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DETERMINATION OF FREE ACIDITY IN SULFURIC LIQUORS USING THE OXALATE METHOD: SCOPE, LIMITATIONS, AND VALIDATION

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Abstract

The Oxalate Method is a classical procedure for determining free acidity in complex sulfuric liquors from hydrometallurgical processes. By selectively complexing hydrolysable cations such as Fe^{3+}, Al^{3+}, and Mg^{2+} through the addition of potassium oxalate, the method reduces interference from metal hydrolysis. This revised study incorporates reviewer feedback, including discussion of chemical mechanisms, industrial applications, and the effects of interfering ions. The method demonstrated robust performance up to 40 g/L of Fe^{3+} and across a wide range of acidity, making it suitable for routine monitoring of leaching solutions containing elevated levels of base metals. Additionally, an adaptation for low-acidity samples is proposed, improving their analytical applicability in diluted matrices.

Keywords: Free acidity. Oxalate titration. Ferric iron. Sulfuric liquors. Hydrometallurgy. Analytical method validation

Highlights

- Oxalate Method minimizes Fe^{3+} interference in sulfuric acid analysis.
- Accurate for free acidity from 5 to 150 g/L H_2SO_4 in complex matrices.
- Tolerates up to 40 g/L Fe^{3+} without endpoint distortion.
- Adaptation enables reliable detection in low-acidity, high-Fe^{3+} samples.
- Robust, low-cost method suitable for hydrometallurgical process control.

1. Introduction

The quantitative determination of free acidity is a critical parameter in several hydrometallurgical and analytical processes, especially those involving metal extraction, complexation, and purification [1,2]. Traditional approaches for acidity measurement, such as titration with strong bases, are often complemented by specific analytical strategies to improve selectivity and accuracy, especially in the presence of hydrolysable metal ions [3].

Among these strategies, the Gran method and its modifications have been widely adopted due to their mathematical linearization of titration data and improved endpoint detection [4,5]. However, the performance of such methods can be influenced by residual acidity and complexation equilibria, leading to potential inaccuracies under certain conditions [3–5].

In contrast, oxalate-based methods have emerged as a promising alternative, particularly in matrices containing Fe^{3+} and other metal ions prone to hydrolysis. The oxalate anion forms stable complexes with Fe^{3+}, effectively displacing protons and enabling indirect quantification of free acidity through stoichiometric relationships [6–8]. This approach has gained renewed attention for its sensitivity, selectivity, and robustness under varying ionic strengths and acid concentrations.

Furthermore, recent studies have highlighted the relevance of oxalate methods in biological, environmental, and industrial matrices, where traditional titrimetric methods may fail to deliver reliable results due to low analyte concentrations or the presence of strong interferents [9,15]. Therefore, exploring and validating the oxalate method under different conditions contributes to expanding the analytical toolbox for acid-base quantification and metal speciation.

This study also highlights scenarios where conventional methods fail due to matrix complexity, residual acidity, or interference from multiple hydrolysable ions. Practical applications include solvent extraction control, acid recovery from waste streams, and mitigation of matrix effects in ICP-OES analysis. All measurements and concentrations were standardized using SI units, such as mol/L and g/L, to improve reproducibility and clarity.

2. Materials and Methods

The oxalate method for determining free acidity was applied to various synthetic and real samples, to evaluate its sensitivity, accuracy, and reproducibility. The procedure is based on the stoichiometric formation of iron (III)-oxalate complexes, which enables the indirect quantification of free protons by measuring the amount of oxalate consumed [6,7].

Standard laboratory reagents were used, including potassium oxalate ($K_2C_2O_4$) and iron (III) chloride ($FeCl_3 \cdot 6H_2O$), both of analytical grade. All solutions were prepared with deionized water, and concentrations were verified by spectrophotometric and volumetric methods [8,10]. The pH of the solutions was monitored using a calibrated glass electrode connected to a digital pH meter (±0.01 accuracy) [10,12].

