International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 09 Issue 03 March 2026
DOI: 10.47191/ijcsrr/V9-i3-14, Impact Factor: 8.048
IJCSRR @ 2026
www.ijcsrr.org

Free Acidity in Hydrometallurgy is not pH: A Critical Review of Measurement Methods, Errors, and Process Consequences

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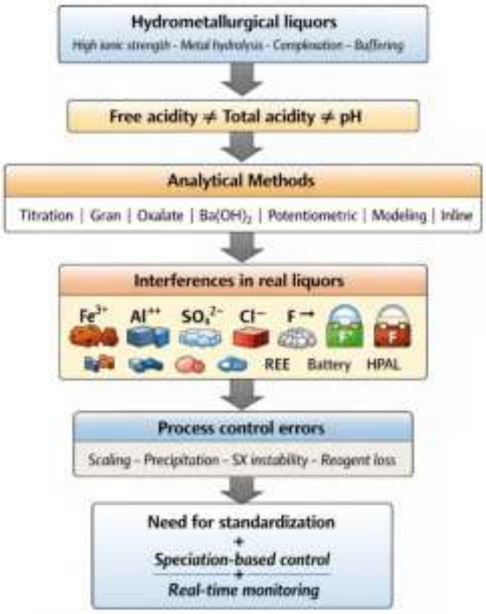
ABSTRACT: Free acidity is a key control parameter in hydrometallurgical processes, governing dissolution, precipitation, solvent extraction, neutralization, and corrosion behavior, yet its determination in real process liquors remains poorly standardized and often misunderstood. In industrial solutions, the distinction between total acidity, free acidity, and active acidity is frequently obscured by high ionic strength, metal hydrolysis, ion pairing, and complexation reactions, making simple pH measurement or conventional titration unreliable. This review critically examines the main analytical approaches used to determine free acidity in hydrometallurgical liquors, including classical acid–base titration, potentiometric and Gran methods, oxalate and complexation-based procedures, $Ba(OH)_2$ and other selective titrations, inline monitoring techniques, and speciation-based modeling calculations. Particular emphasis is given to the effect of interfering species commonly present in industrial circuits, such as Fe^{3+}, Al^{3+}, SO_4^{2-}, Cl^-, and F^-, which strongly influence endpoint detection, hydrogen ion activity, and the apparent acid balance. The review shows that discrepancies between analytical methods are not only experimental but also thermodynamic, arising from differences between proton concentration, activity, and chemically bound acidity. These inconsistencies can lead to significant errors in process control, affecting reagent consumption, precipitation efficiency, scaling, solvent extraction stability, and environmental performance. By comparing reported methods and industrial practices, this work identifies the limitations of current procedures and highlights the need for standardized definitions, speciation-aware analysis, and improved inline monitoring strategies for reliable acidity control in modern hydrometallurgical operations.

KEYWORDS: Free acidity; hydrometallurgy, Oxalate method, Gran titration, Acid dosing; control; circular acid regeneration

Highlights

- Free acidity is not equivalent to pH in hydrometallurgical liquors
- Metal hydrolysis strongly affects titration results
- Oxalate and Gran methods provide improved accuracy
- Industrial liquors require speciation-aware analysis
- Lack of standardization leads to process control errors

Graphical abstract



1. INTRODUCTION

Acidity control is a fundamental parameter in hydrometallurgical processes and directly affects dissolution kinetics, phase stability, impurity control, solvent extraction performance, and environmental compliance. In modern hydrometallurgical flowsheets, acid concentration must be carefully adjusted to maintain reaction selectivity, avoid excessive reagent consumption, and prevent precipitation or scaling phenomena that may compromise plant operation (Free, 2021; Han et al., 2023). The importance of accurate acid control has increased with the growing complexity of industrial circuits, particularly in the processing of low-grade ores, secondary resources, and recycling streams, where solutions frequently contain high concentrations of dissolved metals and strong electrolytes (Tabelin et al., 2021).

In industrial practice, acidity is commonly monitored using titration or pH measurement, but these parameters do not necessarily represent the same chemical quantity. Several definitions are used in the literature and in plant operation, including total acidity, free acidity, active acidity, titratable acidity, and hydrogen ion activity. These terms are often used interchangeably, even though they correspond to different physicochemical concepts. In concentrated hydrometallurgical liquors, the difference between concentration and activity of hydrogen ions becomes significant, and the measured acidity depends strongly on ionic strength, complexation reactions, and hydrolysis equilibria (Free, 2021; Han et al., 2023).

The limitations of pH as an indicator of acidity are particularly evident in strong electrolyte systems, where activity coefficients deviate from unity and the relationship between pH and proton concentration becomes non-linear. In sulfate, chloride, and mixed electrolyte solutions typical of hydrometallurgical operations, ion pairing and complex formation can store or release protons during titration, producing multiple endpoints or apparent buffering regions. As a result, the value obtained in a titration may not correspond to the thermodynamic hydrogen ion activity, nor to the amount of acid effectively available to drive leaching or precipitation reactions (Free, 2021).

Additional complications arise from the presence of hydrolyzable metal ions such as Fe^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+}, and rare-earth elements, which undergo stepwise hydrolysis and form basic salts during neutralization. These reactions consume titrant and may be incorrectly interpreted as free acid, leading to systematic errors in acidity determination. Similar effects occur in fluoride-rich, sulfate-rich, and chloride-rich liquors, as well as in recycling circuits where multiple metals and ligands coexist. Such interferences are widely reported in hydrometallurgical systems including copper leaching, pressure leaching, solvent extraction, acid mine drainage treatment, and battery recycling processes (Tabelin et al., 2021; Arana Juve et al., 2022).

The problem is further aggravated by the absence of standardized procedures for determining free acidity in hydrometallurgical solutions. There is no universally accepted ASTM or ISO method defining the operational meaning of free acidity under high ionic strength conditions. Consequently, different plants and laboratories adopt different titration endpoints, masking agents, or calculation procedures, making comparison between results difficult and sometimes misleading. This lack of standardization can result in over-acidification, poor impurity control, excessive reagent consumption, and instability in downstream separation processes (Han et al., 2023; Shoukang, 2024).

Because of these limitations, the determination of free acidity should not be treated as a simple analytical measurement, but rather as a speciation-dependent parameter that must be interpreted in the context of solution chemistry. Understanding the relationship between hydrogen ion activity, metal hydrolysis, complexation, and titration behavior is essential for selecting the appropriate analytical method and for correctly interpreting acidity values in industrial liquors (Free, 2021; Han et al., 2023).

Therefore, the objective of this review is to critically analyze the concept of free acidity in hydrometallurgical systems, with emphasis on the chemical basis of acidity in concentrated electrolytes, the analytical methods used for its determination, the interferences caused by metal ions and complexing species, and the consequences of incorrect acidity measurement on process control. Special attention is given to titrimetric, potentiometric, and modeling-based approaches, as well as to the lack of standardization in industrial practice.

To ensure transparency and reproducibility in the selection and evaluation of the literature, the review methodology adopted in this work follows systematic review principles based on the PRISMA 2020 guidelines, as described in the next section.

2. METHODOLOGY

This review was conducted as a structured literature review following the principles of the PRISMA 2020 statement for systematic reviews (Page et al., 2021). The objective of the methodology was to identify, screen, and select publications related to the measurement of free acidity, acid speciation, titration methods, and analytical limitations in hydrometallurgical systems.

The literature search was performed using the databases Scopus, Web of Science, ScienceDirect, SpringerLink, and Google Scholar. The search included combinations of the following keywords:

free acidity, hydrometallurgy, acid titration, speciation, hydrolysis, leach liquor, hydrogen ion activity, Gran titration, oxalate method, acid balance, sulfate solutions, chloride leaching, industrial liquors.

Boolean operators were applied to refine the search, using expressions such as:

(“free acidity” OR “acid speciation”)
AND (hydrometallurgy OR leaching)
AND (titration OR hydrolysis OR activity OR analysis)

The inclusion criteria considered publications from 2020 to 2026 on hydrometallurgical systems, acid solutions, analytical methods, chemical speciation, or process control. Studies limited to dilute laboratory systems, biological media, or environmental monitoring without analytical relevance to acid determination were excluded.

The screening process followed the PRISMA 2020 workflow, including identification, screening, eligibility assessment, and final inclusion (Page et al., 2021). After removing duplicates and excluding publications outside the scope of this review, 55 references were selected. The selection process is summarized in Figure 1.

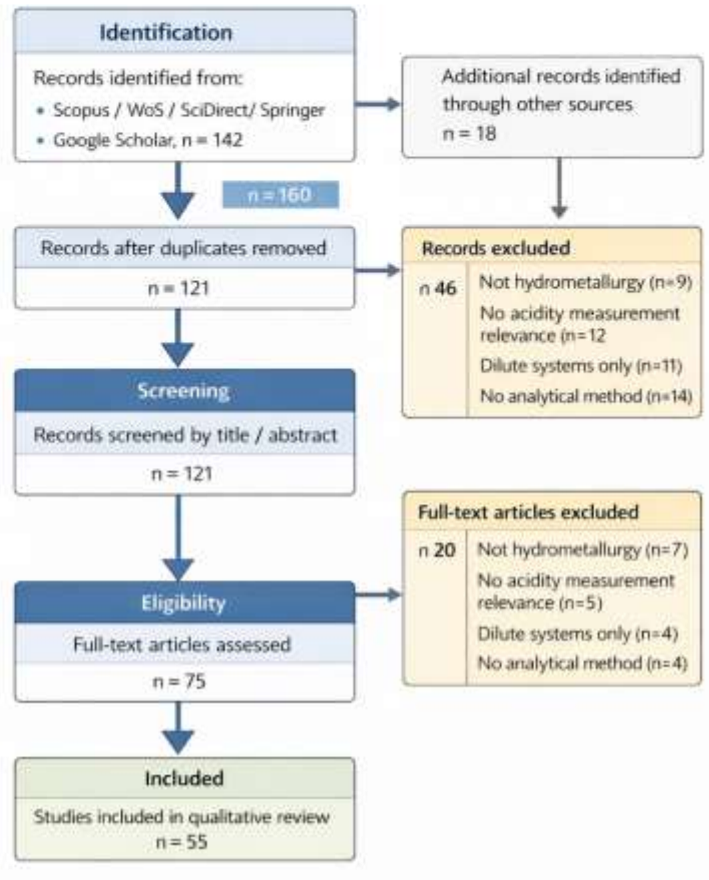


Figure 1. PRISMA 2020 flow diagram of literature selection (55 studies included). Adapted from Page et al. (2021).

