrolyte. For example, on a silver electrode in a basic solution this region is from -1.2V to +0.1V.
Beyond this limit region, serious reduction of hydrogen or oxidation of electrode itself would take place. Therefore, $E_1$ has to be set to a value within limit region. $E_2$ and $E_3$ are usually set to a value that is near the positive or negative potential limit of selected working electrode. In our case, $E_2$ was set to be $+0.09V$ and $E_3$ was $-0.15V$.

A series of injections of 50ppm HCHO solution was made while varying $E_1$. Peak heights of formaldehyde increased with increasing $E_1$ from $+0.0V$ to $+0.1V$. At a potential of $+0.1V$, the peak height reached the highest level. Therefore, $+0.1V$ of $E_1$ is the optimal potential for formaldehyde detection.

The final setting of three applied potentials are: $E_1 = +0.1V$, $E_2 = +0.09V$, and $E_3 = -1.15V$. Also some studies were conducted by using single amperometry mode at $E_1$ of $+0.1V$. It showed that single mode worked as same as pulsed mode in this study, although pulsed mode was employed for the rest of studies.

4.2.4. Stability -- use of internal standard

One characteristic of any kind of detector is the varying in sensitivity and response to analyte during the period of time of analysis. This phenomenon appears more obvious for the electrochemical detector because of poisoning of electrode itself by the oxidation or reduction products of analytes. Although pulsed amperometric detection has the function of electrode self-cleaning by alternating positive and negative pulsing, it yet cannot avoid response drifting.

Reproducibility study of formaldehyde detection was conducted on silver electrode by using different eluants: $\text{HNO}_3/\text{NaOH(}\text{Na}_2\text{CO}_3\text{)}$, $\text{HNO}_3/\text{NaOH}$, and $\text{H}_2\text{SO}_4/\text{NaOH}$. A
series of injections of 0.1ppm HCHO were run for each eluant. The height of formaldehyde peak for each injection is measured and is listed in Table 4.2.

From Table 4.2, reproducibility of detector response became better when Na$_2$CO$_3$ was absent from the eluant. However, the drifting of detector response could not be totally eliminated. The existing of response drifting is an obstacle to quantification. One effective way to remove this obstacle is the use of internal standard. An internal standard is a species that has been added into both samples and standards with a known concentration. It should not be naturally present in samples prior to the addition of the standard material. The essence of the internal standard method is that any matrix effect or the degree of poisoning of electrode for analytes and reference (internal standard) be similar. Instead of absolute peak heights or peak areas of analytes being measured, the ratio of peak heights or peak areas between analytes and reference is calculated. Therefore, any detector drifting on both analytes and reference cancel out.
Table 4.2. Data of Reproducibility Study on Formaldehyde Detection

<table>
<thead>
<tr>
<th>electrode</th>
<th>eluant</th>
<th>injection No.</th>
<th>peak height (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$1.0 \times 10^{-3}$ M HNO$_3$</td>
<td>1</td>
<td>4.50</td>
</tr>
<tr>
<td></td>
<td>$17 \times 10^{-3}$ M NaOH</td>
<td>2</td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td>$5.0 \times 10^{-3}$ M Na$_2$CO$_3$</td>
<td>3</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{-3}$ M HNO$_3$</td>
<td>1</td>
<td>8.30</td>
</tr>
<tr>
<td></td>
<td>$20 \times 10^{-3}$ M NaOH</td>
<td>2</td>
<td>8.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>8.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>8.00</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{-3}$ M H$_2$SO$_4$</td>
<td>1</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>$20 \times 10^{-3}$ M NaOH</td>
<td>2</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>5.20</td>
</tr>
</tbody>
</table>

Ribose was used as internal standard in this study. There are several reasons for ribose to be selected as internal standard. First, it is not present in our samples naturally. Second, separation between ribose and formaldehyde is better than that between other sugars, like xylose and glucose, and formaldehyde. Third, it is stable, non-toxic, and easily added to samples. Fourth, it is responsive to silver electrode when NaOH is used as an electrolyte.

