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A new method of ion chromatography technology for speedy determination and analysis in organic electrosynthesis of glyoxylic acid

Sheng-Pei Chen*, Tao Huang, Shi-Gang Sun

Department of Chemistry, State Key Laboratory of Physical Chemistry of Solid Surfaces, Institute of Physical Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

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Abstract

Based on ion chromatography (IC) technology, we have developed a new method that combines ion chromatography with a conductivity detector to separate and determine the substances of glyoxal, glycolic acid, oxalic acid and glyoxylic acid. The ion chromatography was applied for the first time in quantitative determination of substances involved in electrosynthesis of glyoxylic acid. The method has been applied to separate and analyze simultaneously either glyoxylic acid and glyoxal in electroxidation of glyoxal, or glyoxylic acid and oxalic acid in electroreduction of oxalic acid. An aqueous Na_2CO_3–$NaHCO_3$ or NaOH–Na_2CO_3 solution was confirmed to be the most desirable eluent. The experimental results demonstrated that the detection sensitivity is ahead of ppm grade, and the variation coefficients such as the retention time, the peak height and the peak area outperform 2%. All the recoveries of the detected substances are ranged between 97 and 103%. The method exhibits advantages of high selectivity, high sensitivity, speediness and simple apparatus requirement. Furthermore, simultaneous determination of a mixture of several substances can be achieved by the developed method, and even a neutral molecule of glyoxal can be also determined by choosing an appropriate composition and concentration of eluent.

Keywords: Ion chromatography; Oxalic acid; Glycolic acid; Glyoxylic acid; Glyoxal

1. Introduction

Ion chromatography (IC) was developed by Small et al. in 1975, and is nowadays a routine chromatographic method employed in laboratory for determination and analysis of ions presented in a variety of aqueous solutions. The IC consists of a low ion-exchange capacity resin as stationary phase, a conductometer as detector and a suppressor column to increase the separation speed and detection sensitivity [1]. Gjerde et al. [2] used a low conductivity eluent to develop a non-suppressed IC technique in 1979. Since then IC technique has been extended to determine organic ions. Many efforts were devoted to the development of the IC technology, i.e., the detection techniques and the ion chromatography suppressor, as well as the simultaneous separation and determination of both anions and cations [3–12]. With the development of hardware manipulation, such as the high qualified and specialized ion-exchange resins, the high capacity columns and large loop volume, IC has been applied widely in agriculture, detergent, food, medicine, mining and metal industries, power plant, pulp manufacturing, semiconductor, and especially in environment. Although many standardization and regulatory bodies, e.g. the American Society for Testing and Materials (ASTM), International Organization for Standardization (ISO), and US Environmental Protection Agency (EPA), have approved the analysis methods based upon IC, most of which reported within the last decade [13], the IC has not been yet applied in the field of organic electrosynthesis.

The organic electrosynthesis is of advantage in many respects: (1) the reaction can be conducted in very mild conditions at normal temperature and pressure; (2) the process is brief, i.e., with high production rate and selectivity; (3) it is an intrinsically environment-friend technique, and attracts more and more attentions from synthesis industry, especially from fine chemical industry. Electrosynthesis is becoming an

* Corresponding author. Tel.: +86 592 2180181; fax: +86592 2180181.
E-mail address: shpchen@xmu.edu.cn (S.-P. Chen).

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important approach to the "green synthesis" industry. Glyoxylic acid is an important intermediate in the perfumery, pharmaceutical and fine chemical industries. The production by electroreduction of oxalic acid using high hydrogen overvoltage metal as cathode has been known for about one century, and electroxidation of glyoxal to glyoxylic acid was adopted as well [14]. The major byproducts in electroreduction of oxalic acid to glyoxylic acid are glycolic acid and glyoxal, and the main byproducts in electroxidation of glyoxal to glyoxylic acid are oxalic and glycolic acids. So in the process of electrosynthesis four compounds may co-exist in electrolyte. Since the structures of these four substances are similar, qualitative and quantitative analysis are often difficult to achieve simultaneously.