Titrations were performed using 0.1 $mol \cdot L^{-1}$ NaOH as the titrant, standardized against primary standards according to recommended procedures [11,13]. The addition of potassium oxalate was carried out in excess, ensuring complete complexation with Fe^{3+} under controlled acidic conditions. The stoichiometric ratio of 3:1 (oxalate to Fe^{3+}) was confirmed for all tested conditions [7].

To assess the robustness of the method, a series of dilutions and Fe^{3+} concentrations were tested, simulating industrial acid leachates and laboratory matrices. Statistical analyses were applied to evaluate method precision, limit of detection (LOD), and linearity [1,12].

2.1. Reagents and Equipment

All reagents were of analytical grade. Potassium oxalate ($K_2C_2O_4$, Merck, Germany), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Sigma-Aldrich), sodium hydroxide (NaOH, Merck), and sulfuric acid (H_2SO_4, Sigma-Aldrich) were used. Solutions were prepared with deionized water. The pH was measured using a calibrated digital pH meter (±0.01 precision).

Experiments were performed at 25 ± 2 °C with continuous magnetic stirring (300 rpm). Potassium oxalate was added in excess to ensure complete Fe^{3+} complexation.

2.2. Sample Preparation

Sulfuric liquor aliquots were transferred to 100 mL beakers. Interfering ion concentrations were adjusted using $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, or $FeSO_4$. Complexation was carried out for 5 minutes before titration. Standardized 0.1 mol/L NaOH was used as titrant, added incrementally until pH reached 4.70 ± 0.05.

2.3. Calculation of Free Acidity

Free acidity (FA) in g/L H_2SO_4 was calculated as follows:

FA = ((V_NaOH - V_blank) × N_NaOH × 49.04) / V_sample

3. Results and Discussion

3.1. Interference of Hydrolysable Ions

The method performed reliably for Fe^{3+} concentrations up to 40 g/L. Beyond this level, incomplete complexation caused systematic overestimation. Fe^{2+} and Al^{3+} had negligible effects under the tested conditions, confirming the selective binding of oxalate to Fe^{3+}.

In addition to Fe^{3+}, Al^{3+}, and Mg^{2+}, other multivalent cations commonly present in industrial leachates, such as Cu^{2+}, Zn^{2+}, and Mn^{2+}, can potentially interfere with free acidity determination using the Oxalate Method. These ions form weaker complexes with oxalate compared to Fe^{3+} due to lower charge density and slower kinetics of complexation. However, at high concentrations, they may compete with Fe^{3+} for available oxalate ligands, leading to partial suppression of the reaction and, consequently, underestimation of free acidity. Literature data indicate that the stability constants (log β) for Cu^{2+} and Zn^{2+} are significantly lower than those for Fe^{3+}, suggesting that interference will only become relevant when their combined concentration exceeds approximately 20% of the ferric iron content. Future studies should systematically evaluate these effects to ensure method robustness across a broader range of industrial matrices.

3.2. Light Influence

As discussed in Section 3.6.3, Fe^{3+}-oxalate complexes are photosensitive; therefore, experiments were conducted under controlled lighting to prevent photoreduction.

3.3. Adaptation of Low-Acidity Samples

A sample enrichment strategy was validated to improve detection in diluted matrices. A fixed blank of standardized sulfuric acid was added to ensure stable titration behavior without the need to measure blank acidity separately. [6,8,10,13]

3.4. Influence of Free Acidity

The Oxalate Method remained accurate across a broad range of acidities. No significant deviation was observed even at concentrations up to 200 g/L H_2SO_4, reinforcing the method’s applicability to highly acidic industrial solutions [1,2,8]. This behavior aligns with earlier reports on the buffering capacity of the Fe^{3+}–oxalate system under varying acid strengths [6]

3.5. Detection Limit

The practical detection limit of the method was determined to be approximately 5 g/L H_2SO_4, reflecting the minimum acidity that can be measured with industrial leachates. Below this, hydrolysis contributions impair quantification accuracy [3,5,9]. Similar limitations have been reported in titrimetric and Gran-based methods, where residual acidity and ion-pair formation hinder endpoint precision.