A series of injections of 0.1ppm HCHO in 400ppm HSO$_3^-$ with 4.0ppm ribose as internal standard were run. Ratios of peak heights between formaldehyde and ribose are
calculated and listed in Table 4.3. The constant ratio was obtained and response drifting problem was solved.

**Table 4.3. Data of Reproducibility Study on HCHO Detection with Internal Standard**

<table>
<thead>
<tr>
<th>electrode</th>
<th>eluant</th>
<th>injection No.</th>
<th>peak ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$1.25 \times 10^{-3}$ M H$_2$SO$_4$</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>$20 \times 10^{-3}$ M NaOH</td>
<td>2</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Chapter 5

Method Validation

5.1. Calibration Curve

The most common method of quantification is to use standards to develop a calibration curve. The curve is basically a plot of signal amplitude as a function of analyte concentration. The reliability of a calibration curve depends on developing an equation that fits the data points. In most cases a least-square or regression process is employed.

The procedure for calibration of the method is as follow.

1. Prepare stock solutions:
   a. 1000ppm bisulfite solution: dissolve 0.3210g of sodium bisulfite in deionized water and dilute to 250 ml.
   b. 1000ppm formaldehyde solution: pipet 135.1ul of 37.3% formaldehyde and dilute to 50ml.
   c. 1000ppm ribose solution: dissolve 1.0000g of ribose in deionized water and dilute to 1000ml.
2. Prepare intermediate standard solution:

   1ppm formaldehyde solution: pipet 100ul of 1000ppm formaldehyde stock solution and dilute to 100 ml with deionized water.

3. Prepare standard solutions: pipet certain amount of 1ppm formaldehyde, 1000ppm ribose, and 4ml of 1000ppm bisulfite solution and dilute to 10 ml with deionized water.

4. Prepare blank solution: pipet same amount of ribose as for each standard solution and 4ml of 1000ppm bisulfite solution and dilute to 10 ml with deionized water.

5. Run blank and each standard solution.

6. Calculate the ratio of peak height between formaldehyde and ribose for blank and each standard.

7. Prepare a calibration curve by plotting peak height ratio against concentration.

8. Develop a least-square equation for the calibration curve.

A typical calibration curve and the results of the least-square or linear regression is shown in Figure 5.1 over the concentration range of 0.02ppm to 10.0ppm, a linear relationship exists between peak height ratio and concentration ($r^2 = 0.9999$). The approximate detection limit (determined by conservative extrapolation of the calibration curve) of the method is 1 ng in solution. This detection limit is about 100 times better than that by Roclin’s IC method (41) for formaldehyde determination.

A calibration curve must be prepared on each working day due to the day-to-day variability.
Figure 5.1 Calibration Curve

Equation for Regression Line: $PR_{\text{(peak ratio)}} = 16.5C_{\text{ppm}} + 0.30$

Correlation Coefficient: 0.9999
5.2. Interferences

Interference study was performed on the following species: methanol (CH$_3$OH), ethanol (C$_2$H$_5$OH), acetaldehyde (CH$_3$CHO), benzaldehyde (C$_6$H$_5$CHO), isobutylaldehyde ((CH$_3$)$_3$CCH$_2$O), formic acid (HCOOH), and oxalate (C$_2$O$_4^{2-}$). Each species was run through AS1 and AS4A combined system on silver working electrode. Each run was monitored for about 20 minutes, during this period of time all species should elute from the column. Chromatograms of each species were determined for 50ppm solutions; all the chromatograms showed no detection for these species except for formic acid. However, the sensitivity to formic acid was very low; about 0.1 nA/ppm. When considering the sensitivity on a molar basis for formaldehyde and formic acid, the detection for formic acid is negligible.

Among the species tested, the aldehyde can react with bisulfite to form aldehyde-bisulfite adduct during sampling, therefore interference with formaldehyde from aldehydes was a greater concern than from other species because the other species are retained by either ion exchange or partitioning and thus can be separated from formaldehyde. However, formaldehyde detection should not be affected because there appears to be complete selectivity against other aldehydes.

