Electrochemical Sensors for Bromate Determination

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Potassium bromate (KBrO3), a renowned oxidizing agent, has a huge reputation for being one of the best and least expensive dough-improving substances in the baking industry. As such, its importance in the baking industry cannot be overemphasized. KBrO3 produced the desired result in baking by influencing the physical and chemical properties of macromolecules such as protein and starch often found in the dough. Precisely, the viscosity, extent of gelatinization, swelling characteristics of the dough, and disulfide linkage formation (in gluten proteins) are affected by the use of KBrO3 as an additive in bread baking. Bromate has been found to be a product of water treatment due to bromide ion oxidation that occurs during ozonation.

bromate | electrochemical sensors | electrochemical impedance spectroscopy | metal phthalocyanine | carbon quantum dots

1. Overview

The application of potassium bromate in the baking industry is used in most parts of the world to avert the human health compromise that characterizes bromates carcinogenic effect. Herein, various methods of its analysis, especially the electrochemical methods of bromate detection, were extensively discussed. Amperometry (AP), cyclic voltammetry (CV), square wave voltammetry (SWV), electrochemiluminescence (ECL), differential pulse voltammetry, and electrochemical impedance spectroscopy (EIS) are the techniques that have been deployed for bromate detection in the last two decades, with 50%, 23%, 7.7%, 7.7%, 7.7% and 3.9% application, respectively. Despite the unique electrocatalytic activity of metal phthalocyanine (MP) and carbon quantum dots (CQDs), only few sensors based on MP and CQDs are available compared to the conducting polymers, carbon nanotubes (CNTs), metal (oxide), and graphene-based sensors. This review emboldens the underutilization of CQDs and metal phthalocyanines as sensing materials and briefly discusses the future perspective on MP and CQDs application in bromate detection via EIS.

2. Background

Potassium bromate ($KBrO_3$), a renowned oxidizing agent, has a huge reputation for being one of the best and least expensive dough-improving substances in the baking industry. As such, its importance in the baking industry cannot be overemphasized. $KBrO_3$ produced the desired result in baking by influencing the physical and chemical properties of macromolecules such as protein and starch often found in the dough. Precisely, the viscosity, extent of gelatinization, swelling characteristics of the dough, and disulfide linkage formation (in gluten proteins) are affected by the use of $KBrO_3$ as an additive in bread baking [1]. Bromate has been found to be a product of water treatment due to bromide ion oxidation that occurs during ozonation.

Despite the importance of bromate in food production, numerous reports of its adverse effect on human health abound. Specifically, it has been reported to be connected to renal diseases, anemia, as well as peripheral neuropathy [1][2] if consumed beyond the allowed level of 25 µg L^{-1} by the world health organization (WHO, 1996). It has also been implicated in cancerous growths in laboratory animals. In addition, bromate in drinking water of mice and rats has been linked to an increase in cases of mesotheliomas of the peritoneum, thyroid cell, and renal tumor. Impaired auditory functions of humans and animals are also part of the scientifically confirmed result of a high level of bromate intake [3]. The United States Environmental Protection Agency (USEPA) and WHO have recommended 10 µg L^{-1} (0.078 µM) as the maximum acceptable level (MAL) as a result of its carcinogenicity [4]. Cancer cases as a result of bromate intake from water and food consumption have attained an alarming rate the world over, hence the need to control its concentration in bromate-containing water and food products to ensure consumer safety arises. It is noteworthy that the classification of bromate as a carcinogen in water and food was an outcome of toxicological examinations which confirmed bromate as a class B2 carcinogen (WHO, 1996) [5].

The determination of trace levels of BrO_3 requires reliable, selective, and very sensitive analytical techniques. High-performance liquid chromatography (HPLC), spectrophotometry, liquid chromatography, gas chromatography, and ion chromatography [6][7][8][9] are the analytical techniques that have been used for bromate detection. However, multiple extractions, hydrolysis, special sample preparation, expensive and highly technical instrumentation, low sensitivity, and high-temperature requirements for bromate extraction limit the application of these methods [10].

A model method for bromate determination would be expected to meet the following criteria:

- Ability to determine BrO_3^- down to a limit of detection that is 25% of the MAL
- Short analysis time and cost
- No sample pre-treatment
- Method accessibility

Therefore, the electrochemical method combines these features and is therefore considered one of the most suitable methods for bromate determination [11].

Electroanalytical methods utilize the relationship between an analyte's concentration and potential (or current) change based on its chemical reactions to determine the quantity of an analyte. It is a quantitative means of analysis that basically depends on electrochemical processes in a medium or at the sensor–medium phase boundary. These electrochemical reactions are dependent on chemical composition, structural changes during analysis, or concentration of the analyte.

Electroanalytical methods have some advantages over other analytical techniques. They allow the determination of various oxidation states of an element and not just the concentration of such elements in the solution. Low detection limits, characterization, and information on the kinetics of a chemical reaction can be obtained through electroanalytical methods. Beyond these, this technique offers simplicity, rapid analyte detection, and cost-effectiveness. H_2O_2, hydrazine, dopamine, iodate, epinephrine, nitrite, glutathione, glucose, phthalates, oxalic acid, ascorbic acid, hydroquinone, and citric acid are a few of the analytes that have been analyzed through electroanalytical methods [12][13].

A wide range of materials has been used for the development of chemically modified electrodes for bromate detection. A very low limit of detection has been achieved with these electrodes that ordinarily would not detect this analyte in the unmodified state [14][15]. This present review discusses the electrochemical methods and some other analytical techniques that have been deployed for bromate detection and future perspectives in the determination of the analyte. The performance in terms of sensitivity and detection limit of CNTs, graphene, polymers, quantum dots, and some nanocomposite-modified electrodes for bromate detection are critically discussed in this review.

Electrocatalytic reduction of bromate produces different products, such as HBrO, Br_2, and Br^-. Table 1 below illustrates different reaction processes with their standard potentials (E° values vs. NHE). It could be deduced that the number of electrons involved and the standard potential values greatly determine the electrocatalytic reduction products. For complete electrocatalytic reduction of BrO_3^- to Br^-, the modified electrode must be able to produce 2 or 6 electrons, 4 electrons produce HBrO, while 5 electrons yield Br_2. Common examples of electrocatalytic reduction of bromate with different electrochemical sensors are provided below.

3. Conclusions

In this review, we have summarized the efforts made in the electrochemical detection of bromate with high sensitivity and selectivity by modifying the electrode surface with different modifiers. We also pointed out those techniques and sensors that still need to be exploited for sensitive and selective determination of bromate, such as EIS and carbon quantum dots and metal phthalocyanine.

Owing to the greater advantages of EIS and the extraordinary properties of metal phthalocyanine and carbon quantum dots, more studies on the determination of bromate are expected in the near future based on the usage of EIS with regard to metal phthalocyanine and carbon quantum dots.

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