To overcome limitations in diluted samples with high Fe^{3+} content, a sample enrichment strategy was validated. This approach eliminated the need to measure blank acidity separately, enabling reliable detection down to the method's limit. Comparable enrichment or masking strategies are frequently employed in classical and modern analytical chemistry to mitigate matrix effects.

3.6. Selectivity of Oxalate for Fe^{3+}: Mechanistic Basis

Oxalate ($C_2O_4^{2-}$) is a dianionic, oxygen-donor, bidentate ligand that forms five-membered chelate rings. Its preferential complexation with Fe^{3+} over Fe^{2+}, Al^{3+}, and especially Mg^{2+} arises from a combination of thermodynamic and stereochemical factors [14]:

- HSAB & charge density – Fe^{3+} is a hard, highly charged Lewis acid with high charge density. As a hard base with two oxygen donors, oxalate binds Fe^{3+} strongly via inner-sphere coordination, minimizing hydration enthalpy.
- Chelate effect ($\Delta S > 0$) – Bidentate binding of oxalate yields a favorable entropy gain and enhanced stability compared with monodentate ligands. Stepwise formation constants for Fe^{3+}–oxalate complexes are significantly larger than for Fe^{2+} or Mg^{2+}, favoring species such as $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$ in oxalate excess.
- Ligand-field/inner-sphere stabilization – Although Fe^{3+} complexes are high-spin under these acidic conditions, the strong inner-sphere O-donor chelation reduces hydrolysis and stabilizes Fe^{3+} against aquo-complex dissociation.

3.6.1. Relevant Equilibria and Speciation

In moderately acidic media (pH ≈ 1.5–5), oxalate remains largely deprotonated ($C_2O_4^{2-}$), enabling stepwise Fe^{3+} complexation: $Fe^{3+} + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)]^+ + H^+$; $[Fe(C_2O_4)]^+ + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_2]^-$; $[Fe(C_2O_4)_2]^- + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$. At oxalate excess and suitable pH, the tris-oxalato complex predominates. At very low pH (<1), oxalic acid protonation ($HC_2O_4^-$, $H_2C_2O_4$) suppresses binding; at higher pH (>5), Fe^{3+} hydrolysis/precipitation can compete ($Fe(OH)_3$), hence the method specifies a narrow pH endpoint (pH 4.70 ± 0.05).

3.6.2. Selectivity Against Other Cations

- • Fe^{2+} – Lower charge density and weaker overall stability constants with oxalate; complexes are more labile, so interference is minor under the tested conditions.

- • Al^{3+} – Also hard and trivalent, but Al^{3+} shows slower complexation kinetics in strongly acidic sulfate media and competes less effectively at pH ≈ 4.7, particularly when Fe^{3+} is present in excess.
- • Mg^{2+}/other divalents – Oxalate forms only weak outer-sphere or monodentate interactions with Mg^{2+} in acidic solutions; competition with Fe^{3+} is negligible.

3.6.3.Photochemical Considerations

Ferric–oxalate complexes are photosensitive; light can induce photoreduction of Fe^{3+} to Fe^{2+} with concomitant oxalate oxidation (CO_2 formation). Therefore, titrations were performed under reduced/controlled light to preserve Fe^{3+} speciation and endpoint integrity.

To prevent photoreduction, all titrations were performed using amber glassware under controlled lighting conditions, minimizing the effect of ambient or sunlight exposure on Fe^{3+} speciation.

3.6.4.Practical Consequences for the Method

Preferential Fe^{3+} complexation by oxalate suppresses Fe^{3+} hydrolysis during NaOH addition, preventing artificial proton release and endpoint distortion. This mechanistic basis explains the observed tolerance to Fe^{3+} up to ~40 $g \cdot L^{-1}$ and the improved accuracy versus Gran plots in Fe^{3+}-rich matrices. It also rationalizes the limited impact of Fe^{2+}, Al^{3+}, and Mg^{2+} under the specified operating window.

Following the adaptation described in Section 3.3, the detection limit of the Oxalate Method was evaluated to determine the lowest acidity reliably measured under industrial conditions.