Figure 1 shows the flow diagram of the literature selection process following PRISMA 2020 guidelines (Page et al., 2021). The initial search returned many records, reduced after title and abstract screening. Full-text evaluation assessed relevance to free acidity, acid speciation, titration methods, and hydrometallurgy. After eligibility, 55 references were retained for qualitative analysis.

3. CHEMICAL BASIS OF ACIDITY IN HYDROMETALLURGICAL LIQUORS

Accurate determination of free acidity in hydrometallurgical solutions requires an understanding of the chemical equilibria that control hydrogen-ion activity. Industrial liquors are rarely simple strong-acid solutions. They have high ionic strength, multiple metal ions, complexing ligands, and hydrolysis reactions. Under these conditions, acidity cannot be defined solely by concentration, and analytical results depend strongly on speciation and equilibrium reactions (Liu et al., 2022; Zhou et al., 2024).

Acid–activity coefficients, ion pairing, and metal hydrolysis influence base behavior in concentrated electrolytes. These effects alter titration curves, shift endpoints, and produce apparent acidity that does not correspond to the concentration of free hydrogen ions. Consequently, the concept of free acidity becomes operational and depends on the analytical method used (Yang et al., 2023; Lodeiro et al., 2020).

Understanding these effects is essential for interpreting titration results, selecting analytical methods, and avoiding errors in process control.

3.1. Hydrogen ion activity vs concentration

In dilute aqueous solutions, hydrogen ion concentration and activity are similar. In hydrometallurgical liquors, ionic strength is often high, and activity coefficients deviate from unity. Under these conditions, pH does not directly represent proton concentration.

The Debye–Hückel model describes activity corrections at low ionic strength, while the Pitzer and SIT models are required for concentrated electrolytes. These models show that the effective acidity depends on ion interactions, not only on acid concentration (Lawrence & Roy, 2021; Yang et al., 2023).

Speciation modeling studies in chloride- and sulfate-leaching systems demonstrate that hydrogen ion activity can change even when total acid concentration remains constant (Liu et al., 2022).

Figure 2 shows that the deviation between concentration and activity becomes significant at high ionic strength. This effect is typical of hydrometallurgical liquors and explains why titration and pH measurements may give different acidity values.

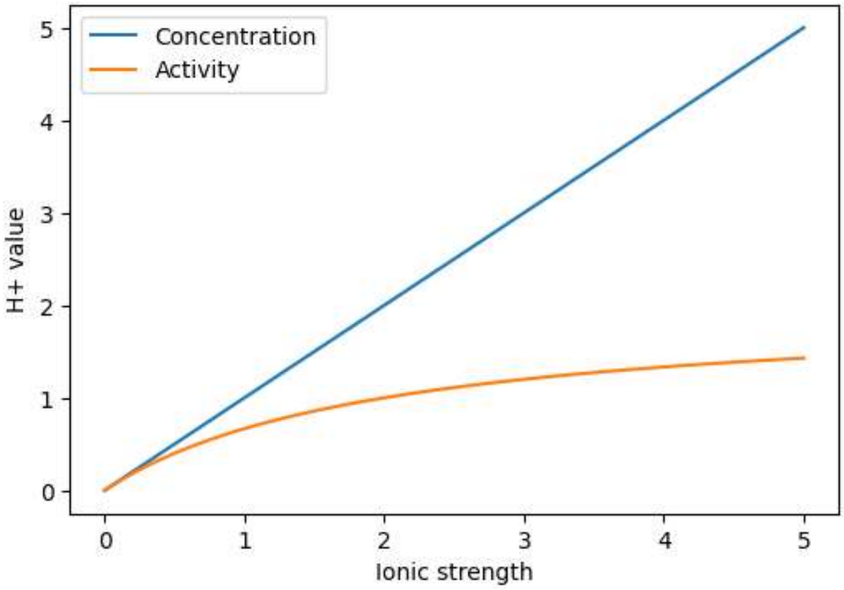


Figure 2. Effect of ionic strength on hydrogen ion activity and concentration in aqueous electrolyte systems. Adapted from Yang et al. (2023).

Figure 2 shows that the difference between concentration and activity becomes significant at high ionic strength. This behavior is typical of hydrometallurgical liquors and explains why titration and pH measurements may yield different acidity values.

3.2. Hydrolysis of metal ions

Hydrolyzable metal ions strongly affect acidity measurements. Ferric, aluminum, copper, zinc, and rare-earth ions undergo stepwise hydrolysis, consuming or releasing protons depending on pH.

Examples include

$Fe^{3+} \rightarrow FeOH^{2+} \rightarrow Fe(OH)_2^{+} \rightarrow Fe(OH)_3$ $Al^{3+} \rightarrow AlOH^{2+} \rightarrow Al(OH)_2^{+} \rightarrow Al(OH)_3$

These reactions occur during titration and may be interpreted as indicating the presence of free acid. As a result, the titration endpoint shifts, and total acidity is overestimated.

Hydrolysis also controls precipitation reactions such as jarosite, basic sulfates, and hydroxides, which consume acid during processing (Rudnik, 2025; Liu et al., 2022).

Metal hydrolysis is one of the main causes of disagreement between titration, pH, and speciation calculations.

3.3. Ion pairing and complexation

In sulfate, chloride, and nitrate systems, acid species exist in multiple forms. Hydrogen ions may be associated with anions or metal complexes.

Examples include

$HSO4^{-}$ / $SO4^{2-}$

HCl / Cl^{-} complexes

HF / F^{-} complexes

NO_3^- complexes

Ion pairing changes the amount of free hydrogen ions available in solution. During titration, these species dissociate, producing additional acidity.

Speciation studies show that complex formation strongly modifies titration curves and buffering regions (Zhou et al., 2024; Guo et al., 2023).

Figure 3 shows the main acid species present in multicomponent hydrometallurgical solutions and their relation to free acidity.

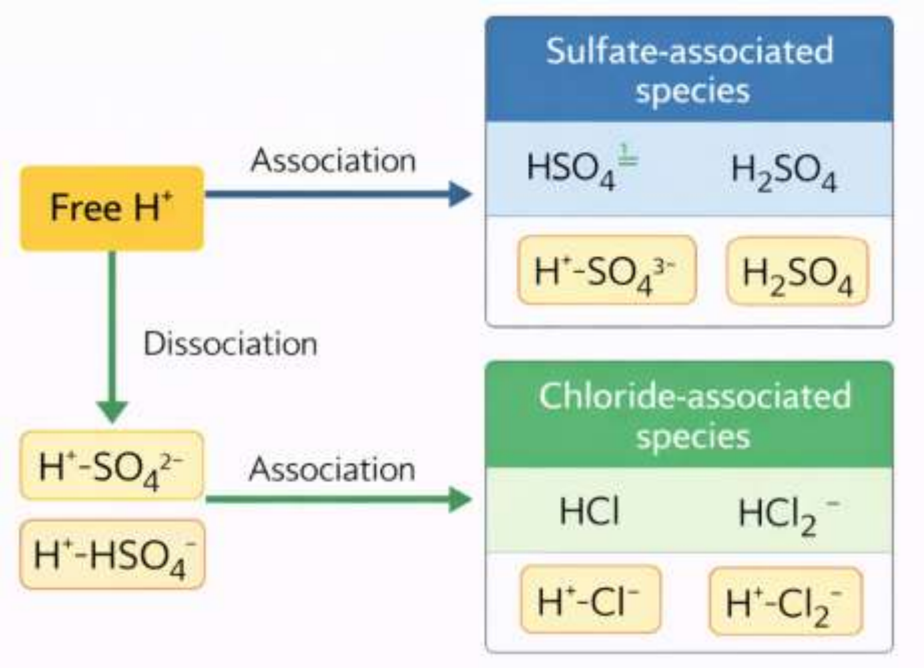


Figure 3. Ion pairing and complexation reactions affecting free acidity in sulfate–chloride systems. Adapted from Zhou et al. (2024).

The diagram shows that a considerable portion of the acidity in multicomponent electrolytes is stored in associated species rather than free hydrogen ions. Ion pairing with sulfate, chloride, and other ligands reduces the measurable free acidity but does not eliminate the proton reservoir. During titration, dissociation of these species may occur, leading to higher apparent acidity values. This effect is particularly relevant in hydrometallurgical liquors with high ionic strength and explains why different analytical methods often produce inconsistent results.

3.4. Acid consumption reactions

In industrial circuits, acid is consumed by neutralization, precipitation, and dissolution reactions. These reactions occur simultaneously with hydrolysis and complexation.

Typical reactions include

Neutralization with oxides or carbonates

Formation of gypsum

Formation of jarosite

Formation of basic sulfates

Formation of metal hydroxides

These reactions reduce free acidity without necessarily changing total acid concentration.

Acid consumption must therefore be interpreted using equilibrium chemistry, not only titration results (Liu et al., 2022; Rudnik, 2025). Table 1 summarizes the main reactions that affect free acidity in hydrometallurgical liquors.

Table 1. Main reactions affecting free acidity in hydrometallurgical systems. Adapted from Liu et al. (2022).