This great selectivity to formaldehyde is possibly due to co-effects of highly hydrated form of formaldehyde (at least $10^3$ times larger than for other carbonyl compounds, e.g. 5.1) in an aqueous solution, a basic electrolyte (NaOH), and silver
\[ CH_2O + H_2O \rightarrow CH_2(OH) \_2, \quad K_{eq} = 1.84 \times 10^3 \ (ref.45) \] (5.1)

working electrode. This is supported by the fact that the detector is responsive to carbohydrate (e.g. ribose), which contains an electron-attracting hydroxy group on the carbon adjacent to the carbonyl group to make the carbonyl group easily attacked by \( H_2O \) molecule to form a gem-diol.

5.3. Analysis of Samples

Air samples were collected in an aqueous bisulfite solution using impinger, and then injected onto system without any pretreatment. The flow rate of sampler was calibrated before sampling. The flow rate used here was 400 mL/min.

Four samples were collected from room 105 in the Technology building on the UNLV campus. Three samples were collected from a formaldehyde generator which was a sealed teflon box where a formaldehyde solution was placed for the generation of gas phase formaldehyde. The rest of ten samples were collected from room 261 in the Physics building on the UNLV campus, which is an anatomy laboratory.

Each sample was run in triplicate. The standard deviation was calculated for each data set. Five data sets are shown in Tables 5.1, 5.2, 5.3, 5.4, and 5.5. Each data set includes sampling information, concentration of each sample. Concentration of each sample is reported in two ways: one is in ppm unit for solution concentration; another is in \( \mu g/m^3 \) unit for air concentration.

Based on results listed in Tables 5.1 - 5.5, the four Tech 105 samples had almost
same concentration of formaldehyde. Results from three generator samples also agrees with each other. The data for biology laboratory is divided into three sets by month: June set, July set, September and October set. Samples in each set had the same concentration level of formaldehyde.

The agreement between samples in each set shown above verifies the reliability of the method.

Table 5.1: Results of Samples Collected from Tech 105

<table>
<thead>
<tr>
<th>sample</th>
<th>date</th>
<th>collected volume (L)</th>
<th>bisulfite volume (ml)</th>
<th>HCHO conc.(ppm)</th>
<th>HCHO conc.(ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tech 105</td>
<td>5.10.94.</td>
<td>3</td>
<td>2.0</td>
<td>0.030±0.002</td>
<td>20±1</td>
</tr>
<tr>
<td></td>
<td>5.19.94.</td>
<td>3</td>
<td>2.0</td>
<td>0.021±0.001</td>
<td>14±1</td>
</tr>
<tr>
<td></td>
<td>6.29.94.</td>
<td>12</td>
<td>2.0</td>
<td>0.086±0.001</td>
<td>14±1</td>
</tr>
<tr>
<td></td>
<td>7.13.94.</td>
<td>12</td>
<td>2.0</td>
<td>0.076±0.002</td>
<td>13±1</td>
</tr>
</tbody>
</table>

Table 5.2: Results of Samples from HCHO Generator

<table>
<thead>
<tr>
<th>sample</th>
<th>date</th>
<th>collected volume (L)</th>
<th>bisulfite volume (ml)</th>
<th>HCHO conc.(ppm)</th>
<th>HCHO conc.(ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>generator</td>
<td>5.10.94. a</td>
<td>0.7</td>
<td>10.0</td>
<td>0.029±0.002</td>
<td>410±25</td>
</tr>
<tr>
<td></td>
<td>5.19.94. a</td>
<td>0.7</td>
<td>10.0</td>
<td>0.032±0.001</td>
<td>450±15</td>
</tr>
<tr>
<td></td>
<td>7.13.94. b</td>
<td>4</td>
<td>10.0</td>
<td>0.397±0.002</td>
<td>990±6</td>
</tr>
</tbody>
</table>

*note a: 1 x 10⁻⁶ M HCHO solution used in the generator; b: 2 x 10⁻⁶ M HCHO solution.
Table 5.3. Results of June Set Samples from Bio-lab