Many existing methods and techniques for the analysis of these four substances (glyoxal, glycolic acid, glyoxylic acid, and oxalic acid) were not satisfactory. Each method may have one or more disadvantages. For example, the potential titration that was applied by Du et al. [15] is difficult to achieve satisfied result though it is a simple method. Another instance, the spectrophotometry that was used by Xu et al. [16] in the process of detection of glyoxylic acid requests that the reaction of 2,4-dinitrophenylhydrazine with glyoxylic acid is carried out first, because of the weak or no absorption of sample in ultraviolet or visible light. Due to the long time of the reaction of glyoxylic acid with 2,4-dinitrophenylhydrazine, the whole analyzing process was too long and introduced therefore large error. Furthermore, methods mentioned above present other disadvantages such as the requirement of many chemical reagents, low sensitivity and the unavoidable interferences. High-performance liquid chromatography (HPLC) [17] is a new efficient technique and has attracted wide attention due to its high sensitivity and precision. It detects the ramification using reversed-phase high performance liquid chromatography with tetrabutylammonium bromide as versus ion. However, in the process of detection of glyoxylic acid in electrolyte, the sample must be transformed into ramification by 2,4-dinitrophenylhydrazine, and the signal interference and spectrum overlap are difficult to overcome. Besides, the equipments are expensive. Hu et al. [18] reported a quantitative detecting method, namely chemically analytical method, which may have significance on both the optimization and evaluation for the process of electrosynthesis. The disadvantages of chemical analytical method are evident in the following aspects: (1) operational steps were fussy, (2) detection was time-consuming, and (3) the results were easy to be interfered. In brief, to develop a fast and precise detection method for the synthesis system becomes a key subject in electrosynthesis of glyoxylic acid.

In this paper, we have developed a new method based on an IC instrument [4,10,13,19,20] that employed a conductivity detector. The method has been applied to determine simultaneously a mixture or an individual of the four substances mentioned previously that co-exist in electrolyte of electrosynthesis of glyoxylic acid. The developed method of IC overcomes the main shortcomings of other determining technologies used in electrosynthesis of glyoxylic acid so far. Both qualitative and quantitative analysis of the electrolyte have been achieved.

2. Experimental

2.1. Instrumentation

An XIC-2100 ion chromatographic instrument (Xiamen University, China) consists of an electrochemical self-regenerating multifunctional suppressor, a two-electrode detector with pulsed data acquisition. The analysis and data collection were carried out by LabNet IC1000 software. The instrument consists of an eluent tank, an advective pump (LC-10AT, SHIMADZU, Japan), a sample valve, a separator column, a suppressor column, a conductivity detector and a computer working station. In this study, an YSA 8 model anion separator column (Ø 4 mm × 250, Beijing Research Institute of Chemical Engineering and Metallurgy, China) was used together with several kinds of eluents. The electrochemical self-regenerating multifunctional suppressor is composed of five thin chambers in sandwich construction, including anion and cation eluent suppressive chambers, anode and cathode chambers, as well as a common electrolyte chamber, all of which are clipped together. An electrochemical process, namely electrolysis of deionized water or detector effluent, is used to regenerate the suppressor for continuous operation. The working current is provided by two separate sources. It can be used for suppressing anion eluent and cation eluent separately or simultaneously. The suppressor has high suppression capacity (60 mmol/l), good reproducibility (RSD = 0.80–0.91%) and good linearity (r = 0.9992) [24].

2.2. Chemicals

Table 1 lists all chemicals (glyoxal, glyoxylic acid monohydrate, glycolic acid, oxalic acid, sodium carbonate, sodium bicarbonate and sodium hydroxide) used in the present studies. The purity and provider of each chemical are also indicated in the table.

2.3. Standard solution and sample preparation

All samples, standard and eluent dilutions were prepared by using Millipore water (18 MΩ cm) provided by a Mill-Q water purification system (Millipore Ltd., Nihon).