Reaction	Effect on free acidity	Effect on titration	Industrial relevance
$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$	Generates H^+ by hydrolysis	Causes delayed endpoint	Common in Cu, Ni, Zn liquors
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$	Releases acidity during titration	Multiple endpoints	Present in laterite and bauxite circuits
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	Stores acidity in paired form	Underestimation at low pH	Typical in sulfate leaching
$H^+ + Cl^- \rightleftharpoons HCl(aq)$	Association reduces free H^+	pH not reliable	Chloride leaching systems
$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$	Consumes acid	Lower titration value	Heap leach, neutralization
$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O$	Strong acid consumption	Fast endpoint shift	Neutralization circuits
$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$	Hydrolysis + precipitation	Endpoint instability	High Fe liquors
$Fe^{3+} + 2SO_4^{2-} + H^+ \rightarrow Fe(SO_4)_2^-$	Acid stored in complexes	Higher apparent acidity	High sulfate liquors
$Na^+ + HSO_4^- \rightleftharpoons NaHSO_4(aq)$	Ion pairing	Alters titration slope	High ionic strength
$REE^{3+} + H_2O \rightleftharpoons REEOH^{2+} + H^+$	Hydrolysis buffering	Slow endpoint	Rare earth leaching
Jarosite formation: $Fe^{3+} + SO_4^{2-} + K^+ + H_2O \rightarrow$ Jarosite $+ H^+$	Generates acidity	Variable results	Pressure leaching
Gypsum formation: $Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$	Removes sulfate	Changes equilibrium	Neutralization / SX

The reactions listed in Table 1 show that the measured acidity depends on the solution's chemical state. This explains why different analytical methods may yield different results for the same liquor.

3.5. Definition of free acidity in real systems

The term free acidity has no universal definition in hydrometallurgy. It may refer to: free hydrogen ions, titratable acidity, thermodynamic acidity, operational acidity, acid available for reaction,

In concentrated liquors, these quantities are not identical.

Analytical methods measure titratable acidity.

Speciation models calculate thermodynamic acidity.

Process control often requires operational acidity.

This difference explains why two laboratories may report different acidity values for the same solution.

Complexation, hydrolysis, and ion pairing must therefore be considered when defining free acidity in industrial systems (Yang et al., 2023; Lodeiro et al., 2020; Liu et al., 2022). Understanding these differences is essential before discussing analytical methods.

To clarify the difference between analytical and thermodynamic definitions, a schematic representation of acidity components in hydrometallurgical liquors is shown in Figure 4.

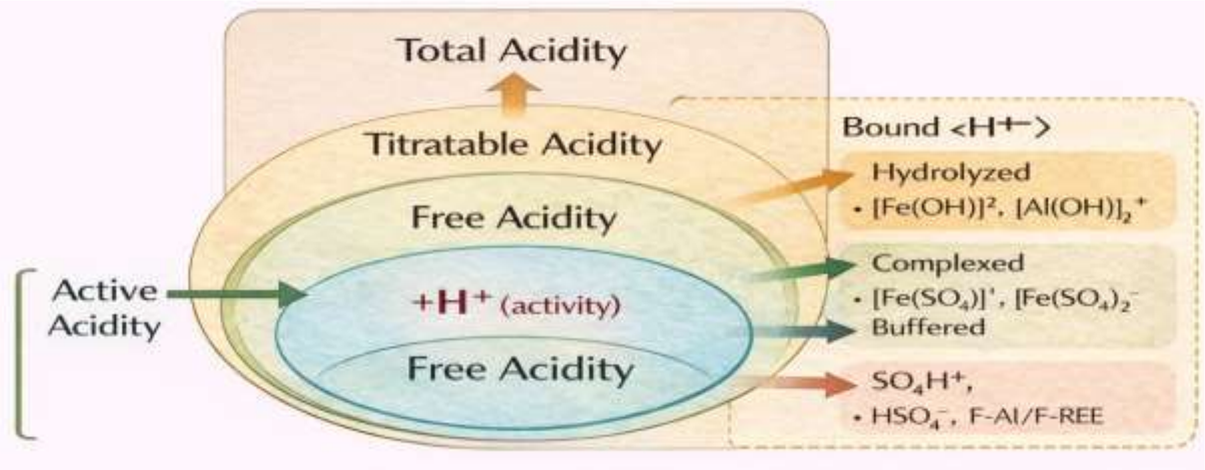


Figure 4. Relationship between total, titratable, free, and active acidity in complex hydrometallurgical liquors. Adapted from Yang et al. (2023) and Liu et al. (2022).

The diagram illustrates that the value obtained by titration does not necessarily correspond to hydrogen ion activity, especially in solutions containing hydrolyzing or complexing metals.

Thermodynamic approaches based on equilibrium calculations and speciation modeling are increasingly used to interpret acidity and alkalinity measurements in complex aqueous systems. These models quantify proton activity, metal hydrolysis reactions, and ion-pairing effects that simple analytical endpoints cannot capture (Yang et al., 2023).

Because free acidity depends on chemical speciation and equilibrium reactions, the analytical method used to determine it becomes critical. The following section reviews the main experimental and instrumental methods used to measure free acidity in hydrometallurgical liquors and discusses their advantages, limitations, and industrial applicability.

4. METHODS FOR THE DETERMINATION OF FREE ACIDITY

The determination of free acidity in hydrometallurgical liquors is mainly based on titrimetric methods. However, endpoint definition, hydrolysis reactions, and complexation effects can significantly affect results. The selected method must match the solution's chemistry.

This section reviews classical and advanced approaches, with emphasis on applicability to industrial systems.

4.1. Classical NaOH titration

Classical acid–base titration with NaOH remains the most widely used method. The endpoint is defined by pH measurement or color indicators. In dilute systems, the method is robust. In concentrated sulfate or chloride liquors, limitations appear.

Indicator-based endpoints may be inaccurate when buffering or metal hydrolysis occurs. Potentiometric endpoints improve reproducibility but do not eliminate interference from hydrolyzable metals (Sharma et al., 2022).

Titrimetric improvements in analytical chemistry have been reported to increase precision and reduce systematic bias (Bashir et al., 2024).

In complex matrices, titration curves may show multiple inflection points. These are often misinterpreted as distinct acid fractions.

4.2. Gran titration

Gran titration applies a mathematical transformation of the titration curve to determine the equivalence volume more accurately. The method reduces subjectivity in endpoint detection.

The principle is based on linearizing the pre-equivalence region. This enables improved determination of the concentration of strong acids in buffered systems.

Figure 5 illustrates the transformation applied in Gran titration and the linear region used to determine the equivalence point.

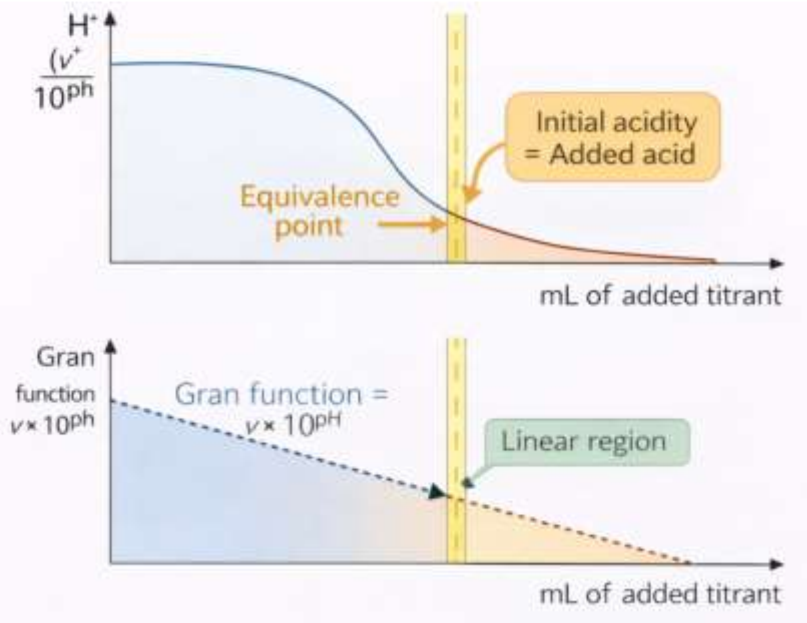


Figure 5. Principle of Gran titration and linearization of the pre-equivalence region. Adapted from Pereira and Santos (2025).

Linear extrapolation minimizes interpretation errors and provides an objective way to determine the equivalence point, especially in strong-acid systems with small pH changes. However, in metal-rich sulfate liquors, the Gran function may deviate from linearity due to hydrolysis of Fe^{3+}, Al^{3+}, and other multivalent ions, which consume hydroxide and alter the pre-equilibrium slope. This can produce discrepancies between the extrapolated intersection and the true free acidity. Distortions arising from ion pairing, sulfate buffering, and changes in activity coefficients at high ionic strength also affect accuracy. Therefore, the Gran method requires careful interpretation in hydrometallurgical liquors, especially when ferric or aluminum levels are high.

Although Gran titration improves precision, it does not eliminate interference from Fe^{3+} or Al^{3+} hydrolysis (Pereira & Santos, 2025). Deviations remain in high-concentration liquors.

4.3. Oxalate method

The oxalate method was developed to minimize $^{+}$ interference from Fe^{3}. Oxalate complexes ferric ions, suppressing hydrolysis during titration. (Verma, 2021; Mwiathi et al., 2022)

This masking step improves endpoint definition and reduces apparent acidity caused by metal hydrolysis. Figure 6 shows the masking mechanism of Fe^{3+} by oxalate during titration.

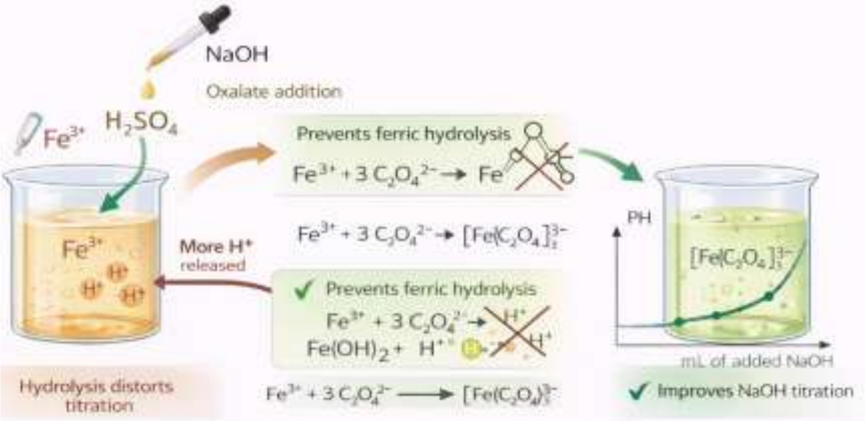


Figure 6. Fe^{3+} masking by oxalate during the titration of sulfuric liquors. Adapted from Pereira et al. (2025).

