

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

Darilena M. Porfirio¹, Paula F. M. Araujo², Diego Santana da Silva³, Walter Santana⁴, Tracy F. S. Fonseca⁵ and Adriano Lucheta⁶

1, 2. Researchers

6. Director

SENAI Innovation Institute for Mineral Technologies, Belém, Brazil

3. R&D Specialist

4. Laboratory Technician

5. Laboratory Manager

Hydro Bauxite & Alumina, Belém, Brazil

Corresponding author: adriano.isi@senaipa.org.br

<https://doi.org/10.71659/icsoba2025-aa017>

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 diasporite during digestion, resulting in the accumulation of gallate $[\text{Ga}(\text{OH})_4]^-$ 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 work 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 $[\text{Ga}(\text{OH})_4]^-$ in alkaline solution. Other species such as $\text{Ga}(\text{OH})^{2+}$, GaO^+ , GaO_2^- , H_2GaO_3^- , $\text{Ga}(\text{OH})_4^-$, 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

determination requires the sample to be acidified to a pH below 3.0 [10]. This procedure oxidizes all gallium to Ga III at a potential close to -0.70 V.

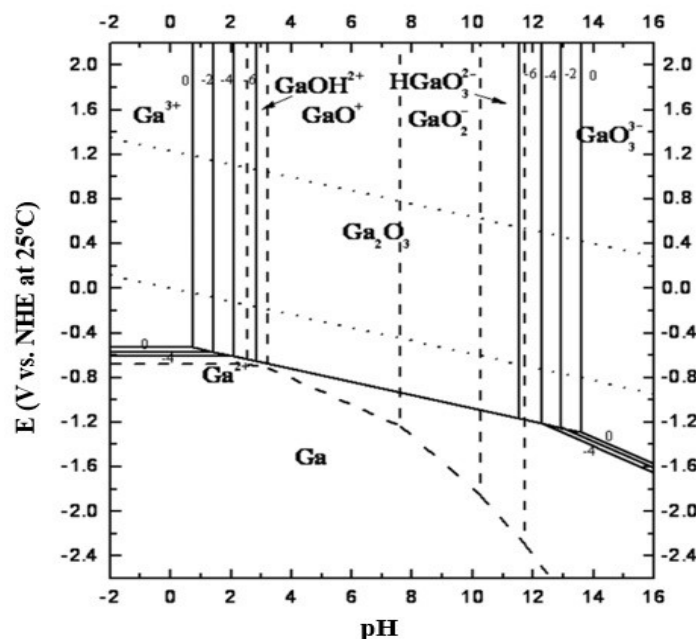


Figure 1. Potential vs. pH for the gallium-water system [10].

1.2 Anodic Stripping Voltammetry (ASV) for Ga Determination

ASV consists of three main steps. The first step corresponds to the pre-concentration of the analyte on the electrode surface by applying a negative potential while stirring. In the second step, known as equilibrium time, stirring is halted and the concentration of the deposited metal reaches equilibrium on the electrode surface. The final step, or stripping step, involves sweeping the potential in the anodic direction, which causes the species to return to the solution [7]. Besides the voltammetric technique, the choices of electrode and data analysis also depend on the analyte and the matrix involved.

In voltammetry, mercury is commonly used as the cathode due to its ability to form amalgams with various metals, making it advantageous for metal determination. Gallium ions can be discharged at a mercury cathode to generate metallic Ga, enabling the pre-concentration of analytes for more sensitive detection [3]. The main advantage is the electrode's ability to easily renew its surface by forming new drops, allowing for continuous electrochemical measurements and the pre-concentration of analytes for more sensitive detection. Mercury electrodes generally exhibit low noise signals, which is advantageous for obtaining clear and precise voltammetric data [11]. Despite its widespread use in electroanalysis, the toxicity of mercury has prompted manufacturers to explore alternatives. As a result, Hg-free sensors such as bismuth drop and glassy carbon electrodes are being developed [11]. These advancements align with the principles of Green Analytical Chemistry, which address concerns about human health, environmental protection, and sustainability. Our team is currently investigating greener options for determining Ga in Bayer liquor, replacing the Hg method. However, in the present work, we applied a hanging mercury drop electrode (HMDE) for this determination, considering all safety and environmental best practices.

