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The Gran Method for Free Acidity Determination in Hydrometallurgical Solutions: Fundamentals, Metal-Ion Interferences, Analytical Limitations, and Industrial Applications—A Critical Review

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Abstract

Free acidity is critical to hydrometallurgical process control, but measurements in metal-rich liquors are complicated by acid dissociation, non-ideal electrode response, complexation, and metal hydrolysis. This critical narrative review examines when a Gran-derived endpoint represents a specified free-acidity measurand. Unlike matrix-specific experimental investigations or broader surveys of acidity methods, its contribution is a Gran-centered methodological and metrological framework linking operational measurand definition, acidic- and basic-branch assumptions, transformed-signal regression, electrode qualification, interference testing, uncertainty, and industrial fitness for purpose. The review distinguishes direct analytical evidence from contextual thermodynamic and process studies. It proposes residual and fit-window diagnostics, matrix-spike and dilution-recovery experiments, orthogonal comparison, and simulation of the actual potentiometric measurement procedure. A numerically linear Gran plot is shown to be an endpoint estimator, not independent evidence of chemical selectivity. Method authorization therefore requires three separate demonstrations: mathematical validity, analytical validity for the defined measurand, and performance across the intended industrial composition envelope. The review identifies an evidence gap in comparative, matrix-resolved performance data and proposes falsifiable validation priorities without claiming new experimental findings.

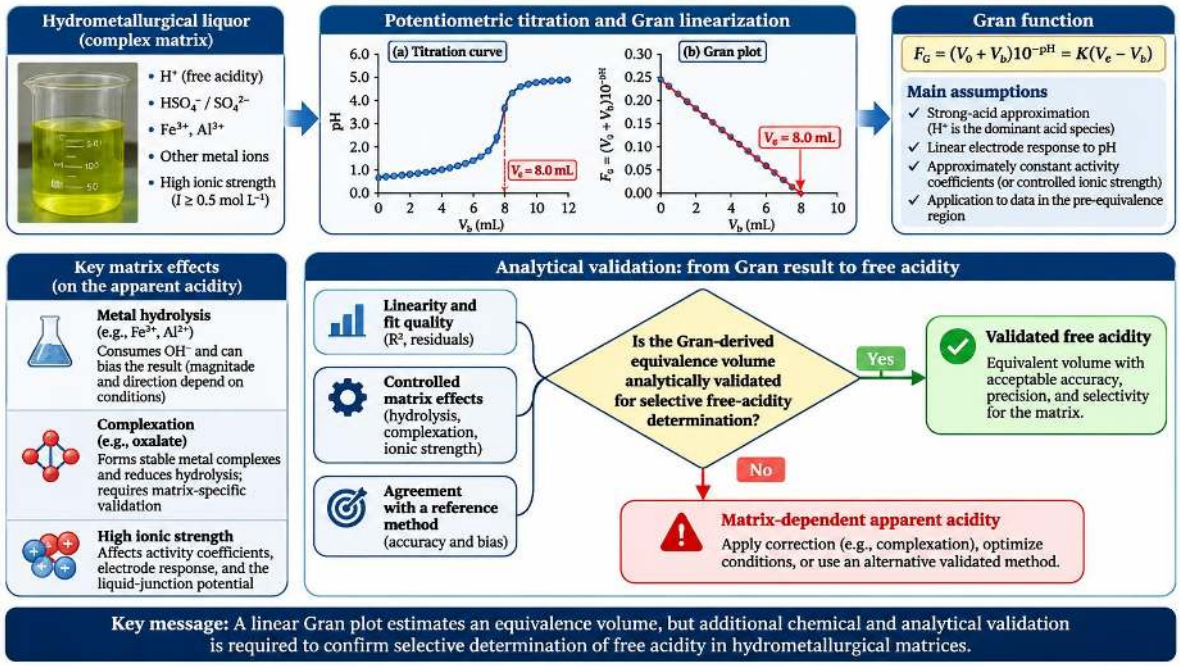
Keywords: Gran method; Free acidity; Hydrometallurgical liquors; Potentiometric titration; Metal hydrolysis; Analytical interferences

Highlights

- Gran-plot linearity is not sufficient evidence of free-acid selectivity.
- Metal hydrolysis and changing activities can distort apparent equivalence volumes.
- Matrix spikes and independent measurements are essential for validation.
- A decision framework links solution chemistry to analytical method choice.

