

Detection of Aldehydes Using Silver Mirror Reaction

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Attention has been recently focused on the harmful effects of aldehydes; hence, various laws regulate the use of most aldehydes. Therefore, a quick, easy, and continuously operating method of detecting aldehydes is required. In this study, we utilized the silver mirror reaction known as a specific reaction of aldehydes to detect aldehydes selectively. We performed the silver mirror reaction on a working electrode surface, and the reaction products which were deposited on the surface were measured by voltammetry. As a result, we could develop a simple measuring method of detecting aldehydes quickly that could distinguish aldehydes from ketones. In addition, we configured the measurement conditions to make the continuous measurement of aldehydes possible. We brought together the reaction field and electrolysis cell, optimized the supporting electrolyte and the mixing ratio of diamine silver ions of ammoniacal silver nitride solution, and improved the controlling sequence of the voltage applied to the working electrode. Consequently, we could continuously measure the level of aldehydes.

1. Introduction

Aldehydes are organic compounds with a distinctive, unpleasant odor, and cause health problems when in food, tap water, and the environment. Therefore, attention has been recently focused on the harmful effects of aldehydes on human health. For instance, the WHO designated formaldehyde, known as the main cause of sick building syndrome, to be “carcinogenic to humans.”⁽¹⁾ Formaldehyde is also legislated not to exceed 0.08 ppm in room air by the Ministry of Health, Labour and Welfare in Japan. Many other aldehydes are regulated by various laws. To satisfy the regulations, a method of monitoring aldehyde levels is necessary.

On the other hand, aldehydes such as formaldehyde, furfural, and acrolein are released into the air during the burning of organic materials, and they also constituent elements of the “burned smell.” Therefore, it is possible to apply a sensor of aldehydes to a fire detecting device. However, it is necessary for this device to detect aldehydes continuously; in other words, monitoring ability is indispensable.

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Currently, a detecting method designated by the Ministry of the Environment is used to measure the level of aldehydes.⁽²⁻⁴⁾ In this method, aldehydes are concentrated by a filter, and then measured by analytical instruments such as a gas chromatography (GC) or high-performance liquid chromatography (HPLC system). Aldehydes are trapped by a filter composed of 2,4-dinitrophenylhydrazine (DNPH) which can derivatize aldehydes. The molecular structure of ketones is analogous with that of aldehydes, as shown in Fig. 1. Thus, derivatization with DNPH cannot distinguish aldehydes from ketones. Therefore, the method needs precision analysis equipment and technical expertise. This causes difficulties in the ready measurement of aldehydes. Furthermore, this method requires considerable time to determine aldehyde quantity and has high inspection costs. Therefore, a quicker and easier method of measuring aldehydes is required. Another available sensor for aldehydes using an electrochemical cell measures the differences in the oxidation-reduction reaction current that is caused by the ON/OFF switching of the DNPH filter.⁽⁵⁾ This performance is not sufficient, because it also cannot separate aldehydes from ketones and its sensitivity is on several tens of ppb order. The gas detector tube⁽⁶⁾ using a color reaction and a chemiluminescence method^(7,8) has problems with the quantitative determination of aldehydes and monitoring technique.

In this study, we utilized the silver mirror reaction, known as a specific reaction of aldehydes, to detect aldehydes quickly, easily, selectively and continuously. The newly developed method has potential as an aldehydes sensor.

2. Experimental Procedure

2.1 Silver mirror reaction

The silver mirror reaction is a reaction in which aldehydes are oxidized by the diamine silver ions ($[\text{Ag}(\text{NH}_3)_2]^+$) of ammoniacal silver nitrate solution (Tollens' reagent) by the following formula.



This reaction is called "the silver mirror reaction" because silver from this reaction attaches onto the glass wall surface like a mirror, as the name suggests. As the above formula indicates, the amount of silver produced depends on the amount of aldehydes;⁽⁹⁾ thus, aldehyde quantity can be determined by measuring the amount of silver formed through this reaction. The reaction is specific to aldehydes.

2.2 Measurement system

The measurement system is shown in Fig. 2. We control a potentiostat (Hokuto Denko, CHABF5001) containing a function generator (FG) using a computer. The potentiostat is connected to three electrodes: a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). A voltage controlled by the FG is applied between the RE and the WE through the potentiostat. The CE makes an electrical connection to the electrolyte so that a current can be applied to the WE. A gold electrode was used for the WE, platinum wire for the CE, and an Ag/AgCl electrode for the RE.