2.4. Operating conditions

Six different composition or concentration eluents for different purposes were used. The eluents were (1) 0.40 mM Na_2CO_3 + 0.50 mM $NaHCO_3$; (2) 4.8 mM Na_2CO_3 + 6.0 mM $NaHCO_3$; (3) 2.0 mM NaOH + 0.05 mM Na_2CO_3; (4) 2.4 mM Na_2CO_3 + 3.0 mM $NaHCO_3$;

Table 1
Chemicals, their purity and provider used in this study

Chemicals	Purity	Company
Glyoxal	40 wt.% solution in water	Aldrich (USA)
Glyoxylic acid monohydrate	98%	Aldrich (USA)
Glycolic acid	99%	Acros (USA)
Oxalic acid	AR, 99.8%	China National Pharmaceutical Group Shanghai Chemical Reagent Company
Sodium carbonate	AR, 99.8%	Shanghai Hongguang Chemical Plant (China)
Sodium bicarbonate	AR, 99%	Shanghai Hongguang Chemical Plant (China)
Sodium hydroxide	AR, 96%	China National Pharmaceutical Group Shanghai Chemical Reagent Company

(5) 1.2 mM Na_2CO_3 + 1.5 mM $NaHCO_3$; (6) 0.60 mM Na_2CO_3 + 0.75 mM $NaHCO_3$. The sampling volume was 100 μl, and the flow rate was 1.5 ml/min. Data collections were carried out at room temperature.

3. Results and discussion

3.1. Influence of eluent composition and concentration on the resolution for qualitative analysis of glyoxylic acid and glycolic acid

For an IC experiment, choosing proper eluent that matches the special characteristics of ion-exchangers in the separator column is a key point. It is known that eluent ions having similar affinity with the analyte ion should be chosen as an eluent [21]. In general, when samples having monovalent and divalent anions are analysed, a mixture of $NaHCO_3$ and Na_2CO_3 as an eluent is widely used. Especially, in the case of the standard analysis method that is well known for the separation of seven different anions in aquatic samples, the corresponding mixed eluents are also employed [12,22,23]. Four eluents were used in this study, which are a mixture of 2.4 mM Na_2CO_3 and 3.0 mM $NaHCO_3$ (eluent A), a solution containing 1.2 mM Na_2CO_3 and 1.5 mM $NaHCO_3$ (eluent B), a solution containing 0.60 mM Na_2CO_3 and 0.75 mM $NaHCO_3$ (eluent C) and a mixture of 0.40 mM Na_2CO_3 and 0.50 mM $NaHCO_3$ (eluent D). The flow-rate was fixed at 1.5 ml/min. The concentration of glyoxylic acid and glycolic acid was 10 mg/l each. The retention time for glycolic acid was 102, 108, 119 and 128 s for the eluents A, B, C and D, respectively. However, with the same eluents A, B, C and D, glyoxylic acid was eluted at retention time of 115, 129, 150 and 168 s, respectively. The lower concentration of eluent was, the longer the retention time. The difference of retention time between glycolic acid and glyoxylic acid was 13, 21, 31 and 40 s for eluents A, B, C and D, respectively. So the difference of retention time increases with the decrease of eluent concentration. Glycolic acid and glyoxylic acid could not be separated when eluent A was used. For eluent B and C, glycolic acid and glyoxylic acid can be basically separated. But when using eluent D, these two analytes can be completely separated very well. As a consequence, it can be easily concluded that the resolution may be improved by changing the concentration of the eluents.

3.2. Qualitative analysis of glyoxylic acid, glycolic acid and oxalic acid

Fig. 1 shows ion chromatograms of glycolic, glyoxylic and oxalic acids. It can be clearly observed that when the sample contains only one substance (glycolic acid, glyoxylic acid or oxalic acid), there is only one peak in the ion chromatograms. The retention time is respectively 90, 99, 558 s for glycolic acid (curve a), glyoxylic acid (curve b) and oxalic acid (curve c) when the eluent of 4.8 mM Na_2CO_3 + 6.0 mM $NaHCO_3$ was used. For a sample of mixture of the two substances (glyoxylic acid and oxalic acid), two corresponding eluting peaks appeared in the ion chromatogram (curve d). Similar