2. Experimental

The protocol presented in this paper was validated by figures of merit recommended by Standard Guidelines [12]. The figures of merit were: (i) Analytical curve (linearity/working range/sensitivity); (ii) Limit of detection (LOD) and limit of quantification (LQ); (iii) Accuracy (recovery); (iv) Precision; and (v) Selectivity. The equipment used was the Metrohm 884 Professional VA, a computer-controlled voltammetric measuring instrument.

2.1 Analytical Curve

The selection of data analysis methods in voltammetry depends on the matrix and the analyte involved. Typical data processing techniques include the standard curve (calibration curve), the internal standard method (pilot ion), and the standard addition method (spiking). For determining Ga III in spent liquor, the standard addition method is particularly recommended, especially for complex matrices, like Bayer liquor.

In this method, the sample undergoes preparation involving pH adjustment and dilution, and it is then added to the electrolytic cell filled with an electrolyte solution. After a voltage-time function (excitation signals) scan, the current is measured. Next, aliquots of standard solution containing the target analyte are added (spikes), and the current is read after each addition. It is good practice to add the standard solution three times, ensuring the aliquot volumes are negligible compared to the total volume in the electrolytic cell. This approach allows any elements in the matrix that might affect the sample's current reading to also consistently influence the measurements after each spike. A graph of current or charge (peak area) *versus* concentration is obtained. The relationship between the quantities is linear, and the concentration of the sample is the modulus of the x-intercept of the graph.

Therefore, each sample will produce its analytical curve. It is important to note that the concentration value refers to the sample-electrolyte solution system (relative concentration). To determine the actual concentration of the sample, a proper conversion must be performed. Additional details will be discussed in the "Results" section.

High-purity (PA) chemical reagents and deionized water were used to prepare. Ga standard solutions were prepared using SPECSOL Standard 1.000 mg/L (998 ± 4 mg/L in 0.1 to 10 % HCl).

2.2 Protocol for Ga Determination in Bayer Spent Liquor

To quantify the total amount of Ga present in the solution by ASV, the sample must be acidified to a pH of 3.0, as previously mentioned. This step ensures the complete oxidation of Ga into Ga (III). A 5 mL of spent liquor sample was acidified with 5 mL of hydrochloric acid (37 %) and the final volume was adjusted to 50 mL using ultrapure water. This new solution will be the bulk sample for Ga determination.

The hanging mercury drop (HMDE) was employed as the working electrode, silver/silver chloride (Ag/AgCl-calomel) served as the reference electrode, alongside a platinum reference electrode. A 35 mL of L-tartaric acid (0.01 M) was used as a supporting electrolyte and pH buffer. Bulk sample aliquots were also introduced into the voltammetric cell, with the total volume being adjusted to 50 mL using ultrapure water. Other relevant data include pre-electrolysis potential set at -1.1 V; scanning range from -1.0 to -0.5 V at a rate of 4 mV/s; enrichment time of 240 seconds; resting time of 10 seconds; nitrogen purge lasting 10 min; and mercury droplet size equal to 4.

It is important to note that the determination of Ga (III) by voltammetry is relatively free from interference. However, one should evaluate the redox potential of inorganic species that may be close to the potential of the analyte being quantified. For Ga (III) in tartaric acid medium, species such as Ni (II), Cd (II), As (III), Co (II), Cu (II), Ti (I), Sn (IV), and Fe (III) have potential near Ga (III). In addition, the presence of Zn (II) in the sample must be investigated once that Zn (II) and Ga (III) form an intermetallic complex close to -1.000 V. Usually, in case of interference, or other conditions resulting in different potential, or an interference buffer can be added. For this protocol, antimony Sb (III) was added to the medium to mitigate any possible interferences [8, 13]. This topic will be further explored in the section on “Selectivity”.

3. Results and Discussion

3.1 Analytical Curve – Linearity / Sensitivity / Working Range

As previously mentioned, the analytical curve for Ga determination by spiking already incorporates the sample into its design. In this way, a single determination curve within the sample, obtained by interpolation, is replaced by individual curves to each sample, requiring the presence of the analyte to be quantified. However, it is important to first establish a blank curve to assess the linearity, working range, and sensitivity of the method [11].