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1. Introduction

Free acidity influences dissolution kinetics, reagent consumption, impurity control, solvent-extraction conditioning, and neutralization requirements. A single acid-strength value may therefore influence both technical decisions and the reconciliation of plant reagent balances. Nonetheless, solutions sampled from leaching and refining circuits are not simple strong-acid standards: they contain sulfate or chloride salts, suspended solids, dissolved transition metals, and sometimes organic complexants. Their hydrogen-ion activity, analytical neutralization demand, and nominal unreacted acid inventory may diverge.

This review is organized around the distinction between measurable electrode response and the intended chemical measurand. The original Gran formulation uses an algebraic transformation to estimate the titration endpoint from measurements on one side of equivalence; it does not itself discriminate protons released from a free mineral acid from those supplied by hydrolysis or other equilibria (Gran, 1952; Michałowski et al., 2005). Reviews and targeted free-acid investigations have repeatedly treated hydrolyzable cations as a particular challenge (Srinivasan & Vasudeva Rao, 2014; von Barsewisch & Hasty, 1985; Pereira & dos Santos, 2025). The original formulation (Gran, 1952) should be interpreted together with later

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methodological discussions (Michałowski et al., 2005; Srinivasan & Vasudeva Rao, 2014), not as evidence that every metal-rich matrix admits the same linear segment.

The distinctive question addressed here is not whether free acidity matters, or whether hydrolyzable metals interfere with titration; those points have already been investigated. A 2025 sulfuric-acid study provides direct evidence under its specific Fe/Al matrix and experimental protocol, while a 2026 broad review considers the wider field of free-acidity measurements. The present review instead asks which mathematical, electrochemical, chemical, and metrological conditions authorize interpretation of a Gran-estimated endpoint as a defined analytical free-acidity measurand. No interference threshold from an individual study is assumed transferable without matrix qualification.

Figure 1 identifies the extrapolation principle, Figure 2 shows the analytical workflow, and Figure 3 isolates the mechanistic routes to endpoint distortion. Tables 1 and 2 distinguish acidity definitions and mathematical assumptions, respectively. Subsequent sections evaluate electrode implementation, metal-ion chemistry, uncertainty, alternative methods, modeling, and industrial deployment. The scope is deliberately critical: supporting process-chemistry papers are not represented as direct demonstrations of analytical accuracy.

2. Review Methodology and Literature Selection

The literature was assembled through targeted, section-specific searches on Gran plots, free-acidity measurement, hydrolysis, ionic strength, alternative titration methods, and hydrometallurgical applications. The initial emphasis was 2020–2026, extended to 2010–2026 where needed, while foundational older studies were retained for historical and mathematical context. This was a critical narrative review rather than a fully reproducible systematic review; database-wide retrieval counts and formal screening-flow statistics were not available. Accordingly, systematic-review status is not claimed.

Each source is interpreted at one of three evidence levels: direct determination or validation of acidity; transferable analytical or thermodynamic methodology; and contextual industrial chemistry. The classes prevent the unsupported inference that an investigation of acid leaching, metal precipitation, or pH control verifies Gran-derived free acidity. Quantitative performance claims are intentionally limited where the supplied bibliography does not include

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primary study data, spike-recovery ranges, or interlaboratory statistics. Reported limits in this review are therefore conditional analytical propositions, not universal measured thresholds.

The reference list comprises 144 entries, including foundational sources and recent metrological guidance from the IUPAC Gold Book and the 2025 Eurachem guide. Bibliographic checks were undertaken for the foundational Gran and Michałowski publications. Full DOI-to-title verification of every remaining citation has not been established; therefore, DOI inclusion alone is not treated as proof of bibliographic accuracy.

3. Free Acidity: Definitions and Chemical Basis

At minimum, industrial reports must state whether "free acidity" denotes the analytical amount of added base required to reach a specified endpoint, the concentration of unbound strong acid species, or an inferred proton balance after speciation correction. These quantities differ from instantaneous hydrogen-ion activity and from total titratable acidity. For a monoprotic acid in an ideal dilute system, concentration and activity may be nearly proportional; for concentrated mineral-acid electrolytes, this equivalence is unjustified without a defined activity model.

As defined in the IUPAC Gold Book, pH is formulated in terms of hydrogen-ion activity rather than the molar inventory of a mineral acid (IUPAC, n.d.). Single-ion activity is convention-dependent and cannot be measured independently as an isolated thermodynamic quantity. A pH value displayed by a commercial meter after calibration in dilute aqueous buffers is therefore an operational electrode response; in concentrated process electrolytes it must not be treated as a matrix-independent free-acid concentration.

For sulfate media, $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ and metal–sulfate association influence both proton availability and the composition of complexes during incremental neutralization. In chloride-rich media, metal–chloride pairing and liquid-junction potentials may dominate different parts of the measurement. Nitric-acid process solutions raise further complications when reactive additives, such as hydrazine, coexist with hydrolyzable ions. These matrix effects make it essential to identify the operational endpoint before selecting the titration algorithm.