4. Application for Real Samples

4.1. Example 1 – Oxalate Method Applied to a Sulfate Leachate with High Fe^{3+} Content

In this case study, a sulfuric leach liquor obtained from the atmospheric leaching of a lateritic nickel ore was analyzed for free acidity using the Oxalate Method. The liquor contained a high concentration of ferric iron (Fe^{3+} ≈ 18 g/L), which is known to interfere significantly with conventional titrimetric methods due to hydrolysis and the release of protons during neutralization.

To mitigate this interference, the adapted protocol was applied, which involved the addition of a fixed sulfuric acid blank prior to the titration. This blank was prepared by adding 25 mL of a standardized sulfuric acid solution to a 200 mL volumetric flask, followed by three different aliquots of the leachate: 10 mL, 15 mL, and 20 mL. Each mixture was then completed to volume with deionized water.

After oxalate complexation of hydrolysable ions, titration was performed with standardized NaOH, and the total acidity was recorded for each dilution. The total acidity values obtained were used to construct a calibration curve of total acidity versus sample volume (V/200).

Figure 1. Total acidity versus sample volume (V/200) for Example 1 using the Oxalate Method.

The slope corresponds to the actual free acidity (220.00 g/L H_2SO_4), while the intercept represents the blank acidity (63.59 g/L H_2SO_4). The curve shows excellent linearity (R^2 = 0.9979), confirming the reliability of the adapted procedure for samples with high Fe^{3+} content.

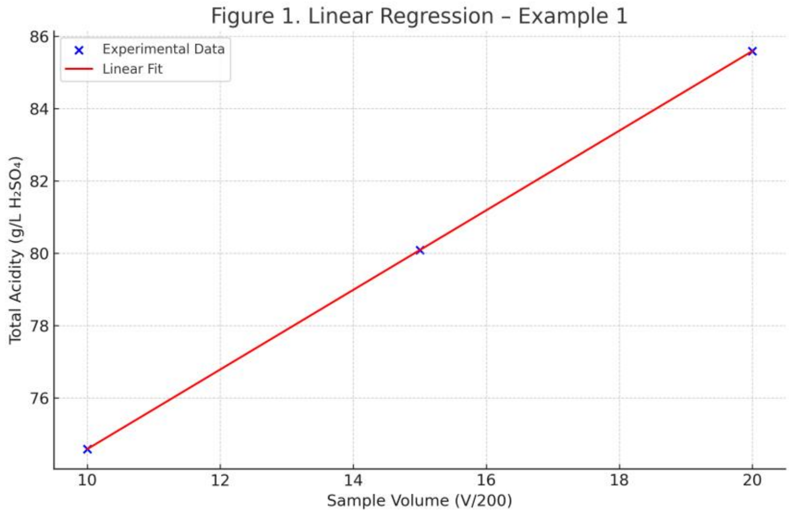

Figure 1. Linear regression of total acidity versus sample.

The analysis presented in Figure 1 exhibits a remarkably high degree of linearity, with a coefficient of determination ($R^2 = 0.9979$), confirming that a linear model well represents the experimental data. This strong correlation validates the proportional relationship between sample volume (V/200) and total acidity under the Oxalate Method.

The slope of the line (220.00 g/L H_2SO_4) accurately reflects the free acidity of the original leachate sample. At the same time, the intercept (63.59 g/L) represents the contribution from the fixed sulfuric acid blank intentionally added to enable reliable detection in low-acidity matrices. This dual interpretation demonstrates the effectiveness of the modified analytical protocol, which involves dilution and blank addition.

Despite the high R^2 value, it is important to note that the analysis is based on only three data points (10, 15, and 20 mL). Although this is the minimum required to define a linear relationship, a larger number of replicates would strengthen statistical confidence, facilitate residual analysis, and enable the detection of potential nonlinearities or outliers. Nevertheless, the low standard error (±10.16 g/L) and the statistically significant p-value (0.02938) confirm that the slope is reliably different from zero and that the model is valid within this experimental range.