Complex formation stabilizes ferric ions in solution and suppresses hydrolysis reactions that would otherwise release additional protons during titration. By preventing the formation of Fe(OH)$^{2+}$, Fe(OH)$_2^+$, and polymeric species, the oxalate ligand reduces secondary hydroxide consumption and sharpens the definition of the equivalence point. This effect is particularly important in sulfate liquors with high Fe^{3+}/H$^+$ ratios, where classical NaOH titration often overestimates free acidity. The use of oxalate also minimizes buffering from ferric hydrolysis and reduces variability between repeated measurements. Validation studies on industrial sulfuric liquors showed improved precision and better agreement with process mass-balance data compared with conventional titration methods (Wu et al., 2020; Pereira et al., 2025).

Validation studies show improved precision compared with conventional titration in sulfate systems (Pereira et al., 2025).

4.4. Ba(OH)$_2$ method

Ba(OH)$_2$ titration reduces sulfate interference by forming BaSO$_4$. This may simplify endpoint detection in high-sulfate media.

However, precipitation reactions may trap acid species and distort stoichiometry, limiting the method to specific matrices.

4.5. Potentiometric titration

Potentiometric titration improves endpoint detection compared with indicators. Glass electrodes measure potential continuously, enabling derivative analysis. Coulometric and electrochemical variants have also been reported for the indirect determination of metal–acid systems (Masac et al., 2021).

Despite improved detection, potentiometric titration remains sensitive to hydrolysis and complexation. Figure 7 shows how metal hydrolysis and complex formation affect the apparent acidity measured during titration. In multicomponent hydrometallurgical liquors, several parallel reactions may occur simultaneously, thereby modifying the concentration of free hydrogen ions during the analytical procedure.

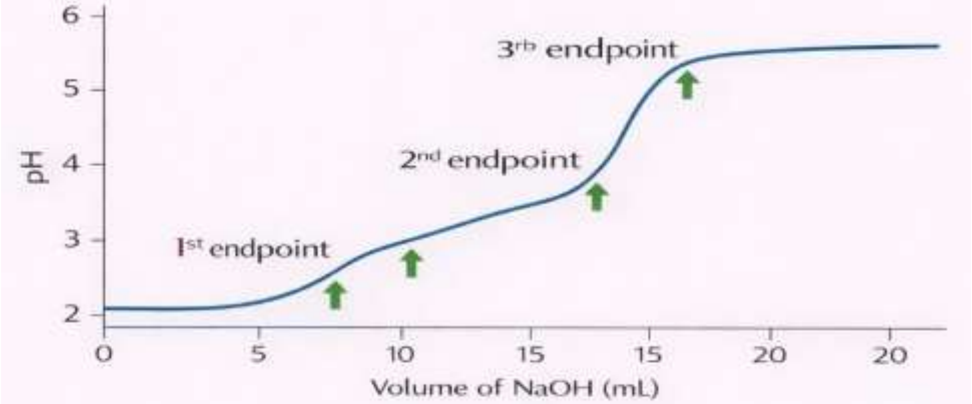


Figure 7. Typical potentiometric titration curve showing multiple endpoints caused by hydrolysis and buffering reactions. Adapted from Bashir et al. (2024), Liu et al. (2022), Yang et al. (2023), Zhou et al. (2024) and Sharma et al. (2022).

The diagram shows that hydrolysis, ion pairing, and complex formation may either release or consume protons depending on solution composition. As a result, the acidity determined by titration does not necessarily correspond to the thermodynamic hydrogen ion activity. These effects are particularly significant in liquors containing Fe^{3+}, Al^{3+}, rare earth elements, sulfate, fluoride, or chloride ligands, where buffering and association reactions strongly influence the endpoint..

4.6. Automatic titrators

Automated titration systems improve repeatability and data logging. They reduce operator bias.

Nevertheless, automation does not correct chemical interferences. It only standardizes execution. Method validation must still account for metal hydrolysis and buffering effects (Bashir et al., 2024).

4.7. Inline probes

Inline pH probes and electrochemical sensors enable real-time monitoring. However, pH alone does not represent free acidity in strong electrolytes.

Industrial deployment requires calibration against titration or speciation models.

4.8. Modeling-based methods

Speciation modeling tools like PHREEQC, HSC Chemistry, Pitzer, and SIT estimate hydrogen ion activity and acid species distribution. These measure thermodynamic acidity, not operational titratable acidity. Model-based interpretation clarifies discrepancies. Table 2 compares methods for determining free acidity.

Table 2. Comparison of analytical methods for the determination of free acidity in hydrometallurgical liquors. Adapted from Sharma et al. (2022); Pereira and Santos (2025); Pereira et al. (2025).

Method	Principle	Advantages	Limitations	Suitable systems
Classical NaOH titration	Neutralization of H^+ with base using indicator or pH endpoint	Simple, fast, low cost	Affected by hydrolysis, buffering, multiple endpoints	Dilute solutions, low metal content
Gran titration	Linearization of pre-equivalence region of potentiometric titration	Higher precision, reduced endpoint error	Distorted by metal hydrolysis and complexation	Moderate ionic strength, sulfate systems
Oxalate method	Complexation of Fe^{3+} to suppress hydrolysis before titration	High precision in Fe-rich liquors	Requires additional reagent, limited to specific systems	Sulfate liquors, Fe^{3+}-rich solutions
$Ba(OH)_2$ method	Precipitation of sulfate before titration	Reduces sulfate interference	Additional step, not universal	High sulfate systems
Potentiometric titration	pH monitoring during titration	Objective endpoint detection	Activity effects at high ionic strength	Laboratory control
Automatic titrators	Automated potentiometric titration	High reproducibility, low operator error	Requires calibration and maintenance	Process laboratories
Inline probes	Continuous pH / conductivity / spectroscopy	Real-time control	Measures activity, not free acidity	Process monitoring
Speciation modeling (PHREEQC / HSC / Pitzer / SIT)	Thermodynamic calculation of species and activity	Accurate in complex systems	Requires data and validation	High ionic strength, multicomponent liquors

The comparison shows no one-size-fits-all method. Method choice must consider ionic strength, metal concentration, and sulfate or chloride levels. In concentrated hydrometallurgical solutions, classical titration may overestimate acidity due to hydrolysis and ion pairing, while masking, Gran transformation, or speciation modeling may be more accurate. These limitations explain the variability in industrial acidity measurements (Sharma et al., 2022; Pereira & Santos, 2025; Pereira et al., 2025).

While analytical techniques attempt to isolate free acidity, their performance is strongly controlled by matrix composition. The next section examines the main interferences observed in industrial liquors and how they affect acidity determination and process control.

5. INTERFERENCES IN INDUSTRIAL LIQUORS

Industrial liquors may contain several interfering species simultaneously. Figure 8 summarizes the main sources of error in free acidity determination.

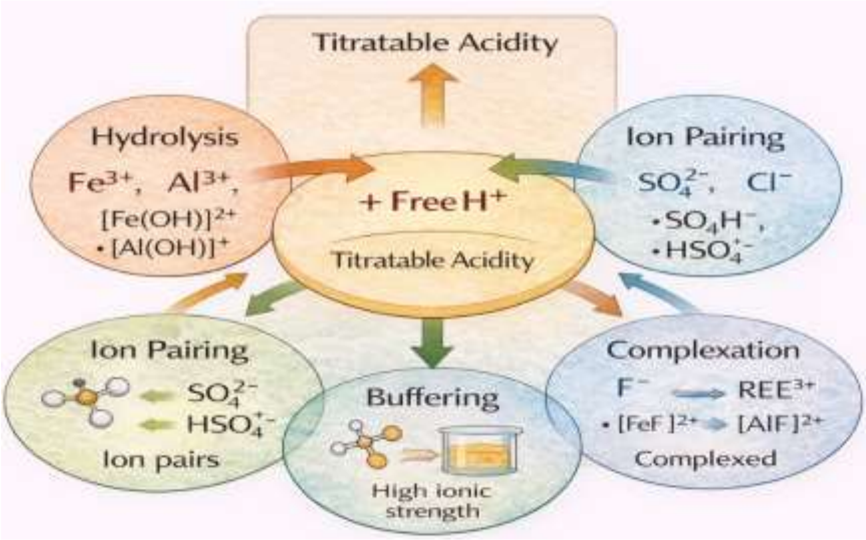


Figure 8. Main sources of interference in free acidity determination in hydrometallurgical liquors. Adapted from Liu et al. (2022), Zhou et al. (2024), and Rudnik (2025).

The figure shows that errors in acidity determination are usually caused by hydrolysis, complexation, or buffering reactions rather than by analytical limitations alone. Industrial hydrometallurgical liquors rarely behave as simple aqueous acid solutions.

High ionic strength, multivalent metals, hydrolysis reactions, and complexation strongly influence the chemical definition of acidity and the analytical response observed during titration. Consequently, the measured free acidity may differ from the thermodynamic hydrogen-ion activity, particularly in sulfate, chloride, fluoride, and mixed-electrolyte systems (Liu et al., 2022; Arnold et al., 2022; Zhou et al., 2024; Yang et al., 2023).

Interferences become more severe in real process liquors, where iron, aluminum, rare-earth elements, and transition metals coexist at high concentrations. These species undergo hydrolysis, ion pairing, and complex formation, which may consume or release protons during titration and thereby distort the analytical endpoint (Lodeiro et al., 2020; Chernyaev et al., 2022; Guo et al., 2023; Rudnik, 2025).

Table 3 lists the main interfering species found in industrial liquors and their effect on free acidity determination.

Table 3. Main interferences affecting free acidity determination in hydrometallurgical liquors. Adapted from Liu et al. (2022); Zhou et al. (2024); Yang et al. (2023); Rudnik (2025).