The blank curve was prepared by adding 20 mL aliquots of ultrapure water and adding 2, 4, 6, and 8 mL aliquots of Ga standard solution (40 mg/L). Figure 2 presents the voltammogram obtained after each Ga addition. The peak corresponding to Ga (III) is very pronounced. The curve presents very good linearity and sensitivity as shown by the high coefficient of determination ($R^2 = 0.986$). The working range until 10 mg/L of Ga (III) was acceptable; higher concentrations may compromise the solution ideality (Debye-Hückel limit) [11]. Once the sample is included in the construction of the analytical curve, the linearity and working range always need to be verified. If these parameters were compromised by adding the sample, the sample must be diluted to maintain the quality of these figures.

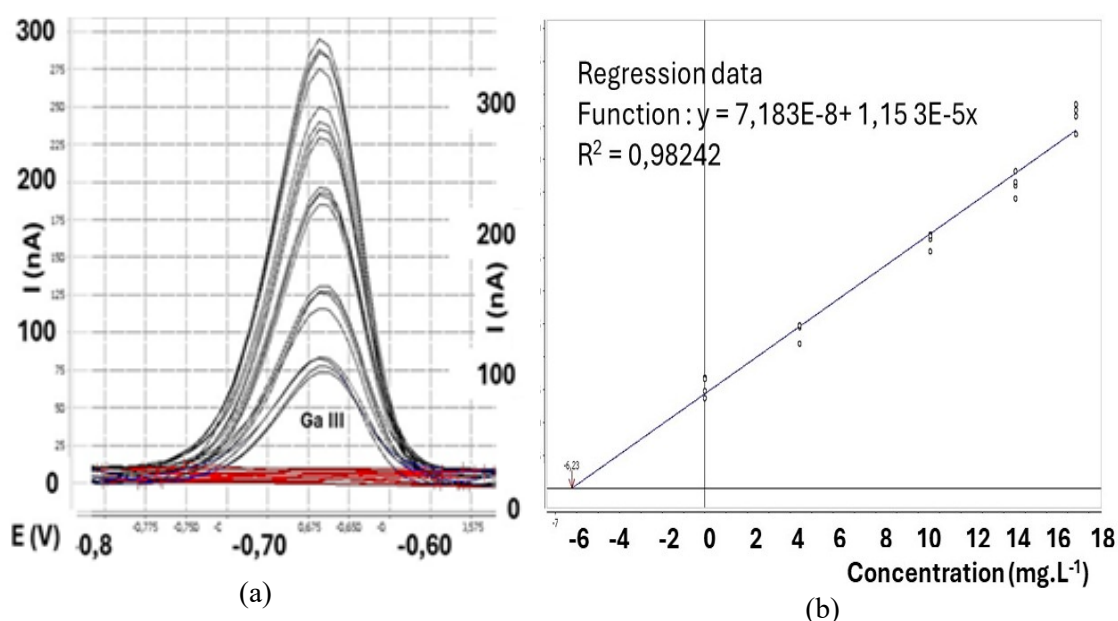


Figure 2. (a) Voltammogram of the standard solution; (b) analytical curve.

3.2 Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of detection (LOD) refers to the smallest concentration of an analyte in a sample that can be detected but not necessarily quantified. In contrast, the limit of quantification (LOQ) is the lowest concentration of an analyte that can be quantitatively determined with acceptable precision and accuracy. These parameters reflect the capability of the method to measure low concentrations of Ga, as well as the purity of the reagents, the efficiency of the cleaning and decontamination procedures of the glassware utilized. Both LOD and LOQ are calculated based on the standard deviation of the blank sample. Specifically, the LOD is defined as three times the standard deviation of the blank, while the LOQ is ten times the standard deviation of the blank [12].

Table 1 presents the results for LOD and LOQ. Under the environmental conditions evaluated, the method can detect Ga III concentration higher than 0.209 mg/L and quantify it with acceptable precision and accuracy at concentrations greater than 0.387 mg/L.

Table 1. Limits of detection (LOD) and quantification (LOQ) for the analytical system.

LOD	$3 \times Sd$	Current	1.18×10^{-8} A
		Ga	0.209 mg/L
LOQ	$10 \times Sd$	Current	$3.9 \cdot 10^{-8}$ A
		Ga	0.387 mg/L

3.3 Accuracy (Recovery)

A Certified Reference Material (CRM) or standard solution is usually used for evaluating the recovery, i.e., for assessing the analytical method regarding random and systematic errors. The criteria for validation of this figure, based on the Horwitz equation ($S_R = 2 C^{0.85}$), state that the acceptable coefficient of variation is greater as the analyte concentration decreases. For the determination of gallium (Ga III), the concentration varies in the range of mg/L, so recovery values between 80 and 110 % are considered acceptable according to standard guidelines [12].