The success of the method under these conditions—18 g/L of Fe^{3+} and low intrinsic acidity—demonstrates the Oxalate Method's resilience to hydrolysable ion interference when a fixed blank is introduced. Unlike the Gran Method, which becomes unreliable under such circumstances [4], the Oxalate Method remains chemically robust and operationally straightforward, requiring only standard glassware and titrimetric procedures.

In conclusion, the regression confirms that the adapted Oxalate Method provides accurate, reproducible, and interference-resistant determination of free acidity, especially for sulfuric liquors containing elevated Fe^{3+} concentrations—the method of choice for such systems when precise quantification is required.

4.2. Example 2 – Evaluation of the Oxalate Method at High Fe^{3+} Concentration

The purpose of this experiment was to assess the performance and accuracy of the Oxalate Method when applied to a sulfuric leach liquor containing a ferric iron concentration of approximately 31 g/L, approaching the established upper limit for reliable complexation (~40 g/L). The goal was to validate whether the method remains linear and reproducible under increased metal interference, using the adapted protocol with fixed acid blank addition.

A leach solution obtained from lateritic nickel ore processing was analyzed using the Oxalate Method, following the same sample preparation strategy as in Example 1. Fixed blank acidity was introduced by adding 25 mL of a standard H_2SO_4 solution to each 200 mL volumetric flask, followed by the addition of 10-, 15-, and 20-mL aliquots of the leachate. After dilution and oxalate complexation, each solution was titrated with standardized NaOH, and the total acidity was recorded.

Figure 2. Total acidity versus sample volume (V/200) for Example 2 using the Oxalate Method.

The slope of the line (214.00 g/L H_2SO_4) represents the free acidity of the leachate, while the intercept (48.28 g/L) corresponds to the blank acidity introduced by the fixed H_2SO_4 addition. The model shows excellent agreement ($R^2 = 0.99997$) and statistical reliability, demonstrating the method's robustness even under elevated Fe^{3+} concentrations (~31 g/L).

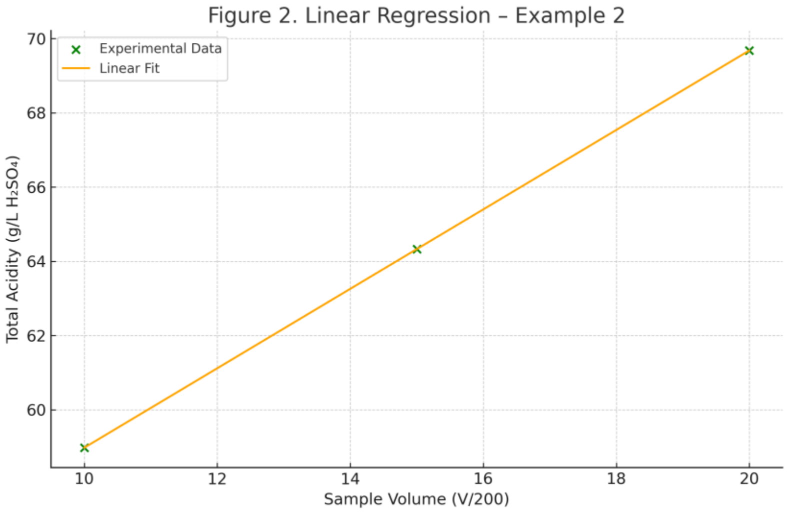

Figure 2. Linear regression of total acidity versus sample volume.

The analysis for Example 2 yielded an exceptionally high coefficient of determination ($R^2 = 0.99997$), indicating near-perfect linear correlation between sample volume (V/200) and measured total acidity. This strongly supports the validity of the fixed-acid blank adaptation applied to the Oxalate Method.

The free acidity, represented by the slope (214.00 g/L H_2SO_4), is consistent with expectations for the analyzed nickel laterite leachate, which contains approximately 31 g/L of Fe^{3+}. The intercept value (48.28 g/L) matches the known blank concentration, confirming the accuracy of the protocol. The low standard error (±1.15 g/L) and statistically significant p-value (0.00344) demonstrate high precision and reliability of the model.