System	Main interfering species	Mechanism	Effect on acidity measurement	Typical processes
Iron-rich	Fe^{3+}, Fe^{2+}	Hydrolysis / complexation	Apparent increase in acidity	HPAL, SX, leaching
Aluminum-rich	Al^{3+}	Hydrolysis / polymerization	Buffering effect	Bauxite, REE
Fluoride	HF, AlF_x, FeF_x	Complex formation	Hidden acidity	REE, Ti, Nb
Chloride	Cl^{-} complexes	Ion pairing	Activity change	Cu, Ni, Co
Sulfate	HSO_4^{-} / SO_4^{2-}	Association	Delayed dissociation	Most hydromet
Rare earth	REE^{3+}	Strong hydrolysis	Endpoint shift	REE refining
Battery recycling	Ni^{2+}, Co^{2+}, Mn^{2+}	Complexation	Variable endpoint	LIB recycling
Heap / HPAL / SX	Mixed ions	Multiple equilibria	Non-linear titration	Cu, Ni, Co

The data in Table 3 show that acidity measurement in industrial liquors depends not only on proton concentration but also on metal speciation and ionic interactions. These effects explain the poor reproducibility often observed when different analytical methods are applied to the same solution (Dutta et al., 2021).

5.1. Iron-rich liquors

Iron is one of the most important sources of interference in acidity determination.

Ferric ions undergo extensive hydrolysis according to reactions such as:

$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$

During titration, these reactions may release protons, causing an apparent increase in acidity. In sulfate media, additional association reactions with SO_4^{2-} further complicate the system (Liu et al., 2022; Li et al., 2024; Zhou et al., 2024).

In strongly acidic leach liquors, iron hydrolysis may occur close to the titration endpoint, producing curvature in the potentiometric curve and affecting the equivalence point.

5.2. Aluminum-rich liquors

Aluminum behaves similarly to ferric iron but with different hydrolysis constants.

Al^{3+} forms hydroxo-complexes and polymeric species that act as buffers during titration. This buffering effect makes endpoint detection difficult, especially in high-aluminum sulfate liquors (Lodeiro et al., 2020; Mwiathi et al., 2022).

These effects are common in bauxite processing, rare earth leaching, and aluminum-bearing ores.

5.3. Fluoride systems

Fluoride forms strong complexes with Fe^{3+}, Al^{3+}, and rare earth ions.

These complexes reduce the concentration of free hydrogen ions while still contributing to titratable acidity. As a result, pH measurement alone may underestimate acidity, while titration may overestimate it (Guo et al., 2023).

Fluoride systems are common in rare-earth processing, titanium production, and niobium or tantalum hydrometallurgy.

5.4. Chloride systems

Chloride media are common in copper, nickel, and cobalt hydrometallurgy. High chloride levels increase ionic strength, promote ion pairing, and influence activity coefficients, shifting titration curves (Liu et al., 2022). In concentrated chloride solutions, the gap between hydrogen ion concentration and activity makes pH unreliable for indicating free acidity.

5.5. High sulfate systems

Sulfate systems are the most common in hydrometallurgy.

The equilibrium between H_2SO_4, HSO_4^-, and SO_4^{2-} leads to partial association of hydrogen ions, which may dissociate during titration and contribute to apparent acidity (Yang et al., 2023).

This effect is particularly important in leach liquors, solvent extraction raffinate, and electrolyte solutions.

5.6. Rare earth liquors

Rare earth ions exhibit strong hydrolysis and complexation behavior.

REE^{3+} species may release protons during titration, causing large deviations between true acidity and measured acidity.

These effects are well known in sulfate and chloride rare earth liquors and often require masking agents or speciation modeling for accurate acidity determination (Zhou et al., 2024).

5.7. Battery recycling liquors

Battery recycling solutions have high concentrations of Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, and Al^{3+}, which form complexes with various ligands, creating multiple equilibria that influence titration curves and endpoint detection (Rudnik, 2025). Due to this complexity, acidity measurement often needs potentiometric titration with chemical modeling.

5.8. HPAL, SX, and heap leach liquors

High-pressure acid leaching (HPAL), solvent extraction (SX), and heap leaching produce concentrated multicomponent solutions containing sulfate, chloride, iron, aluminum, and transition metals, causing significant deviations between measured and actual acidity (Liu et al., 2022; Yang et al., 2023).

In these systems, classical titration alone is often insufficient, and combined methods such as masking, the Gran transformation, or thermodynamic modeling are required. Figure 9 summarizes the key chemical mechanisms responsible for interference in acidity determination in industrial liquors.

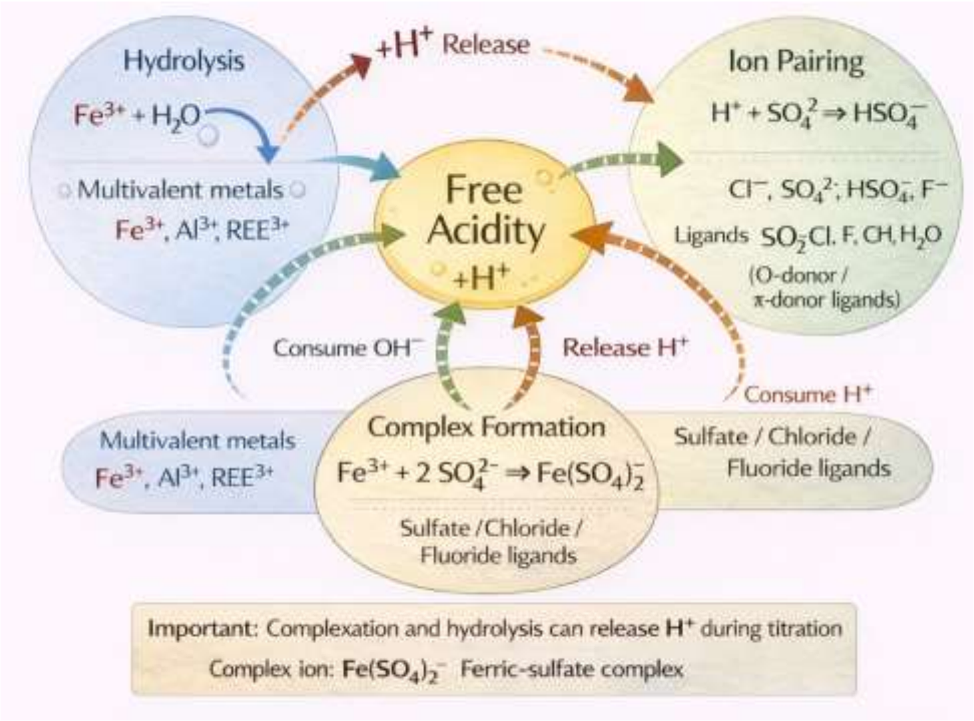


Figure 9. Main interference mechanisms affecting free acidity determination in hydrometallurgical liquors. Adapted from Liu et al. (2022); Zhou et al. (2024); Yang et al. (2023).

The diagram shows that hydrolysis, ion pairing, and complex formation may either consume or release protons during titration. These effects explain why a single analytical procedure cannot define free acidity.

The presence of multiple interferences in real liquors makes the choice of analytical method critical. The following section compares the main methods for determining free acidity and discusses their applicability across different hydrometallurgical systems.

6. COMPARISON OF ANALYTICAL METHODS

Different analytical methods used to determine free acidity may produce significantly different results when applied to industrial hydrometallurgical liquors. The discrepancy is caused by hydrolysis reactions, ion pairing, precipitation, and buffering effects that occur during titration. Because each method responds to a different chemical definition of acidity, the selection of the analytical procedure must consider the composition of the solution and the purpose of the measurement.

In industrial systems such as acid leaching, solvent extraction, recycling, and wastewater treatment, inaccurate acidity determination may affect process stability, metal recovery, and reagent consumption. Reviews on hydrometallurgical processing and acid recovery show that reliable chemical control requires analytical methods compatible with high ionic strength and multicomponent solutions (Wang et al., 2023; Kumar Vinayak et al., 2025; Dobre et al., 2024).

The most common methods include classical titration, Gran titration, oxalate masking, $Ba(OH)_2$ titration, potentiometric titration, automated titrators, inline probes, and speciation modeling. Each method measures a different operational definition of acidity.

Table 4 compares the primary analytical methods used to determine free acidity in hydrometallurgical liquors and highlights their applicability to industrial systems.

Table 4. Comparison of analytical methods for the determination of free acidity in hydrometallurgical solutions. Adapted from Wang et al. (2023), Kumar Vinayak et al. (2025), and Dobre et al. (2024).

Method	Principle	Advantages	Limitations	Industrial use
NaOH titration	Neutralization to defined endpoint	Simple, low cost	Strong interference from hydrolysis and complexation	General laboratory use
Gran titration	Linearization of pre-equivalence region	Improved endpoint detection	Distorted by hydrolysis and ion pairing	Sulfate liquors
Oxalate method	Masking of Fe^{3+} by complexation	High precision in Fe-rich systems	Requires additional reagent	Iron-rich liquors
$Ba(OH)_2$ method	Precipitation of sulfate as $BaSO_4$	Clear endpoint in sulfate media	Errors due to co-precipitation	High-sulfate solutions
Potentiometric titration	Electrode potential monitoring	Accurate endpoint detection	Does not eliminate hydrolysis effects	Laboratory / plant
Automatic titrator	Controlled potentiometric titration	High reproducibility	Same chemical limitations	Quality control
Inline probe	Continuous pH measurement	Real-time monitoring	Does not measure free acidity	Process control
Speciation modeling	Thermodynamic equilibrium calculation	Predictive capability	Requires reliable data	Research / process design

The comparison shows that no single method is universally applicable. Classical titration is simple but sensitive to hydrolysis. Gran titration improves endpoint detection but may fail in iron-rich liquors. Oxalate masking reduces ferric interference and is more reliable in sulfate media. Modeling-based approaches provide thermodynamic interpretation but require accurate input data. Similar conclusions have been reported in reviews of hydrometallurgical processing, acid recovery, and solution treatment (Wang et al., 2023; Kumar Vinayak et al., 2025; Dobre et al., 2024).

Errors in acidity determination are not only analytical issues but may directly affect industrial performance. The next section discusses how incorrect measurement of free acidity influences process control, reagent consumption, precipitation behavior, and overall hydrometallurgical efficiency.

7. IMPACT OF ACIDITY MEASUREMENT ERRORS ON PROCESS CONTROL

Errors in determining free acidity can directly affect hydrometallurgical process performance. In industrial circuits, acidity controls dissolution rate, precipitation, solvent extraction stability, corrosion, and reagent consumption. When the analytical value does not reflect the actual free acid available in solution, the process may be operated outside the optimal range (Pereira & Barbosa, 2017).