The recovery of Ga was assessed using 2 mL (triplicate) of the standard solution at 50 mg/L. It is important to note that the standard solution used was prepared independently from the calibration solution. The individual recovery values fell within the acceptable criteria limits. The average concentration determined was 47.7 mg/L, resulting in a recovery of 95.5 %.

3.4 Precision (Repeatability, Intermediate Precision, and Reproducibility)

Precision is determined through reproducibility, intermediate precision, and repeatability. It should be noted that, in the ISI-TM laboratory, only two technicians are qualified to run VA 884 Professional analyses. Therefore, for this work, reproducibility will not be assessed. The intermediate precision refers to the continuous evaluation of the method over time. Therefore, a quality control procedure will be implemented but it will not be present in this work.

Repeatability is assessed using standard deviation, coefficient of variation (CV), or Z-score, with standard solutions or certified reference materials (CRMs) typically employed for this purpose. Like "Recovery," the standard guidelines accept coefficient of variation (CV) values ranging from 7.3 to 15 %, or Z-scores within the interval of $-2 \leq Z \leq +2$ for measurements in the ppm and ppb range [12]. This figure will be analyzed through the standard solution (50 mg/L). Table 2 presents the results. Although the coefficient of variation slightly exceeds the allowable limit at 15.96 %, the results can still be regarded as satisfactory due to the analysis of the relative error (4.54 %) and the Z-score (0.30).

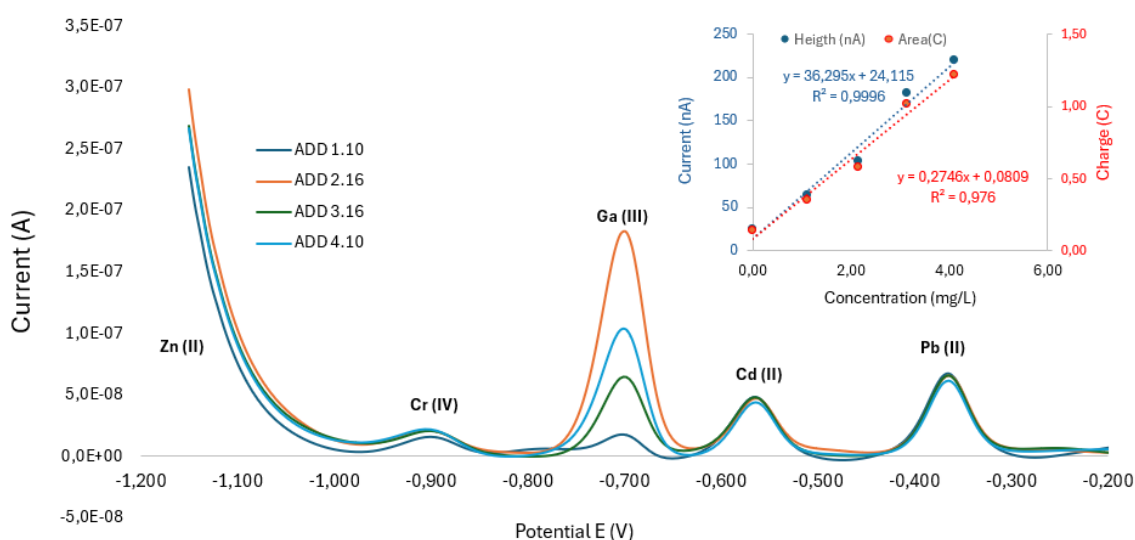
Table 2. Parameters for variability analysis – Standard Solution

% Error (Ref- μ) / Ref	(50 – 47.73) / 50	4.54 %
CV = sd / μ	7.62 / 47.73	15.96 %
Z = (Ref- μ) / sd	(50-47.73) / 7,62	0.30

3.5 Selectivity

Selectivity is the degree of reliability with which the method can quantify the analyte in the presence of other species that potentially interfere. The ions Ni (II) and Cd (II) may interfere in the analysis. The presence of Zn (II) in the sample must be investigated once that Zn (II) and Ga (III) form an intermetallic complex close to -1.000 V. Species As (III), Zn (II), and Co (II) could be tolerated in ratios of 1:3, 1:2, and 1:5, respectively. The ions Cu (II), Ti (I), Sn (IV), and Fe (III) could be tolerated up to ratios of 1:200, 1:200, 1:100, and 1:50, respectively[8, 13].