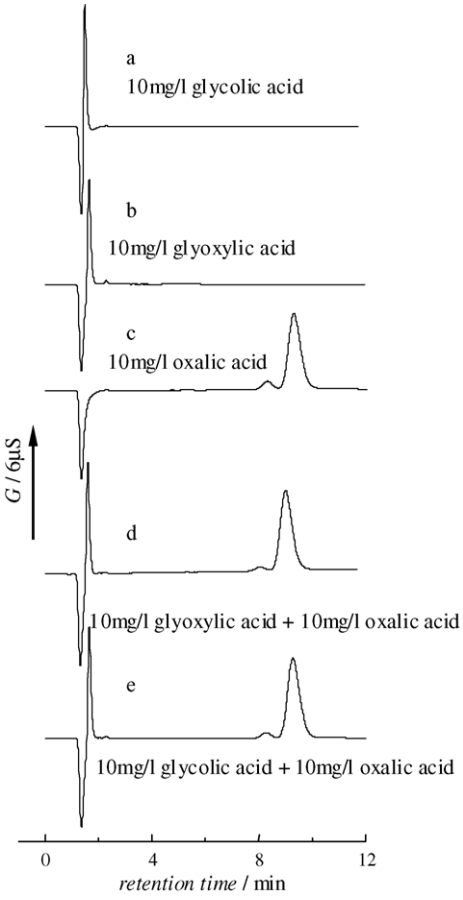
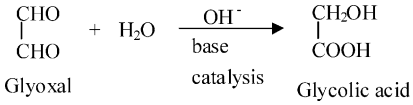


Fig. 1. Ion chromatograms. Eluent: 4.8 mMNa_2CO_3 + 6.0 mM$NaHCO_3$. Suppressing current: 60 mA; flow rate: 1.5 ml/min; sampling volume: 100 μl; conductivity detector.

result has been obtained for the sample of mixture of glycolic acid and oxalic acid (curve e). Experimental results of Fig. 1 demonstrated that the selectivity of the current method for detecting glyoxylic acid and oxalic acid or glycolic acid and oxalic acid is fairly good. Under these experimental conditions, oxalic acid has been completely separated from glycolic acid and glyoxylic acid, while it is not the cases of glycolic acid and glyoxylic acid. Since low concentration of eluents leads to long retention time, glycolic acid and glyoxylic acid can be completely separated by using low concentration of eluent, e.g. 0.40 mM Na_2CO_3 + 0.50 mM $NaHCO_3$ (seen in Section 3.1).

3.3. Qualitative analysis of glyoxal

Glyoxal does not exist in the form of an ion. According to the detecting principle of ion chromatography, the substance of glyoxal could not be directly detected. However, glyoxal is an active molecule that can be easily converted to glycolic acid by catalyst of strong base such as sodium hydroxide. In the glyoxal molecule, one –CHO will be oxidized and the other will be reduced. As a result, the conversion of glyoxal to glycolic acid in the presence of strong base will take place.



An appropriate concentration of sodium hydroxide as eluent allows the conversion of glyoxal into glycolic acid to be done in the separator column, then the product glycolic acid in the ion chromatographic system can be detected. There is only one downward peak assigned to water in the ion chromatogram when the eluent of 2.4 mM Na_2CO_3 + 3.0 mM $NaHCO_3$ is used. Taking the eluent of 2.0 mM NaOH + 0.05 mM Na_2CO_3 as eluent, it appears nevertheless a clear, strong and upward eluting peak with retention time of 2.6 min (shown in Fig. 2). The retention time for this peak is in accordance with that of glycolic acid in the same experimental condition. Further studies demonstrated that during the process of eluting, the conversion of glyoxal to glycolic acid was occurred.

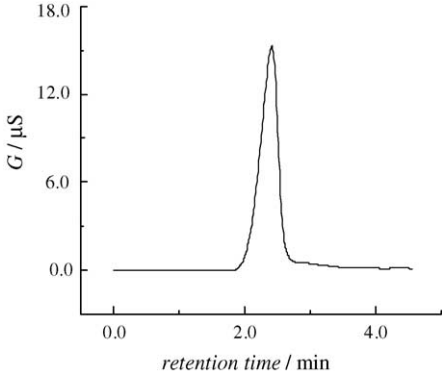


Fig. 2. Ion chromatogram. Solution: 20 mg/l glyoxal; eluent: 2.0 mM NaOH + 0.05 mM Na_2CO_3. Flow rate: 1.5 ml/min; conductivity detector; suppressing current: 40 mA; sampling volume: 100 μl.