Incorrect acidity measurement may lead to over-acidification, insufficient neutralization, scaling, reduced metal recovery, or excessive reagent consumption. These effects are particularly relevant in heap leaching, pressure leaching, solvent extraction, electrochemical recovery, and recycling circuits (Thomas, 2021; Harvey et al., 2025; Ibrahim et al., 2025).

Hydrometallurgical systems often operate near equilibrium limits. Small errors in acidity can shift speciation, alter precipitation conditions, and change metal distribution between phases. The consequences of incorrect acidity measurement propagate through several unit operations, as summarized in Figure 10.

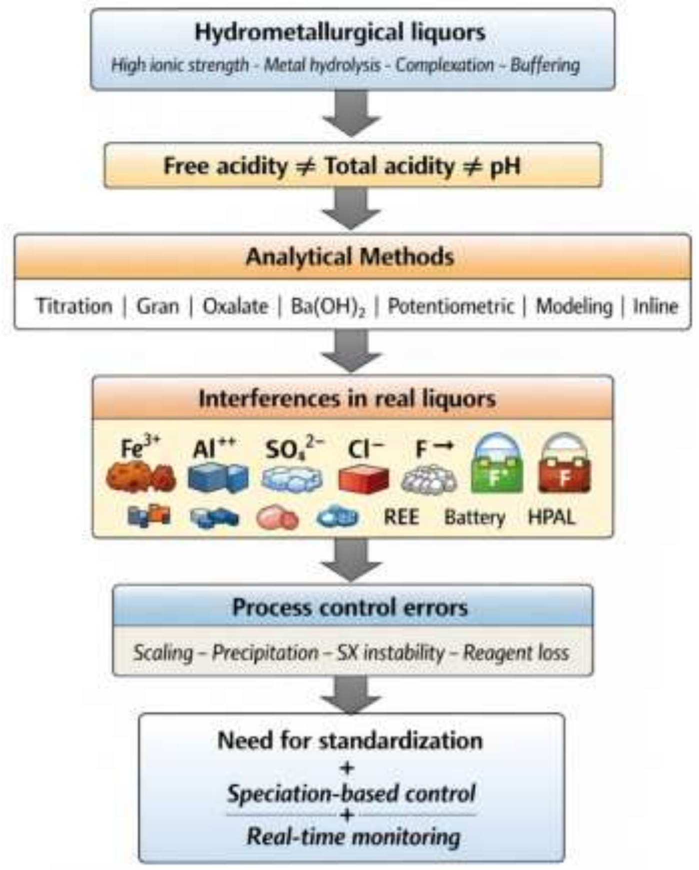


Figure 10. Consequences of incorrect free acidity determination on hydrometallurgical process stability. Adapted from Thomas (2021) and Ibrahim et al. (2025).

This scheme highlights that small analytical errors may generate large operational problems, especially in high-acid circuits.

7.1. Over-acidification and reagent consumption

Overestimating free acidity leads to excessive acid addition. This increases operating costs and may dissolve unwanted gangue minerals. Carbonates, silicates, and secondary precipitates consume acid without contributing to metal recovery. Studies of heap leaching show that inaccurate estimation of acid consumption results in inefficient operation and higher reagent demand (Thomas, 2021). Excess acid also increases ionic strength and may destabilize downstream separation steps.

7.2. Precipitation failure and hydrolysis control

Many hydrometallurgical steps rely on controlled hydrolysis or precipitation. These include iron and aluminum removal, jarosite formation, gypsum precipitation, and rare-earth separation.

If free acidity is underestimated, precipitation may begin prematurely.

If free acidity is overestimated, precipitation may not occur. Incorrect acidity values therefore affect solid–liquid separation and impurity control (Silva et al., 2020).

7.3. Solvent extraction instability

Solvent extraction is highly sensitive to acidity. Distribution coefficients depend on proton concentration and on complex formation.

Incorrect acidity measurement may cause phase disengagement problems, third phase formation, loss of selectivity, and organic degradation

These effects are common in copper, nickel, cobalt, and rare-earth circuits.

Acid control is also critical during acid stream recycling or in closed-loop operations (Wang et al., 2023).

7.4. Scaling, corrosion, and equipment damage

Acidity influences scaling reactions such as gypsum, basic sulfates, and hydroxides.

Incorrect acidity measurement may lead to deposition inside pipes, reactors, and heat exchangers.

Corrosion rate also depends on acid concentration. Excess acid increases material degradation, while insufficient acid may promote precipitation (Nogueira et al., 2020).

Electrochemical acid recovery studies show that precise pH and acidity control reduce scaling and improve process stability (Ibrahim et al., 2025). Figure 11 summarizes the primary process problems caused by inaccurate determination of free acidity in hydrometallurgical circuits.

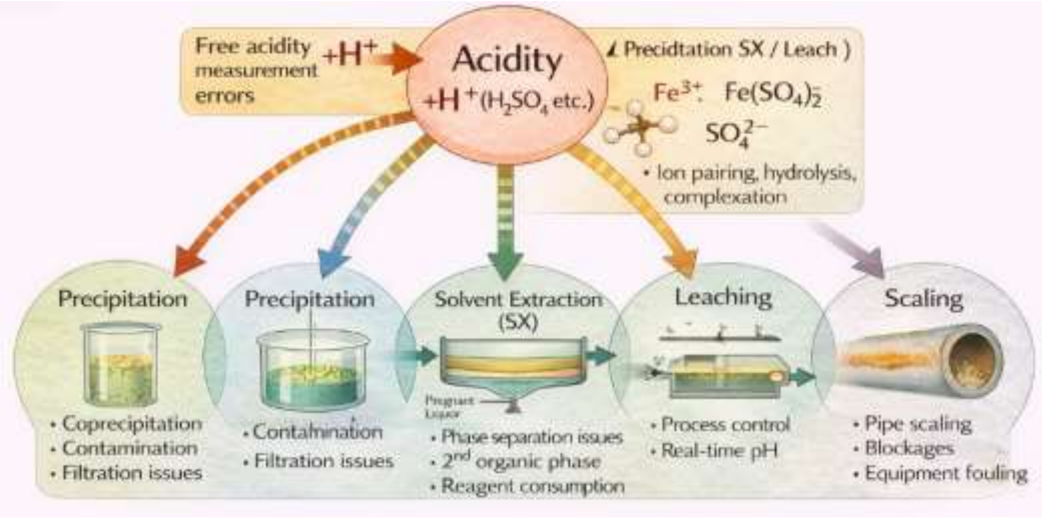


Figure 11. Effect of free acidity measurement errors on hydrometallurgical process control. Adapted from Thomas (2021), Harvey et al. (2025), and Ibrahim et al. (2025).

The diagram shows that acidity affects several unit operations at once. An analytical error may propagate through the circuit, causing multiple operational problems.

7.5. Process modeling and dynamic control

Modern hydrometallurgical plants increasingly rely on dynamic models to control acid balance. These models require reliable analytical data. Simulation studies of heap leach operations show that inaccurate acidity inputs lead to incorrect predictions of metal recovery and acid consumption (Harvey et al., 2025).

Model-based control is effective only when the measured acidity reflects the actual chemical state of the solution (Canales et al., 2024). Table 5 summarizes the main industrial consequences of inaccurate acidity determination.

Table 5. Industrial consequences of errors in free acidity determination. Adapted from Thomas (2021), Harvey et al. (2025), and Ibrahim et al. (2025).

Analytical error	Chemical mechanism	Process effect	Typical circuit
Overestimated acidity	Hydrolysis	Over-acidification	Heap leach
Underestimated acidity	Complexation	Precipitation failure	Iron removal
Wrong endpoint	Buffering	SX instability	Cu SX
pH only	Activity ignored	Scaling	HPAL
No masking	Fe^{3+} hydrolysis	Acid excess	Sulfate liquor

The table shows that analytical errors may affect not only laboratory results but also plant operation, reagent consumption, and equipment integrity. Reliable determination of free acidity is therefore essential for process control.

The effects discussed above are supported by experimental and industrial studies reported in the literature. The following section presents selected case studies in which different methods of acidity determination produced different results and led to different process interpretations.

8. CASE STUDIES FROM LITERATURE

Differences between analytical methods become more evident when applied to real hydrometallurgical systems. Laboratory titration procedures often assume simple acid solutions, while industrial liquors contain multiple metals, complexing ions, and precipitation reactions. As a result, the measured acidity may depend strongly on the method used (Moghadam et al., 2026).

Several studies in leaching, pressure leaching, chloride systems, battery recycling, and acid recovery demonstrate that pH, classical titration, and speciation modeling may lead to different interpretations of the same solution chemistry (Godirilwe et al., 2021; Karppinen et al., 2024; Lim et al., 2025).

These case studies highlight the need to relate analytical results to the solution's chemical state rather than to a single numerical acidity value.

8.1. Industrial leaching systems

In pressure leaching of complex sulfide ores, iron hydrolysis and chloride complexation change the effective acidity during the reaction. Studies on high-pressure leaching of copper ores showed that acid consumption cannot be predicted only from titration because hydrolysis reactions release or consume protons during the process (Godirilwe et al., 2021).

Similar effects were observed in chloride–ferric systems used for arsenic immobilization, where acidity controls both dissolution and precipitation equilibria (Godirilwe et al., 2024).

In atmospheric leaching of sulfide tailings, oxidants, metal ions, and sulfate concentration modify speciation, leading to differences between measured and effective acidity (Karppinen et al., 2024).

Heap and dump leaching studies also show that gangue minerals consume acid in ways not detected by simple titration methods (Lizama, 2021).

8.2. Influence of metal ions and impurities

Several hydrometallurgical studies demonstrate that dissolved metals strongly affect acidity measurements. In oxygen pressure leaching of zinc oxide dust, the presence of iron and silicon changed the acid balance and altered the interpretation of titration data (Bai et al., 2025).

Fluoride, chloride, and sulfate species may also modify proton activity and buffering behavior. In magnesium recovery from serpentine tailings, fluoride addition changed reaction mechanisms and acid consumption, affecting the calculated acidity (Peng et al., 2021).

Copper smelting waste acid treatment shows similar behavior, where competing reactions between Cu^{2+}, As species, and sulfate alter the effective acidity of the solution (Sun et al., 2024).