Therefore, a mixture of possible interferents with redox potentials closer to the Ga (III) potential were tested (Zn (II) at 50 mg/L; Cu (II), Cd (II), and Pb (II) at 10 mg/L). Figure 3 presents the results. There was no change in the Ga (III) measurement capacity. Despite good selectivity, Sb(III) will be used as an interference buffer because of the complexity of the spent liquor.


Figure 3. Voltammogram of Ga in the presence of possible interfering agents.

3.6 Determination of Ga in Spent Liquor

Once the analytical curve for determining Ga considers the sample in its construction, one should guarantee that the sample is enough diluted to maintain the reading within the working range. In our study, 3 dilutions (1:15; 1:10; 1:7.5) of the original sample were tested. The best results were achieved with a dilution of 1:10, so the protocol presented here considers this value for preparation of the bulk sample for Ga determination.

As the pre-electrolysis potential of -1.1 V was used, the simultaneous deposition of Zn and Ga occurred at -1.000 V, the Ga-Zn (3:2) intermetallic compound was deposited [8]. The interference could be eliminated by the addition of Sb (III) as follows:



The reactivity was verified, now with the presence of the sample by adding a mixture of possible interferences in the presence and absence of Sb (III). Figure 4 shows that there is no overlapping in the redox potential of these species with Ga (III).

