Determination of Gallium in Bayer Spent Liquor by Voltammetry (ASV)

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Abstract

Gallium (Ga) is considered a critical metal, applied to integrated circuits, optical devices such as LEDs, and as a doping element in silicon-based photovoltaic cells, with a rising global demand. Gallium is a rare, widely dispersed trace element closely related to minerals of Al and Zn due to geochemical affinity. Most of the world's Ga is associated with bauxite and zinc ores, with Bayer's spent liquor being one of the most promising sources of this metal. Accurate determination of Ga content is the first step in evaluating the feasibility of its extraction. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a widely used technique employed for the determination of multiple and trace elements, particularly in bauxite. However, in Ga determination from Bayer spent liquor, the high concentration of easily ionizable elements, such as sodium, may affect the precision of ICP-OES due to matrix effects. Otherwise, voltammetric methods offer a more selective, sensitive, interference-free, and cost-effective alternative for determining Ga from spent liquor. In addition, Ga electrochemical behaviour can be studied using voltammetry, which aids in the development of a potential Ga concentration process. This work presents a validated analytical method for determining Ga in liquid matrix by Anodic Stripping Voltammetry (ASV). Unequivocal separations of the element peaks were obtained by observing their characteristic potentials, allowing for distinct identification of the analyte Ga (III) and other potentially interfering chemical species. Here, we introduce a measurement system capable of performing routine and research tests, addressing current and future challenges in determining Ga in matrices such as Bayer spent liquor.

Keywords: Voltammetry, Gallium, Spent liquor, Rare earth, Critical mineral, Bauxite.

1. Introduction

Gallium was discovered in 1875 by the French chemist Paul-Émile Lecoq de Boisbaudran while he was studying a zinc-containing mineral (sphalerite). The chosen name is derived from the Latin word Gallia, the ancient name for the region now known as France. Gallium is one of the metals with the lowest melting point (29.76 °C) and a high boiling point (2 204 °C). When solid, it is brittle and can break easily. Due to its wide temperature range in which it remains liquid, gallium was initially used in high-temperature thermometers and in metal alloys that needed to melt easily. However, since the 1960s, as semiconductor technology improved, the applications for gallium have significantly increased. Today, the demand for gallium-based products continues to rise, particularly in intelligent materials, integrated circuits, optical devices such as LEDs, and as a doping element in silicon-based photovoltaic cells [1].

Gallium does not exist in elemental form in nature, and its occurrence as a natural mineral is rare and scattered. Gallium is usually associated with its neighbours in the periodic table sharing similar properties, including atomic radius, trivalent oxidation state, tetrahedral or octahedral coordination, and amphotericity, such as zinc (Zn), aluminium (Al), and germanium (Ge). The most common minerals in which gallium (Ga) can be found are germanite, gallite, sphalerite, and bauxite [1, 2].

Bauxite is one of the primary sources of Ga worldwide. The Bayer process for alumina production results in the release of Ga from gibbsite, boehmite, or diaspore during digestion, resulting in the accumulation of gallate $[Ga(OH)_4]^-$ in the spent liquor. For this reason, gallium production associated with the Bayer process proves to be both technically and economically feasible. To extract Ga from Bayer spent liquor, various techniques are employed, including ion exchange, solvent extraction, electrochemical deposition, and fractional precipitation. However, there is no universal process for recovery of Ga from Bayer process. The main challenges include high costs, low recovery rates, and contamination issues [3–5].

Accurate determination of total Ga is the first step in assessing the feasibility of its recovery. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is widely employed to determine multiple and trace elements. In this method, excited electrons emit energy at specific wavelengths as they return to their ground state. Each element produces a unique spectrum, allowing for the determination of concentration based on optical emission. However, the presence of different species in spent liquor creates a complex matrix and interferences can occur, for high TDS (total dissolved solids), suspended solids, high salts, viscosity, density, volatility, and particularly due to the high concentration of easily ionizable elements, such as sodium. Causes are the effects of suppression or enhancement of signal, instability of signal, drift during analysis; sample and standard failures, and more frequent maintenance [6].

Voltammetry techniques are electroanalytical methods used to determine the concentration of electroactive species based on the principles of oxidation-reduction and mass transfer. The potential of interest is related to the redox potential of the electroactive species being quantified at a specific pH. The concentration of the species is determined by the current generated as a function of the rate at which the species is transported to the electrode surface through mass transport phenomena [7]. Both the analyte and the matrix dictate the appropriate voltammetry technique to use. Anodic Stripping Voltammetry (ASV) is commonly employed to determine trace metals, including Ga III [8, 9]. This works aims to demonstrate that ASV provides a selective, sensitive, interference-free, and cost-effective alternative for measuring Ga III in spent liquor.

1.1 Electrochemistry of Gallium

Gallium oxides, like aluminum oxides, are amphoteric. Thus, Ga can exist in different ionic species in an aqueous solution depending on the pH value. The most stable oxidation state of gallium is "+3", which corresponds to the presence of solvated (Ga^{3+} or Ga III) ions in acidic solution and gallate ions $[Ga(OH)_4]^-$ in alkaline solution. Other species such as $Ga(OH)^{2+}$, GaO^+, GaO_2^-, $H_2GaO_3^-$, $Ga(OH)_4^-$, $HGaO_3^{2-}$, and GaO_3^{3-} may occur as the pH transitions from acidic to basic. Consequently, the electrochemical behavior of gallium varies significantly [8].

Chung and colleagues investigated the redox behaviors of various ionic species of gallium, as illustrated in the Pourbaix diagram (Figure 1). For quantitative determination, it is essential to ensure that all species are identified under stable and appropriate conditions, considering the type of electrode, redox potential, and possible interferences from other species. A method for gallium

Table 3. Results – Total Ga in spent liquor.

Replicates	Voltammetry Reading (mg/L)	Sample Concentration (mg/L)
1	28.32	283.2
2	25.70	257.0
3	20.84	208.4
4	21.55	215.5
5	24.49	244.9
Average	24.18	241.8
Sd	3.06	30.6
CV	12.7 %	12.7 %

4. Conclusions

The protocol outlined in this document is easily reproducible. It was developed by established guidelines and best practices for analytical methods. All figures related to the validation process yielded satisfactory results. Control charts accomplishing concentration and position of the peak potential will be prepared to ensure long-term stability of the measurement. Additionally, opportunities for replacing mercury with alternative materials as the working electrode should be explored.

ASV voltammetry is an effective method for addressing both current and future inquiries related to the determination of Ga (III). The developed method and established analytical conditions create a measurement system that meets the needs for testing Bayer liquor samples, both routinely and for research purposes. Moreover, the electrochemical behavior of Ga can be studied using voltammetry, which supports the development of alternative methods for concentrating Ga in processes.

As global demand for gallium increases, the ASV is an alternative to ICP-OES and other methods of spectrochemical analysis that are prone to errors due to ionization interference in complex samples such as Bayer liquor.

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