8.3. Chloride and hydrochloric systems

Hydrochloric leaching routes are particularly sensitive to the definition of acidity. In hydrometallurgical production of TiO_2 from ilmenite, controlling hydrochloric acid concentration determines dissolution rate, impurity behavior, and precipitation stability (Dong et al., 2025).

Because chloride forms strong complexes with metal ions, titration results may not reflect the actual free acid available for reaction. This system illustrates the limitation of pH-based control in concentrated electrolytes.

8.4. Recycling and secondary resources

Battery recycling, waste acid treatment, and secondary metal recovery often involve highly complex liquors. These solutions contain multiple metals, organic ligands, and high concentrations of sulfate or chloride.

Review studies on lithium-ion battery recycling show that acid balance must be evaluated using speciation models rather than relying solely on titration, because hydrolysis and complexation control metal recovery (Das et al. 2023, Lim et al. 2025).

Similar observations were reported in hydrometallurgical recovery of metals from waste solutions, where phase separation and crystallization depend on accurate control of acidity (Wang et al., 2023).

Figure 12 compares the interpretations of acidity obtained from pH measurements, titration, and speciation modeling in multicomponent hydrometallurgical systems.

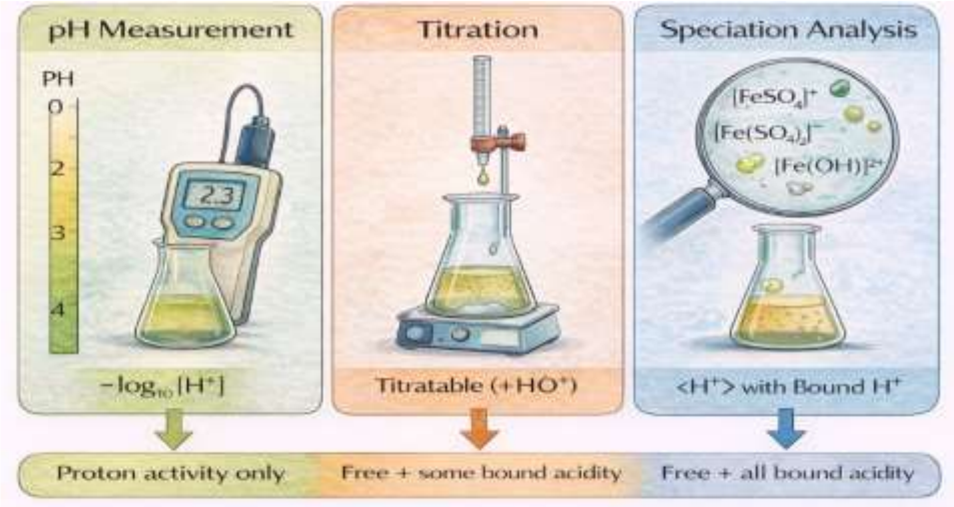


Figure 12. Comparison between pH, titration, and speciation-based interpretation of acidity in hydrometallurgical solutions. Adapted from Karppinen et al. (2024) and Lim et al. (2025).

The diagram shows that different analytical approaches may yield different conclusions about the same solution. This explains why process control based solely on pH or titration may fail in complex liquors.

8.5. Laboratory vs industrial measurements

Laboratory experiments use simplified solutions, whereas industrial liquors contain solids, colloids, and multiple ionic species. In bioleaching and galvanic leaching, acidity varies during the reactions due to mineral and redox changes, making endpoint detection difficult (Ma et al., 2021). Lab-measured acidity often can't be directly applied in plant operations.

Figure 13 illustrates the difference between acidity measured in laboratory solutions and that observed in industrial liquors.

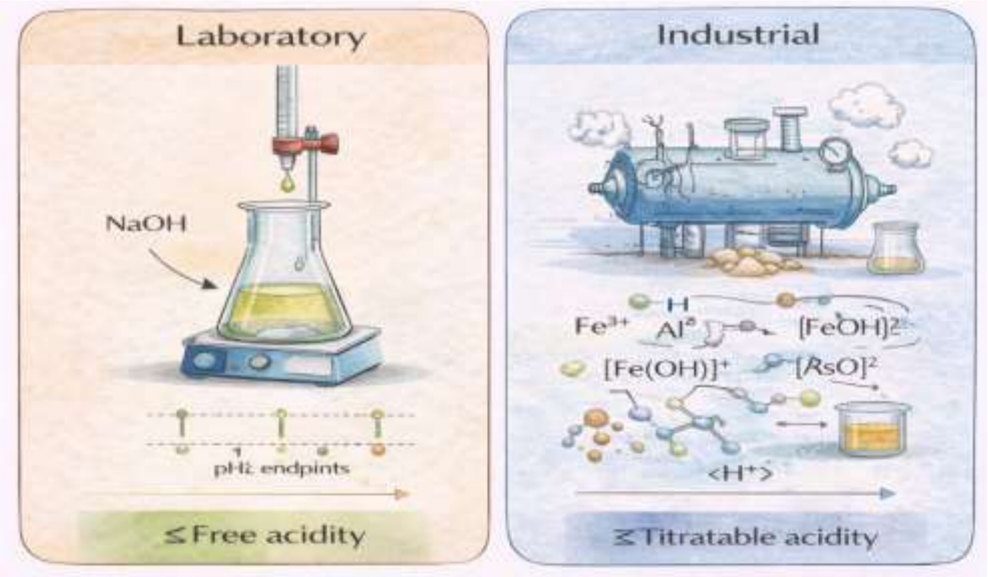


Figure 13. Difference between laboratory and industrial acidity behavior in hydrometallurgical systems. Adapted from Bai et al. (2025) and Dong et al. (2025).

Industrial solutions show buffering, hydrolysis, and precipitation effects that are not present in simplified laboratory systems.

Table 6 summarizes selected case studies where the determination of acidity affected the interpretation of hydrometallurgical results.

Table 6. Case studies showing the influence of acidity determination method on hydrometallurgical interpretation. Adapted from Bai et al. (2025), Godirilwe et al. (2021), Dong et al. (2025), Lim et al. (2025), and Sun et al. (2024)

System	Method used	Problem observed	Cause
Heap leach	Titration	Acid excess	Gangue reaction
HPAL	pH	Precipitation error	Hydrolysis
Chloride leach	Titration	Wrong endpoint	Complexation
Battery recycle	pH	SX instability	Speciation
Waste acid	Titration	Acid imbalance	Multiple ions

The case studies confirm that the definition of free acidity depends on solution chemistry, analytical method, and process conditions. These differences explain the lack of consistency in reported acidity values.

The results discussed above show that the absence of a universal definition of free acidity leads to inconsistent analytical results and operational difficulties. This limitation highlights the need for standardized procedures and clear reporting criteria, as discussed in the next section.

9. NEED FOR STANDARDIZATION

The previous sections show that the concept of free acidity is not uniform in hydrometallurgical practice. Different plants use different titration procedures, different endpoints, and different definitions of acidity. As a result, acidity values reported in the literature are often not directly comparable.

Unlike other analytical parameters, there is no universal standard for the determination of free acidity in process liquors. No ASTM or ISO method specifically defines how acidity should be measured in multicomponent hydrometallurgical solutions. In practice, each operation adopts its own procedure, often based on historical experience rather than chemical definition. (Jianxun & Haiqiong, 2025)

Similar problems have been reported in other analytical fields where different national and industrial standards coexist, producing inconsistent results. Comparative studies of analytical standards show that the absence of harmonized procedures leads to systematic differences in measured values and difficulties in data comparison (Jianxun & Haiqiong, 2025).

This situation is also observed in hydrometallurgy, where the same solution may give different acidity values depending on the method used.

9.1. Lack of a universal definition of free acidity

The term free acidity is used with different meanings in the literature. In some cases, it refers to titratable acid. In others, it refers to hydrogen ion activity. In industrial practice, it may represent the acid available for reaction.

These definitions are not equivalent. Hydrolysis, ion pairing, and complexation may consume or release protons during titration, causing the measured acidity to differ from the thermodynamic acidity.

Because of this, reporting only the acidity value without the method used may lead to incorrect interpretation of process conditions.

9.2. Absence of standardized analytical procedures

Most hydrometallurgical plants use modified titration methods, often without detailed description of endpoint, indicator, or masking agents.

Gran titration, oxalate masking, and potentiometric titration may produce different results for the same solution. Differences become larger in liquors containing Fe^{3+}, Al^{3+}, fluoride, or high sulfate concentration.

In other analytical fields, standardization has been achieved by defining the method, endpoint, and reporting format. Similar approaches are required for acidity determination (Jianxun & Haiqiong, 2025). Figure 14 shows how different analytical definitions of acidity yield different reported values and why standardization is necessary.

Figure 14. Effect of different analytical definitions on reported acidity values and need for standardization. Adapted from Jianxun and Haiqiong (2025).

The diagram shows that the lack of a common definition prevents direct comparison between laboratories and industrial plants. Standardization must include both the analytical method and the chemical definition.

9.3. Proposed definition of free acidity

Based on the analysis presented in this review, free acidity in hydrometallurgical systems should be defined as:

Free acidity = hydrogen ions available for reaction under specified analytical conditions.

This definition requires that the analytical method be reported together with the result.

Recommended reporting should include

- method used
- titrant
- endpoint definition
- masking agents
- temperature
- ionic strength (if known)
- presence of metals or fluoride

Without this information, acidity values cannot be compared.

9.4. Recommended analytical methods

Different methods may be appropriate for different systems.

Suggested guidelines

Low metal concentration
→ classical titration or potentiometric titration
High Fe^{3+} or Al^{3+}
→ oxalate masking method
High ionic strength
→ Gran titration or modeling
Complex liquors
→ speciation modeling + titration

Process control
→ automatic titration or inline sensors

These recommendations are not strict rules, but they provide a basis for harmonization.

Table 6 proposes a minimum set of information that should be reported when free acidity is measured in hydrometallurgical studies.

Table 7. Recommended reporting rules for free acidity determination in hydrometallurgical systems. Adapted from Jianxun and Haiqiong (2025).