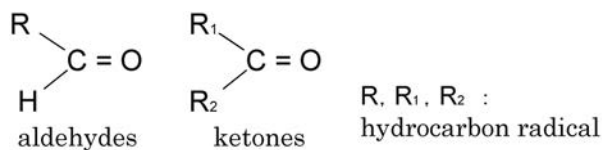


Fig. 1. Structural formulae of aldehydes and ketones.

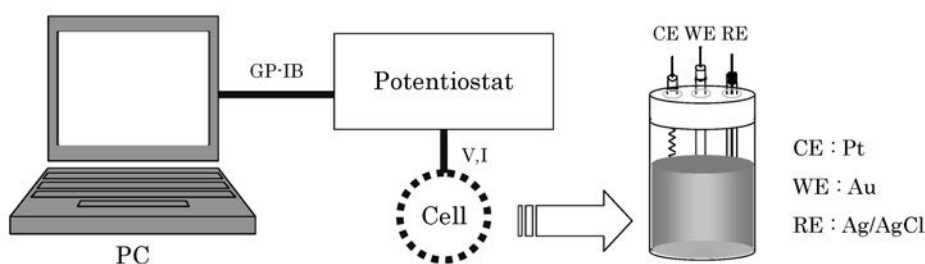


Fig. 2. Measurement system. WE, RE, and CE are connected to a potentiostat. The potentiostat generates the voltages and measured the currents. The measurement process is controlled by a computer connected to instruments via the GP-IB with LabVIEW.

2.3 Measuring method

First, we mixed specified volumes of Tollens' reagent and an aliquot of the sample on the electrode surface. If aldehydes exist in the sample solution, the silver mirror reaction takes place, and silver precipitates onto the electrode surface. Second, we analyzed the silver deposited on the electrode surface by voltammetry to determine the quantity of aldehydes in the sample solution.

Voltammetry is an electrochemical method that is commonly used to analyze electrode reactions in oxidation-reduction systems. When we control the electrode potential and apply electrolysis, an oxidation-reduction reaction occurs on the electrode surface at a certain voltage. If we observe a current at that instant, we can evaluate the reaction on the electrode surface, and some components of the solution in contact with the electrode. The current-voltage curve recorded during voltammetry is called a voltammogram, and the

peaks of the reaction current appear generally at a target-specific voltage. The integrated current, i.e., the amount of electrical change, is proportional to the concentration of the reacting species. Therefore, we can determine the quantity of the reacting species selectively.⁽¹⁰⁾

For convenience, we label the method in which a solution for silver mirror reaction and an electrolysis solution are separated as the 2-phased measuring method. The method by which they are mixed is labeled the 1-phased measuring method. In the 1-phased measuring method, there is a probability of disturbance of the silver mirror reaction by the supporting electrolyte in the electrolysis solution. Therefore, we apply the 2-phased measuring method first to verify that the method of this study can determine the quantity of aldehydes. In the 2-phased measuring method, note that only the WE is in the reaction field; electrolytes and the other electrodes cannot contribute the silver mirror reaction.

3. Results and Discussion

3.1 *Voltammogram of silver mirror reaction products*

The voltammogram on the electrode on whose surface the silver mirror reaction was carried out with 100 ppm acetaldehyde is shown in Fig. 3. It took 5 min to complete the reaction after mixing the reagent and acetaldehyde on the electrode surface. There is a peak current at approximately 0.2 V. This peak value depends on the concentration of the acetaldehyde. Therefore, it is believed that the peak current at approximately 0.2 V is the current from an oxidation reaction of the silver deposited on the electrode surface by the silver mirror reaction.

3.2 *Investigation of silver mirror reaction time*

When we mix the reagent and a sample on the electrode surface, aldehydes in the sample solution cause the silver mirror reaction. Silver precipitates on the surface after a period of time. The reaction time is expected to be strongly connected to the amount of silver deposited. The relationship between peak current and reaction time is shown in Fig. 4, in which a sample of 100 ppm acetaldehyde was applied.

As can be observed in the figure, the amount of silver deposited onto the surface is dependent on the reaction time. When the reaction time is 1 min, the peak current is sufficiently large to be detected. Thus, deposition from the reaction can be observed in a shorter time than expected. When the reaction time is longer, a larger peak current is obtained; however, we defined the reaction time as 5 min because of the need for speed and precision.