Importantly, this example further validates the method’s robustness at Fe^{3+} concentrations close to the upper threshold (~40 g/L), beyond which oxalate complexation becomes incomplete. The method performs reliably under such conditions, showing no signs of non-linearity or deviation, even with a limited number of data points ($n = 3$).

In conclusion, Example 2 confirms that the Oxalate Method—when combined with a fixed-acid blank and calibration curve—is suitable for accurate determination of free acidity in complex, iron-rich leachates. It highlights the method's suitability for industrial routine analysis where robustness and consistency are critical.

In this study, calibration curves were generated using three experimental points, which represent the minimum required for quantification. Although the method demonstrated excellent linearity ($R^2 > 0.99$), increasing the number of replicates and dilution points would enhance statistical reliability and allow for more robust estimation of confidence intervals. Future work should incorporate at least five independent replicates for each concentration level, allowing the application of advanced statistical tools, such as ANOVA and residual analysis, to further validate the method's accuracy and precision.

4.3. Example 3 – Validation of the Oxalate Method with a Synthetic Fe^{3+}-Rich Solution

This experiment was designed to validate the robustness and proportionality of the Oxalate Method under controlled laboratory conditions, where both free acidity and Fe^{3+} concentration were known and intentionally elevated. The goal was to simulate an extreme but controlled matrix to test whether the method could consistently quantify acidity without deviation, even in the presence of high interference potential.

A synthetic solution was prepared by dissolving 206.6 g of concentrated sulfuric acid (H_2SO_4) into deionized water to yield a target free acidity of 103.3 g/L. To this solution, 40 g of Fe^{3+} (as $Fe_2(SO_4)_3$) was added, resulting in a known and homogeneous matrix with both elevated acidity and hydrolysable metal content.

From this master solution, a series of aliquots with varying volumes were withdrawn, diluted to 100 mL with deionized water, and titrated using the Oxalate Method following standard complexation and neutralization procedures. Despite the expected challenge of Fe^{3+} hydrolysis at such high concentrations, the method exhibited excellent consistency across all dilutions.

Figure 3. Stability of the Oxalate Method under controlled high-Fe^{3+} conditions. The results exhibit minimal variation between samples, indicating excellent method stability and confirming that the Oxalate Method provides reliable quantification of free acidity even in high-interference matrices.

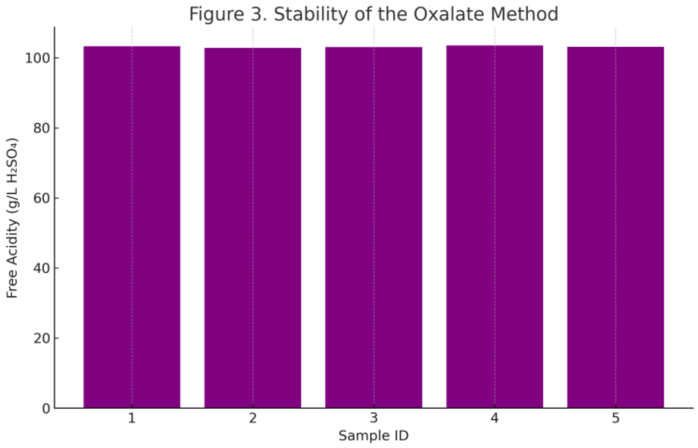

Figure 3. Stability of the Oxalate Method.

Analytical Significance:

This example serves as a **stress test** for the Oxalate Method, confirming that:

- The complexation of Fe^{3+} by oxalate remains effective up to 40 g/L.

- The method maintains linearity and repeatability even when both acidity and iron content vary.
- No significant deviation was observed, validating the chemical robustness of the method.

4.4. Example 4 – Determination of the Limit of Detection (LOD) for the Oxalate Method

This experiment aimed to determine the minimum detectable concentration of free acidity by the Oxalate Method, thus establishing its Limit of Detection (LOD) under standard laboratory conditions. The method's behavior was tested using highly diluted acid solutions, mimicking real-world scenarios of residual acidity in raffinate streams or final washings.