Item	Requirement
Method	Must be specified
Titrant	Must be specified
Endpoint	Must be defined
Masking agent	Must be reported
Temperature	Recommended
Ionic strength	Recommended
Metal concentration	Recommended
Fluoride / chloride	Recommended
Model used	If applicable

Standardized reporting rules would enable comparisons across studies and improve the reproducibility of hydrometallurgical data. Clear identification of the analytical method, chemical environment, and operating conditions is essential to distinguish among free, titratable, and thermodynamically defined acidity. Without this minimum dataset, reported acidity values may reflect methodological artifacts rather than true solution chemistry.

Standardization alone will not solve all the limitations of acidity determination. New analytical tools, real-time sensors, and speciation modeling are increasingly used to improve process control. These developments are discussed in the next section.

10. FUTURE TRENDS

The limitations discussed in the previous sections indicate that conventional titration methods are insufficient for modern hydrometallurgical operations. Increasing process complexity requires real-time monitoring, better chemical modeling, and integration with automated control systems.

Recent developments include inline analytical sensors, chemometric data processing, speciation modeling, and digital twins. These tools allow continuous estimation of effective acidity instead of periodic laboratory measurements (Khalid & Santos 2025).

10.1. Inline sensors and spectroscopic monitoring

Inline monitoring methods are being developed to replace manual titration. Spectroscopic techniques combined with chemometric modeling can estimate acid concentration without sampling.

Raman spectroscopy, for example, has been successfully applied to online monitoring of organic acids using multivariate calibration models, showing that indirect analytical signals can be used to predict acid concentration in complex solutions (Heller et al., 2022).

In hydrometallurgical systems, similar approaches can be used to estimate acidity, sulfate concentration, or metal speciation.

Automated ion chromatography has also been applied to continuous monitoring of process water in concentrator plants, enabling real-time detection of sulfur species and other ions that affect the acidity balance (Kokko, 2023).

These developments indicate that future acidity control will rely on online data rather than manual titration.

Figure 15 shows a simplified scheme of inline monitoring combined with chemometric modeling for real-time estimation of acidity.

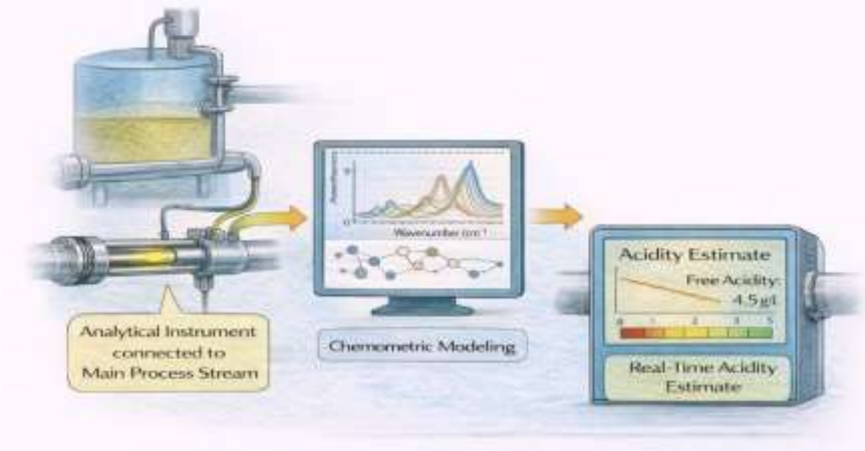


Figure 15. Concept of inline analytical monitoring and chemometric modeling for real-time acidity estimation. Adapted from Heller et al. (2022) and Kokko (2023).

The diagram shows how spectroscopic or chromatographic signals can be converted into acidity values through calibration models, enabling continuous control of hydrometallurgical circuits.

10.2. Speciation modeling and thermodynamic calculation

Speciation modeling is increasingly used to interpret acidity measurements. Programs such as PHREEQC, HSC Chemistry, and Pitzer-based models allow calculation of hydrogen ion activity, complexation, and hydrolysis equilibria.

These tools can predict effective acidity even when titration results are ambiguous.

In high-ionic-strength systems, modeling may provide more reliable information than direct measurement. The combination of titration and modeling is expected to become standard in complex hydrometallurgical circuits.

10.3. Digital twins and process simulation

Digital twins are being introduced in metallurgical plants to simulate process behavior in real time. In such systems, measured variables are combined with thermodynamic models to estimate hidden parameters such as free acidity.

When integrated with speciation modeling, digital twins can predict precipitation, scaling, or acid consumption before they occur. This approach reduces reagent use and improves process stability.

Figure 16 illustrates the integration of inline sensors, thermodynamic modeling, and process control in a digital twin framework.

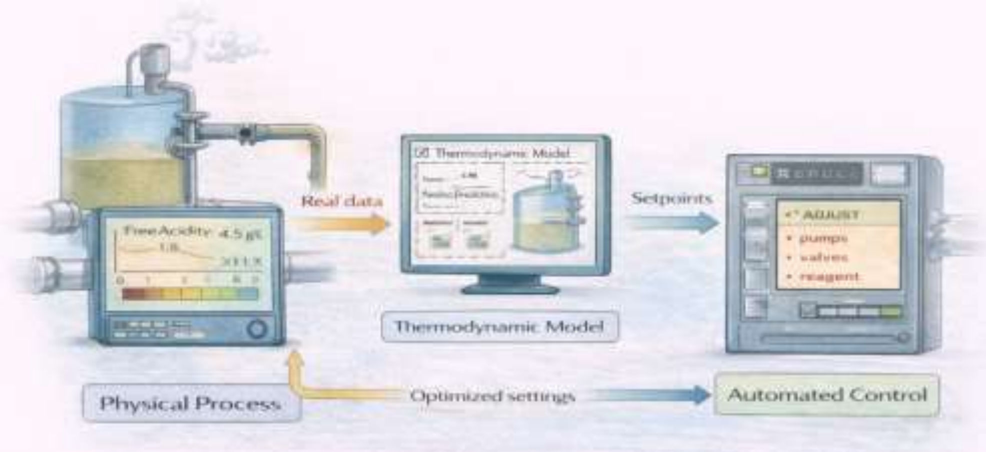


Figure 16. Integration of inline monitoring, thermodynamic modeling, and automated control in digital twin-based hydrometallurgical operation. Adapted from Heller et al. (2022) and Kokko (2023).

The scheme shows how measured data are combined with equilibrium calculations to estimate effective acidity and adjust operating conditions in real time.

10.4. Automatic titration and process automation

Automatic titrators are already used in many plants, but future systems will combine automatic titration with data processing and modeling.

Possible developments include

- automatic endpoint recognition
- correction for hydrolysis and buffering
- real-time calculation of free acidity
- integration with plant control systems

These tools will reduce operator dependence and improve reproducibility.

10.5. Artificial intelligence and data-driven control

Machine learning and chemometric models are being used to interpret complex analytical signals. Instead of measuring acidity directly, the system predicts acidity from multiple variables.

Examples include

- spectroscopy + regression
- ion chromatography + modeling
- process data + AI
- digital twin + control loop

These approaches are particularly useful in systems where classical titration fails.

The evolution from manual titration to automated and model-based control confirms that free acidity is not a simple analytical parameter. The final section summarizes the main conclusions of this review and proposes recommendations for future work.

11. CONCLUSIONS

Determining free acidity in hydrometallurgical systems is complex and often underestimated. While acidity is vital in processes like leaching, solvent extraction, and purification, measuring it in industrial liquors is challenging. Hydrolysis of metal ions, ligands, high ionic strength, and electrolytes causes deviations between hydrogen ion concentration, activity, and titratable acidity. Consequently, titration or pH readings may not accurately reflect the solution's true chemical state.

This review shows that free acidity can't be defined solely by analytical endpoints. In sulfate, chloride, or fluoride media, metal hydrolysis, ion pairing, and complex formation change proton activity, affecting titration. Thermodynamic interpretation using activity coefficients, equilibrium, and speciation is often needed to understand acidity in complex hydrometallurgical liquors. These effects are especially important with multivalent ions or high sulfate levels, where buffering and polymerization impact measurements.

Classical NaOH titration is popular for its simplicity, but it is sensitive to interferences and endpoint issues. Enhanced techniques improve precision but face limits in hydrolysis and complexation. Masking strategies help in industrial systems with interfering metal ions. Advanced methods such as potentiometry, automation, and modeling offer higher resolution but require calibration and interpretation.

Industrial experience shows that errors in acidity measurement can have significant operational impacts. Overestimating acidity can cause excess reagent use, corrosion, and environmental issues, while underestimating can lead to incomplete leaching, precipitation problems, scale, or process instability. Since hydrometallurgical reactions rely heavily on solution chemistry, even small inaccuracies can greatly affect process stability and metallurgical performance.

A central finding of this review is the absence of a universal definition of free acidity in hydrometallurgy. In practice, different operations apply different analytical procedures, titration endpoints, masking reagents, and calculation approaches. The lack of widely accepted standardized procedures complicates comparison between studies and may hinder the interpretation of experimental and industrial data. The establishment of clearer terminology, standardized reporting practices, and recommended analytical protocols would therefore represent an important step toward improving reproducibility and process control.

Future advances in acidity measurement will likely combine advanced analytical tools with digital monitoring, including inline sensors, automated titration, spectroscopy, and real-time modeling. Coupled with automation and predictive control, these methods can enable continuous estimation of acidity, real-time process adjustments, and greater stability in hydrometallurgical operations.

Free acidity in hydrometallurgical systems isn't the same as pH and can't be defined by a single method. Accurate measurement requires considering chemical speciation, hydrolysis, complexation, and activity effects. Lack of standardization hampers research and industry. Developing unified definitions, better reporting, and integrated monitoring is crucial for improved acidity control.

DECLARATIONS

Author contributions – Antonio Clareti Pereira

Conceptualization:

Methodology: Literature review and analysis: Writing – original draft preparation: Writing – review and editing.

All authors have read and approved the final manuscript.

FUNDING

The authors received no specific funding for this work.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No new data were generated or analyzed in this study. All information used in this review is derived from published literature sources cited in the reference list.

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Cite this Article: Pereira A. C. (2026). Free Acidity in Hydrometallurgy is not pH: A Critical Review of Measurement Methods, Errors, and Process Consequences. International Journal of Current Science Research and Review, 9(3), pp. 1233-1260. DOI: https://doi.org/10.47191/ijcsrr/V9-i3-14