3.3 *Quantitative and selective detection of aldehydes*

We measured the following four samples to confirm the selective detection of aldehydes:

- acetaldehyde (aldehydes)
- propionaldehyde (aldehydes)
- acetone (ketones)
- methylisobutylketone (ketones)

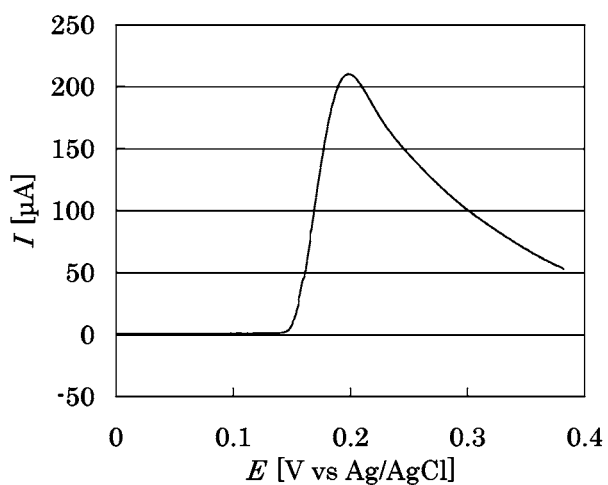


Fig. 3. Voltammogram obtained for reaction product using 100 ppm acetaldehyde.

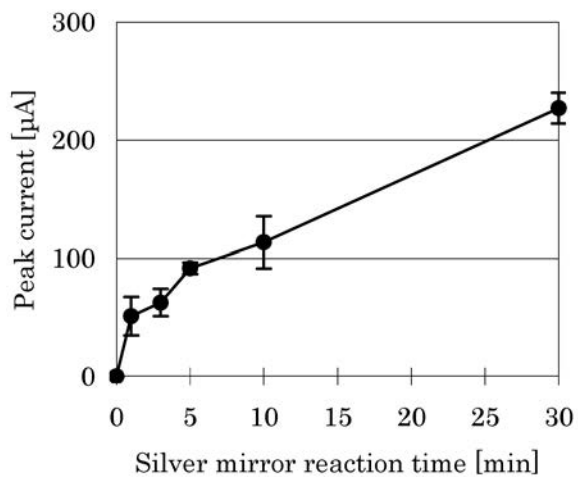


Fig. 4. Relationship between peak current and reaction time.

We investigated the concentration dependence of the peak current obtained at approximately 0.2 V using each sample. As shown in Fig. 5, the peak currents of the aldehydes depend on their concentrations. In contrast, the reaction currents caused by the ketones were scarcely observed, and did not depend on their concentrations. Therefore, we conclude that a measuring method using the silver mirror reaction is selective for aldehydes. If organic acid affects the measurement results, incorporating traps using a DNPH filter and alkaline beads in the reaction will solve this problem. Therefore, aldehydes can be measured selectively, quantitatively, and qualitatively.

3.4 Continuous batch measurement

We brought together the reaction field and electrolysis cell for the purpose of continuous measurement. In fact, the major difference between the 1-phased and the 2-phased measuring methods is whether CE, RE and a supporting electrolyte exist in the silver mirror reaction field. The supporting electrolyte is particularly indispensable and has the potential to cause the silver mirror reaction by itself. We fixed some measurement conditions and procedures to fit this method. We repeated a cyclic scan of the potential and observed the voltammogram until the waveform became stable. Then, we mixed a sample into the electrolysis solution. We detected a mutation of the waveform when we mixed the sample. By this method, we could measure the analyte continuously.

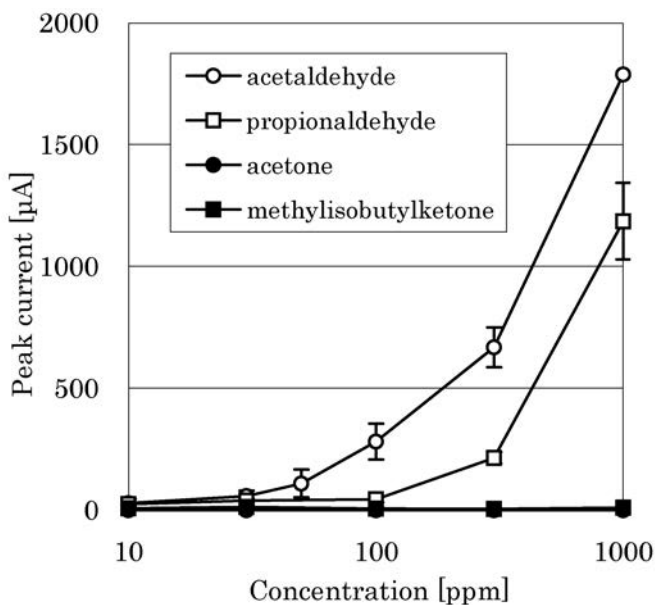


Fig. 5. Selectivity of present method for aldehydes.