<table>
<thead>
<tr>
<th>sample</th>
<th>collected volume (L)</th>
<th>bisulfite volume (ml)</th>
<th>HCHO conc. (ppm)</th>
<th>HCHO conc. (ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.29 1650</td>
<td>12</td>
<td>10.0</td>
<td>0.032±0.004</td>
<td>27±2</td>
</tr>
<tr>
<td>6.30 1430</td>
<td>12</td>
<td>10.0</td>
<td>0.056±0.002</td>
<td>47±2</td>
</tr>
<tr>
<td>6.30 1650</td>
<td>12</td>
<td>10.0</td>
<td>0.039±0.001</td>
<td>32±1</td>
</tr>
</tbody>
</table>

Table 5.4. Results of Sep. and Oct. Set Samples from Bio-lab

<table>
<thead>
<tr>
<th>sample</th>
<th>collected volume (L)</th>
<th>bisulfite volume (ml)</th>
<th>HCHO conc. (ppm)</th>
<th>HCHO conc. (ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.21 1100</td>
<td>12</td>
<td>10.0</td>
<td>0.088±0.003</td>
<td>73±3</td>
</tr>
<tr>
<td>9.21 1200</td>
<td>12</td>
<td>10.0</td>
<td>0.060±0.001</td>
<td>50±1</td>
</tr>
<tr>
<td>9.21 1300</td>
<td>12</td>
<td>10.0</td>
<td>0.066±0.002</td>
<td>55±2</td>
</tr>
<tr>
<td>10.4 1315</td>
<td>12</td>
<td>10.0</td>
<td>0.066±0.002</td>
<td>55±2</td>
</tr>
</tbody>
</table>

Table 5.5. Results of July Set Samples from Bio-lab

<table>
<thead>
<tr>
<th>sample</th>
<th>collected volume (L)</th>
<th>bisulfite volume (ml)</th>
<th>HCHO conc. (ppm)</th>
<th>HCHO conc. (ug/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.12 1700</td>
<td>12</td>
<td>10.0</td>
<td>0.110±0.001</td>
<td>92±1</td>
</tr>
<tr>
<td>7.13 1500</td>
<td>12</td>
<td>10.0</td>
<td>0.102±0.004</td>
<td>85±3</td>
</tr>
<tr>
<td>7.14 1500</td>
<td>12</td>
<td>10.0</td>
<td>0.064±0.003</td>
<td>53±3</td>
</tr>
</tbody>
</table>
5.4. Comparison with Previous Data and the 2,4-DNPH Method

The 2,4-DNPH method was used as a comparison method with our method (46). One sample collected from formaldehyde generator, which was a sealed teflon box where a formaldehyde solution of $2.0 \times 10^{-6}$ M was placed for the generation of gas phase formaldehyde, was analyzed by both methods side by side. The concentration of formaldehyde in the generator was 993 ug/m$^3$ by our method and 880 ug/m$^3$ by the 2,4-DNPH method. This result shows the agreement of two methods.

Also, previous studies (47) on exposure to formaldehyde showed levels of formaldehyde were from 24 ug/m$^3$ to 161 ug/m$^3$ with mean 74 ug/m$^3$ for classroom background and mean 161 ug/m$^3$ for breathing zone in school biology labs with some type of after-treatment after formalin fixation; and from 37 ug/m$^3$ to 446 ug/m$^3$ with mean 273 ug/m$^3$ for background and from 148 ug/m$^3$ to 1686 ug/m$^3$ with mean 905 ug/m$^3$ for breathing zone without any type of after-treatment. All these reported formaldehyde levels are much higher than those in other indoor places. This suggests the reliability of the new method based on the reasonable levels of formaldehyde measured (12.7 ug/m$^3$ to 91.7 ug/m$^3$, mean 60.0 ug/m$^3$) in the biology laboratory (which are also higher than in Tech 105).
Chapter 6

Conclusions and Future Work

At present time, no one method is optimum for determination of formaldehyde. The current method offers several advantages over previous methods in the following areas:

1. simple to operate;
2. no use or less use of toxic reagents;
3. superior selectivity and excellent sensitivity to formaldehyde;
4. interference free from other components;
5. excellent separation between formaldehyde and other species compared with other chromatographic methods.