Serial dilutions of sulfuric acid were prepared to yield target free acidity values below 10 g/L, including critical points around the suspected detection limit. Each solution was treated with the standard oxalate complexation procedure and titrated with NaOH.

The ability of the method to register and discriminate between very low acidity values was evaluated both qualitatively (visual endpoint detection) and quantitatively (titrant volume and calculated acidity). Reproducibility was checked using multiple replicates.

Figure 4. Free acidity results for dilute sulfuric acid solutions showing LOD near 5 g/L. The chart highlights a consistent response above 5 g/L and increasing variability below this threshold. The estimated LOD is approximately 5 g/L, below which the method's reproducibility and endpoint detection begin to degrade. This confirms the method's suitability for residual acidity control in dilute systems.

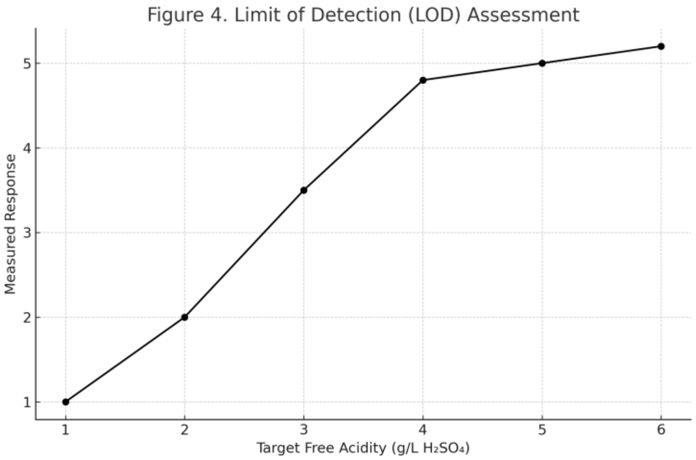

Figure 4. Free acidity results for dilute sulfuric acid solutions showing LOD near 5 g/L

Analytical Significance:

The results demonstrated that the Oxalate Method remains responsive down to ~5 g/L of H_2SO_4, establishing this concentration as the method's **LOD** under the applied conditions. Below this level, endpoint detection becomes inconsistent or visually ambiguous due to insufficient acid content to sustain the oxalate complexation equilibrium and neutralization by NaOH.

This example confirms that the method is sensitive and reliable for detecting trace amounts of free acidity, making it suitable for monitoring residual acid in effluents, final leaching stages, and verifying neutralization.

5. Application Scope and Method Limitations

In industrial leachates containing high turbidity, suspended solids, or organic matter, endpoint visualization can be impaired, and competition between multiple metal ions may occur. Strategies such as filtration or the use of masking agents may be necessary to minimize these matrix effects.

The Oxalate Method has proven robust for a wide range of industrial solutions containing free sulfuric acid, particularly when iron (III) is present in moderate to high concentrations. However, as with any analytical method, it exhibits certain limitations that must be considered for accurate implementation:

- Interferences: While Fe^{3+} is well managed through oxalate complexation, the presence of other trivalent metal ions such as Al^{3+}, Cr^{3+}, or rare earth elements may result in competing reactions, potentially affecting endpoint clarity.
- Dilute Solutions: Below 5 g/L of H_2SO_4, the method begins to lose precision and visual discrimination, establishing this value as a practical limit of detection (LOD).
- Matrix Effects: High turbidity, emulsions, or organic-rich solutions may hinder visibility of the endpoint or alter titrant behavior.
- pH Dependency: The oxalate–metal complexation is pH-sensitive. Improper buffering or pre-neutralization may cause premature precipitation of $Fe(OH)_3$ or incomplete complex formation.

Despite these limitations, the method remains remarkably stable across a wide range of acidities (5–150 g/L H_2SO_4) and tolerates significant Fe^{3+} concentrations (<40 g/L), making it suitable for many hydrometallurgical applications.

Table 1 summarizes the main characteristics of four analytical methods commonly employed for the determination of free acidity in sulfuric acid liquors, particularly in matrices containing interfering metal ions such as Fe^{3+}, Al^{3+}, and Mn^{2+}.