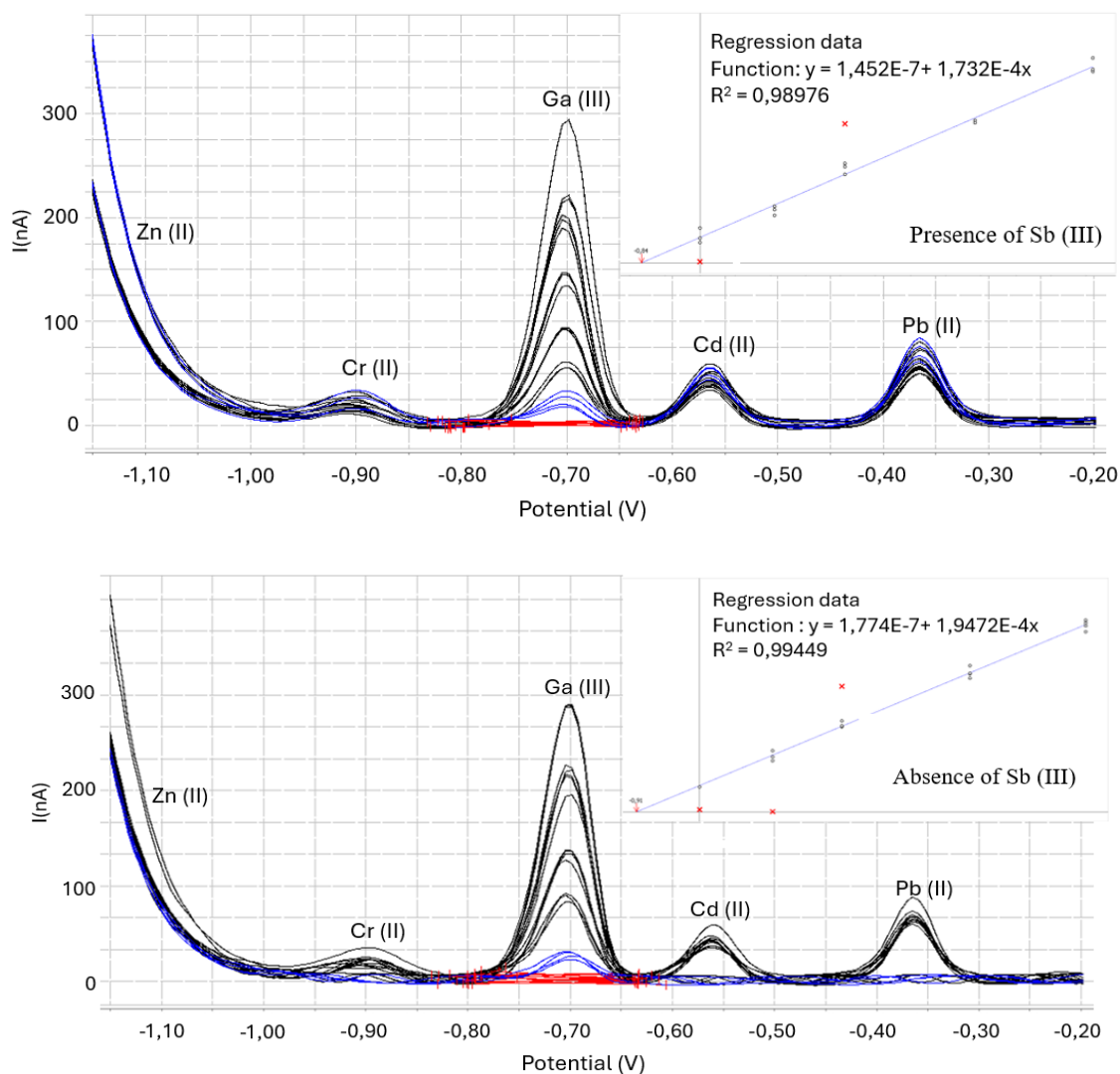


Figure 4. Voltammogram of Ga (III) in the spent liquor - Sb (III) effect.

After completing the method validation and protocol development, the Ga total concentration in the spent liquor sample was determined. Five different aliquots were analyzed. The results, along with the actual concentrations, are presented in Table 3. The coefficient of variation was less than 15 %, which is an acceptable value for repeatability according to standard guidelines [12].

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.

References

1. N. K. Foley and B. Jaskula, Gallium -A smart metal, *USGS Publications Warehouse, U.S. Geological Survey* (2013), 2013-3006. <https://doi.org/10.3133/pp1802H>
2. O. Chernov and A. Chagnes, Processing and extraction of critical raw materials from residues, *Mining and Processing Residues*, (2023), 71-183. <https://doi.org/10.1016/B978-0-323-95175-3.00003-9>
3. Z. Zhao et al. Recovery of gallium from Bayer liquor: A review, *Hydrometallurgy*, Vol. 125-126, (2012), 115-124. <https://doi.org/10.1016/j.hydromet.2012.06.002>
4. L. Qu et al., A review of the current state of research on gallium recovery from Bayer liquor, *The Journal of The Minerals, Metals & Materials Society (TMS)*, Vol. 76, (2024), 6084-6098. <https://doi.org/10.1007/s11837-024-06578-3>
5. L. Yuxin et al., A critical review of gallium production: Resources and extraction technologies, *Minerals Engineering*, Vol. 228, (2025), 109320. <https://doi.org/10.1016/j.mineng.2025.109320>
6. J. Vind et al., Distribution of selected trace elements in the Bayer Process, *Metal*, Vol. 8(5), (2018), 327. <https://doi.org/10.3390/met8050327>
7. S. Sharma, M.G.H. Zaidi and S. Mehtab, Voltammetry: an electrochemical analytical method. *In book: Research Trends in Chemical Sciences*, Chapter: 7, (2020), 127-140.

8. Y. Chung and C. Lee, Electrochemistry of gallium, *Journal of Electrochemical Science and Technology*, Vol. 4(1), (2013), 1-18. <https://doi.org/10.5229/JECST.2013.4.1.1>
9. S. Pysarevska and L. Dubenska. Advances in the electrochemical determination of gallium (III), *Chemistry of Metals and Alloys*, Vol. 11, (2018), 34-41. <http://doi.org/10.30970/cma11.0370>
10. S. S. Deshpande and A. P. Joshi, Trace level determination of gallium by differential pulse anodic stripping voltammetry. *Indian Journal of Chemistry*, Vol. 26A, (1987), 797-798.
11. Metrohm, Green alternative methods for voltammetric analysis in different water matrices. *Blog*, https://www.metrohm.com/pt_br/applications/whitepaper/wp-087.html (accessed on 8 May 2025).
12. DOQ-CGCRE-008 (2020) Standard guidelines: Guidance on Validation of Analytical Methods standards ABNT NBR ISO/IEC 17000 e ABNT NBR ISO/IEC 17025 Rev. 9.
13. Metrohm - Application Bulletin 36/2. Polarographic analyses half-wave potentials of metal ions.