In the 1-phased measuring method, Tollens' reagent is used in the electrolyte. Thus, the silver mirror reaction always occurs when aldehydes are mixed into the electrolyte. Therefore, we are able to detect aldehydes whenever continuous measurement is performed.

In the 1-phased measuring method, Tollens' reagent and a supporting electrolyte coexist in the electrolysis cell. The type of supporting electrolyte must be considered because some electrolytes influence or degrade the solution of the silver mirror reaction. We mixed Tollens' reagent and one of the following supporting electrolytes to determine if the silver mirror reaction took place. In the case of K_2SO_4 , the reaction took place. In the case of an acetic acid buffer solution, the reaction took place slowly. In the case of KCl, the solution became clouded soon after mixing Tollens' reagent with KCl and shaking; however, silver did not precipitate onto the electrode surface. It is believed that diamine silver ions in Tollens' reagent combine with chloride ions to form compounds, and thus, in this case, aldehydes do not cause silver to precipitate. In the case of a phosphate buffer solution, after mixing Tollens' reagent and aldehydes, yellow crystals were formed and silver did not precipitate. Therefore, we used K_2SO_4 as the supporting electrolyte for the 1-phased measuring method.

On the other hand, the concentration of KCl used for the RE was saturated to obtain a stable potential of the RE in the 2-phased measuring method, because chloride ions have no adverse effects on the silver mirror reaction. In the 1-phased measuring method, the silver mirror reaction might be disturbed because chloride ions seep from the RE and mix with diamine silver ions. Thus, the concentration of KCl in the RE was changed from saturation to 10 mM in the 1-phased measuring method.

A critical problem is the stability of the waveform of the voltammogram when cyclic voltammetry is carried out continuously to detect aldehydes. We envisaged that applying a constant voltage to the electrodes inhibited the reaction products from depositing on the electrode surface and disturbed the stabilization. To solve the problem, we improved the control sequence of the applied voltage. We maintained the electrode potential at the open electrode after one cycle of the potential scan, and provided adequate time for the reaction products to be deposited on the electrode surface. The potential range was determined to be centered on the self-potential. Furthermore, the mixing ratio of Tollens' reagent was modified so that the amount of diamine silver ions and, thus, that of the produced silver were increased under the influence of the ammonia level of Tollens' reagent. Thus, the standard deviation at the potential where the peak current was observed could be suppressed to less than 3%.

After this improvement, we mixed acetaldehyde into the electrolysis cell after the waveform of the voltammogram had been stabilized. The voltammogram obtained from each concentration of acetaldehyde by continuous measurement is shown in Fig. 6. The peak current at approximately 0.3 V depends on the concentration of aldehydes. The temporal alteration of the peak current value at approximately 0.3 V is shown in Fig. 7. The peak current was stable until we added acetaldehyde. Although the change in the peak current was small when we measured low-concentration acetaldehyde, the peak current change was obvious when we measured 10 ppm acetaldehyde. The increments of the peak current from the baseline depend on the concentration of the acetaldehyde, as shown in Fig. 8.

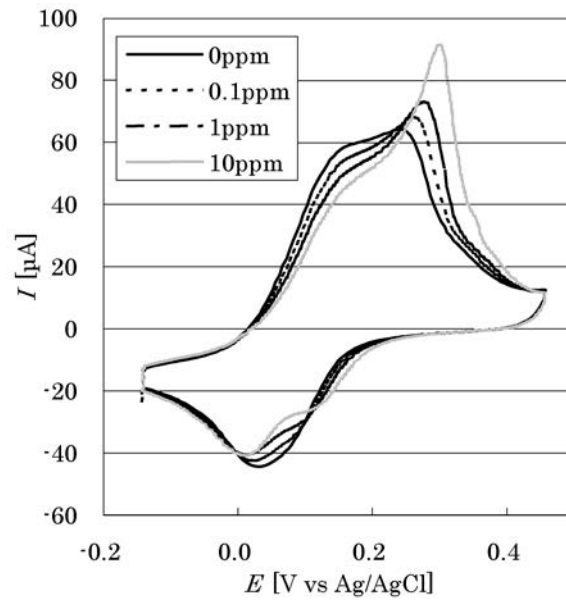


Fig. 6. Voltammogram by continuous measurement.