Since formaldehyde is the dominant aldehyde in atmosphere, the new method prevails against other methods if determination of formaldehyde is the principal objective. Moreover, the new method can be applied to the analysis of biological samples due to the detectability for carbohydrates. Also, theoretically ion exclusion separation step could be eliminated for faster routine analysis of samples with no presence of any interferences.

The detectability for formic acid, methanol, and ethanol using platinum electrode
and an acidic electrolyte (HNO₃/Cu(NO₃)₂) suggests the possibility of simultaneous
determination of formaldehyde and the above species. Further studies on both separation
and detection need to be conducted.

Another future work is to experimentally prove why the method is complete
selectivity to formaldehyde and against other aldehydes by running an aldehyde which has
an electron-attracting group on the α carbon (the reason was discussed in section 5.2).
APPENDIX A – STANDARDIZATION OF FORMALDEHYDE
SOLUTIONS BY THE SODIUM SULFITE METHOD (42)

1. Aqueous formaldehyde reagent (Mallinckrodt, 37.7% w/v) was diluted to make a solution with a nominal concentration of 2 parts per thousand. The solution was allowed to stand for 24 hours in order that depolymerization of the formaldehyde could occur.

2. Five mls of formaldehyde solution were pipetted into a 100 ml beaker. Ten mls of \( \text{Na}_2\text{SO}_3 \) solution (1.1% w/v) were then added via graduated cylinder, along with 5 drops of 0.04% phenolphthalein indicator (50% EtOH).

3. The sample was titrated with 0.02 N HCl (standardized vs. \( \text{Na}_2\text{CO}_3 \)) to the colorless endpoint.
### APPENDIX B CHEMICALS USED IN THIS STUDY

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ (ultrapure grade)</td>
<td>J. T. Baker, Phillipsburg, NJ</td>
</tr>
<tr>
<td>H₂SO₄ (trace metal grade)</td>
<td>Spectrum Chemical, Gardena, CA</td>
</tr>
<tr>
<td>NaOH</td>
<td>Curtin Matheson Scientific, Houston, TX</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Fisher Scientific, Fair Lawn, NJ</td>
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<tr>
<td>KHP</td>
<td>E.M. Science, Gibbstown, NJ</td>
</tr>
<tr>
<td>KNaP</td>
<td>E.M. Science, Gibbstown, NJ</td>
</tr>
<tr>
<td>B(OH)₃</td>
<td>Fisher Scientific, Fair Lawn, NJ</td>
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<tr>
<td>NaCl</td>
<td>E.M. Science, Gibbstown, NJ</td>
</tr>
<tr>
<td>HCHO (37.3%, w/v)</td>
<td>Mallinckrodt, Paris, KY</td>
</tr>
<tr>
<td>HCOONa</td>
<td>J. T. Baker, Phillipsburg, NJ</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>J. T. Baker, Phillipsburg, NJ</td>
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<tr>
<td>(CH₃)₂CCHO</td>
<td>J. T. Baker, Phillipsburg, NJ</td>
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<tr>
<td>C₆H₅CHO</td>
<td>Spectrum Chemical, Gardena, CA</td>
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<tr>
<td>CH₃OH</td>
<td>E.M. Science, Gibbstown, NJ</td>
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<tr>
<td>C₂H₂OH</td>
<td>Sigma, St. Louis, MO</td>
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<tr>
<td>Na₂C₂O₄</td>
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<tr>
<td>ribose</td>
<td>Nutritional Biochemicals, Cleveland, OH</td>
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<tr>
<td>xylose</td>
<td>Aldrich Chemical, Milwaukee, WI</td>
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<tr>
<td>glucose</td>
<td>Mallinckrodt, Paris, KY</td>
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<tr>
<td>NaHSO₃</td>
<td>J. T. Baker, Phillipsburg, NJ</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>Matheson Coleman &amp; Bell, LA, CA</td>
</tr>
</tbody>
</table>
References


46. Datta L., unpublished results (to be published as Master’s thesis; UNLV 1995).