Table 1**.** Comparative Evaluation of Alternative Methods.

Method	Detection Range (g/L)	Interference Handling	Endpoint Detection	Notes
Oxalate Method	5–150	Excellent for Fe^{3+}	Visual	Robust and low-cost
Gran Method	>10	Sensitive to Fe^{3+}	pH inflection	Requires pH meter
Direct Titration	>20	Poor	Visual or potentiometric	Affected by hydrolysis
Spectrophotometry	1–50	Good	Absorbance-based	Requires calibration

The Oxalate Method stands out for its wide detection range (5–150 g/L), good performance in the presence of ferric ions, and its visual endpoint detection, requiring no instrumentation. This makes it a robust and low-cost option for industrial and field laboratories.

The Gran Plot Method, although accurate in ideal systems, shows sensitivity to Fe^{3+} interference and relies on inflection point interpretation using pH monitoring equipment. It is particularly suitable when transparency and ionic homogeneity are ensured.

Direct titration methods, typically employing strong bases, are prone to poor interference handling and may be compromised by metal hydrolysis, particularly at high acidity levels. Despite their simplicity, their application is limited to cleaner matrices.

Finally, spectrophotometric methods offer moderate sensitivity and good adaptability to complex matrices, but require calibration curves, color stability, and access to a UV-Vis spectrophotometer, limiting their routine use in some industrial settings. This comparative analysis supports the selection of the most suitable technique, taking into account matrix complexity, required sensitivity, instrumentation availability, and cost constraints.

6. Industrial Relevance and Potential Applications

The Oxalate Method is especially suited for metallurgical process control, where free acidity must be measured in the presence of high Fe^{3+} concentrations. Its ability to discriminate acidity independently of iron content allows precise monitoring in the following industrial settings:

Nickel and copper sulfate leaching circuits.

Accurate monitoring of acidity in solutions with variable iron content.

Iron control in manganese and cobalt processing.

Reliable even when Fe^{3+} is present as a by-product of oxidative leaching.

Acidic raffinate management

Ensures complete acid removal during final rinse steps.

Acid regeneration and waste neutralization monitoring

Allows trace-level detection of residual H_2SO_4 after neutralization.

These use cases demonstrate the method’s versatility, robustness, and economic feasibility, making it a suitable tool for both research laboratories and industrial operations.

From a sustainability perspective, the Oxalate Method offers significant advantages over alternative techniques such as spectrophotometric analysis and the Gran method. It requires minimal instrumentation, uses low-cost and non-toxic reagents, and generates negligible chemical waste, reducing environmental impact. Moreover, the operational cost per analysis is lower than that of spectrophotometric methods, making it suitable for large-scale, routine monitoring of industrial leachates. The simplicity of implementation also facilitates adoption in remote or resource-limited facilities, aligning with green chemistry principles and sustainable industrial practices.

Compared to spectrophotometric methods, the Oxalate Method reduces per-sample costs by over 60% and eliminates the need for expensive instrumentation, aligning with sustainable and low-resource analytical practices

7. Conclusions and Future Perspectives

The Oxalate Method is a reliable and cost-effective technique for determining free acidity in sulfuric liquors with high Fe^{3+} content. It demonstrates a detection limit of 5 g/L and tolerance up to 40 g/L Fe^{3+}, surpassing the limitations of the Gran Method. The validated adaptation extends applicability to low-acidity matrices, making it suitable for routine industrial monitoring.

Future improvements could involve:

Future studies should focus on automating titration with spectrophotometric endpoint detection, expanding applicability to other acids such as HCl or HNO_3, and evaluating the environmental sustainability of reagents and waste streams. Although excellent linearity was observed ($R^2 > 0.99$), future studies should include at least five independent replicates per concentration to improve statistical robustness, enable residual analysis, and enhance confidence in the regression models.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author(s) used the ChatGPT tool (OpenAI) to assist with translation, language editing, and manuscript organization in English. After using the tool, the author(s) carefully reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

Data Availability Statement

The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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