Table 2
The linear range, calibration curve equation and correlation coefficient for determining glyoxylic acid and glyoxal

Substance	Linear ranges (mg/l)	Calibration equation (y: μS·s; x: mg/l)	Correlation coefficients (r)
Glyoxylic acid	2–12	$y = -4.91432 + 7.87795x$	0.9996
Glyoxal	2–12	$y = -6.22516 + 13.37112x$	0.9998

3.4. Ion chromatography with conductivity detector applied in electrosynthesis of glyoxylic acid through oxidation of glyoxal

3.4.1. Quantitative analysis of glyoxylic acid and glyoxal

The method performance is evaluated by analyzing a mixture sample containing the 4 substances encountered in electrosynthesis. Calibration curves for glyoxylic acid and glyoxal were obtained from standard solutions prepared with Millipore water. The linear range, correlation coefficient and the calibration equation for the two substances are listed in Table 2. The calibration curves for glyoxylic acid and glyoxal present a good linearity, and the correlation coefficients (r) of the calibration curves are respectively 0.9996 and 0.9998 for glyoxylic acid and glyoxal.

3.4.2. Ion chromatography served practically in electroxidation of glyoxal to glyoxylic acid

For the effective application of ion chromatography, which combines suppressor column and conductivity detector in organic electrosynthesis processes, we applied the method to detect and analyze the electrolyte containing glyoxal and glyoxylic acid. The detailed steps were as following: (a) preparing a sample solution mixing the four substances, in which the concentrations of glyoxal, glyoxylic acid, chloride and oxalic acid are 4, 10, 5 and 1 mg/l, respectively; (b) detecting the solution by using the method of ion chromatography; (c) confirming the species existing in the sample solution and calculating the concentration of each substance with the help of each calibration equation. The results are listed in Tables 3 and 4. It can be seen that the detecting results were close to the given quantities and the standard deviations were allowable. Furthermore, all the recoveries of the detected substances are ranged between 97 and 103%,

Table 3
The analysis data of glyoxal

No.	Analyzer (mg/l)	Real (mg/l)	RSD (%)
1	4.17		4.2
2	4.10		2.5
3	4.15	4.00	3.7
4	4.06		1.5
Average	4.12		3.0

Table 4
The analysis data of glyoxylic acid

No.	Analyzer (mg/l)	Real (mg/l)	RSD (%)
1	9.85		−1.5
2	9.93		−0.6
3	9.90	10.0	−0.9
4	9.89		−0.8
Average	9.88		−1.1

or 100 ± 3%. In a word, ion chromatography possesses good performance in simultaneously detecting and analyzing electrolyte of practical electrosynthesis.

3.5. Ion chromatography with conductivity detector applied in study of electroreduction of oxalic acid to glyoxylic acid

3.5.1. Qualitative and quantitative detection of oxalic acid

In the process of electroreduction of oxalic acid to glyoxylic acid, the main species existing in electrolyte are glyoxylic acid (product), oxalic acid (reactant), tetrabutylammonium bromide (additive) and glycolic acid (byproduct). The main objective of analysis is to determine each content in the electrolyte, i.e. glyoxylic acid, oxalic acid and glycolic acid. After electrolyzing, the electrolyte was diluted for 2500-fold with Millipore water. The ion chromatogram is shown in Fig. 3. The experimental conditions are 4.8 mM Na_2CO_3 + 6.0 mM $NaHCO_3$ (eluent), 1.5 ml/min (flow rate); 60 mA (suppressing current), 100 μl (sampling volume), conductivity detecting. Six peaks appeared in the ion chromatogram of Fig. 3. Peaks 1, 2, 3, 4, 5 and 6 can be assigned respectively to H_2O, glycolic acid together with glyoxylic acid, Br^-, unknown substance, $SO_4^{2-}$and oxalic acid. It can be clearly seen that three ions (Br^-, SO_4^{2-}, $C_2O_4^{2-}$) were well separated in addition to glycolic acid together with glyoxylic acid. The standard calibration curve for oxalic acid exhibits a good linearity. The calibration equation has been

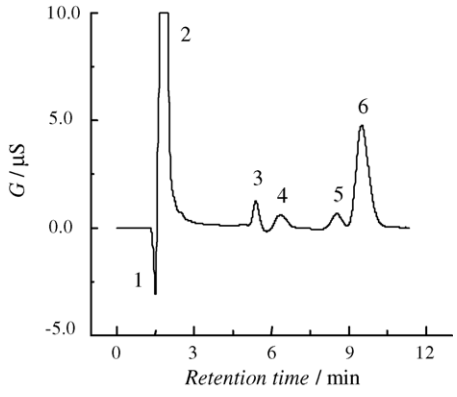


Fig. 3. Ion chromatogram of anionic species in electrolyte of oxalic acid electroreduction to glyoxylic acid. Eluent: 4.8 mM Na_2CO_3 + 6.0 mM $NaHCO_3$; flow rate: 1.5 ml/min; suppressing current: 60 mA; sampling volume: 100 μl; conductivity detector peak identities: (1) H_2O; (2) glycolic acid and glyoxylic acid; (3) bromide; (4) unknown; (5) sulfate; (6) oxalic acid.