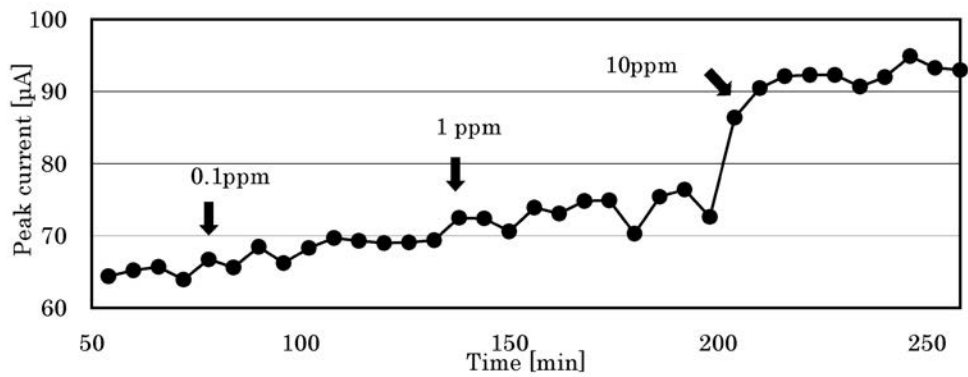


Fig. 7. Time course of peak current.

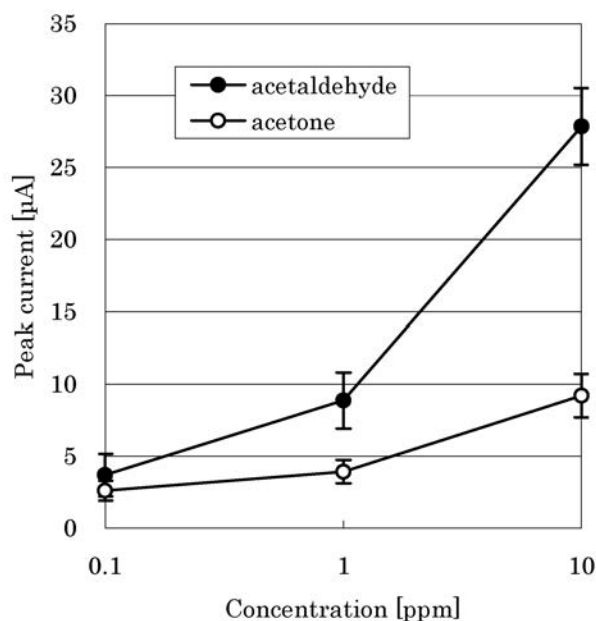


Fig. 8. Peak current values as functions of aldehyde and acetone concentrations in continuous measurement.

Therefore, aldehydes can be continuously measured by the 1-phased measuring method. The peak current corresponding to 0.1 ppm acetaldehyde is approximately 4 μA , which is an easily detectable value. Because the lower bound of the current measurement by this system is about 0.1 μA , it is believed that we can, in principle, detect concentrations of ca. 10 ppb.

4. Conclusions

We developed a simple measuring method of detecting aldehydes rapidly, easily and sensitively. The silver mirror reaction, which is specific to aldehydes was used to measure aldehyde concentration selectively. Thus, we could detect aldehydes rapidly, separating and distinguishing them from ketones. The amount of deposition of the silver mirror reaction products on the electrode surface may be increased by the optimization of electrode surface geometry, the shape of the reaction vessel, and the conditions of electrochemical measurement. Thus, this method could have higher sensitivity by these ingenuity.

Furthermore, we tried the 1-phased measuring method for continuous measurement. Various interactions, such as the reaction of the supporting electrolyte with Tollens' reagent, might give false information, because the measurement is carried out while the silver mirror reaction takes place in the electrolysis cell. Then, we considered a supporting electrolyte, and improved the control sequence of the voltage applied to the WE and the mixing ratio of Tollens' reagent. As a result, aldehydes could be continuously measured by the 1-phased measuring method. This result indicates the possibility of aldehyde monitoring. Automatically refreshing the electrode surface will permit the monitoring of aldehydes using this method.

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