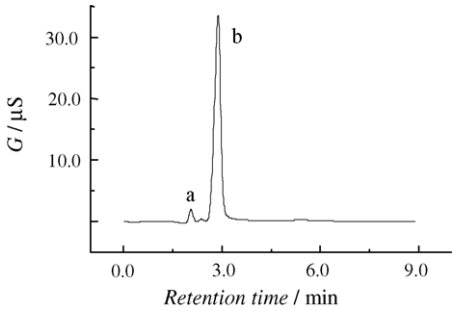


Fig. 4. Ion chromatogram of anionic species in electrolyte. Eluent: 0.40 mM Na_2CO_3 + 0.50 mM $NaHCO_3$; flow rate: 1.5 ml/min; suppressing current: 40 mA; sampling volume: 100 μl; conductivity detector; peak identities: (a) glycolic acid; (b) glyoxylic acid.

formulated as $y = -7.64616 + 13.74619x$ (y: peak area, μS·s; x: concentration, mg/l). The correlation coefficient (r) of the calibration curves is 0.9998. We can measure the area of peak 6 in Fig. 3 by integration, and then calculate the concentration of oxalic acid by applying the calibration equation using the peak area values. The concentration of oxalic acid thus determined is 11.84 mg/l after a dilution for 2500-fold.

3.5.2. Qualitative and quantitative detection of glycolic acid and glyoxylic acid

It can be observed that the peak of glycolic acid overlaps with that of glyoxylic acid when a solution of 4.8 mM Na_2CO_3 + 6.0 mM $NaHCO_3$ was used as eluent. Such overlap of peaks arises difficulties for qualitative and quantitative analysis of glycolic acid and glyoxylic acid. However, when using 0.40 mM Na_2CO_3 + 0.50 mM $NaHCO_3$ as eluent, glycolic acid and glyoxylic acid can be completely separated and simultaneously detected. The electrolyte was diluted for 10,000-fold, and the results of ion chromatography are shown in Fig. 4. Peak a in Fig. 4 can be assigned to glycolic acid, and peak b may be attributed to glyoxylic acid. The peak b is even stronger than the peak a. It demonstrates that glyoxylic acid is the main product in the electrolyte of electroreduction of oxalic acid, and the amount of byproduct of glycolic acid is quite few. The calibration equations for glycolic acid and glyoxylic acid have been confirmed respectively as $y = -6.84015 + 9.43841x$ and $y = -8.20365 + 8.59481x$ (y: peak area, μS·s; x: concentration, mg/l). The correlation coefficient r for glycolic acid is 0.9995, and that for glyoxylic acid is 0.9985. Using the peak areas to calculate the concentration of glycolic acid or glyoxylic acid by applying the corresponding calibration equation, the concentration of glycolic acid has been determined to be 2.543 mg/l, and that of glyoxylic acid is 52.11 mg/l after a dilution for 10,000-fold.

4. Conclusions

In the current study, ion chromatography has been applied for the first time in electrosynthesis of glyoxylic acid (electroxidation of glyoxal to glyoxylic acid or electroreduction of

oxalic acid to glyoxylic acid). A new method has been developed based on ion chromatography technology. which allows the determination separately/simultaneously of substances involved in electrosynthesis of glyoxylic acid. Both qualitative and quantitative experimental results confirmed that the developed method of ion chromatography is a real-time, speedy, new detection and analysis technique. The results demonstrated furthermore that IC can be employed to determine not only acid species (glycolic acid, oxalic acid and glyoxylic acid) but also neutral molecule glyoxal, which is significant for analyzing electrolyte in electroxidation of glyoxal to glyoxylic acid.

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