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Table 1 summarizes distinct measurands to avoid reporting a chemically ambiguous number as "free H_2SO_4".

Table 1. Definitions and operational interpretation of acidity

Quantity	Operational meaning	Principal limitation
Hydrogen-ion activity	Electrochemical activity influencing the indicator electrode	Not a direct molar inventory of strong acid
Free mineral acid	Defined concentration of analytically available unbound mineral acid	Depends on aqueous speciation and convention
Titratable acidity	Base demand to a stated endpoint	May include hydrolysis and weak-acid contributions
Apparent Gran acidity	Value inferred from extrapolated Gran equivalence volume	Chemical selectivity must be independently demonstrated

Note. Conceptual synthesis; definitions and reporting conventions should be explicitly fixed for each matrix.

4. Fundamentals and Mathematical Development of the Gran Method

For an idealized strong monoprotic acid of initial volume V_0 and a strong-base titrant volume Vb, the analytical excess acid before equivalence is proportional to (Ve − Vb), where Ve is the ideal equivalence volume. With calibrated pH and approximately constant activity factors, the pre-equivalence Gran function can be written as $F_G = (V_0 + Vb) \times 10^{\wedge}(-pH) = K(Ve - Vb)$. Its linear extrapolation to $F_G = 0$ estimates Ve. This relationship is a limiting case; a real electrode follows a Nernst-type activity response, and liquid-junction effects or changes in activity coefficients make K composition-dependent.

Nomenclature should not obscure method selection: Gran I and Gran II denote historically distinct linearization procedures, and modified Gran I formulations introduce additional assumptions or corrections (Michałowski et al., 2005). In this review, $F_G = (V_0 + V_b)10^{-pH} = K(V_e - V_b)$ is specifically the idealized pre-equivalence acidic-branch Gran-type relation. It is not presented as an all-purpose Gran I/Gran II equation. Post-equivalence or basic-branch processing requires its own derived transformation and activity assumptions. In sulfate/bisulfate media, the monoprotic expression is only a limiting illustration, not a complete process-electrolyte model.

The measured electrode potential can be expressed as $E = E° + (RT/F)\ln(a_{H^+}) + E_j$ using an appropriate sign convention for the cell configuration. In this expression, E_j represents a possibly varying junction contribution. The fitted Gran function inherits these response

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imperfections, so regression correlation alone cannot establish the correct equivalence volume. Pre- and post-equivalence transformations are not interchangeable, and extrapolation beyond the stable region may amplify small potential errors.

A composition-independent E_j may shift an electrode response without changing its shape. In contrast, a junction potential that varies during titrant addition can deform the potential–volume curve and bias its extrapolated endpoint. Analysts should therefore retain measured E versus V_b alongside instrument-converted pH, with electrode and reference types, junction construction, buffer standards, Nernst slope, offset, conditioning time, drift, and temperature. Matrix-specific checks are required after routine buffer calibration.

A defensible analysis evaluates multiple plausible linear segments, inspects signed residuals and leverage, reports uncertainty in the x-intercept, and tests whether inferred acid concentration is stable under reasonable dilution and fit-window changes. Weighting should reflect the error structure in potential or derived Gran coordinates rather than being selected solely to maximize the coefficient of determination. Figure 1 illustrates idealized linearization; its axes are schematic and contain no reported experimental data. Reports on Gran plotting and potentiometric data reduction (Andrade, 2020; Granholm et al., 2015) motivate transparent fit selection, but do not establish matrix-specific limits of bias.

For a fitted line $F_G = mV_b + b$, the extrapolated endpoint is $V_e = -b/m$. First-order uncertainty propagation gives $u^2(V_e) = u^2(b)/m^2 + b^2u^2(m)/m^4 - 2b\ \mathrm{Cov}(m,b)/m^3$; the covariance term must be retained. Because transforming potential or pH into F_G changes the error distribution, heteroscedasticity, non-Gaussian errors, and shared uncertainty in added volume may invalidate ordinary unweighted least squares. Weighted or generalized least squares, resampling from original potential–volume observations, or nonlinear fitting of the untransformed measurement model should be compared where warranted. A descriptive fit-window sensitivity statistic is $S_{window} = [\max(V_e) - \min(V_e)]/\mathrm{mean}(V_e)$, computed over chemically admissible windows; it has no universal pass/fail cutoff. Automated selection must enforce minimum observations, chemically reasonable bounds, residual/leverage checks, and window stability, rather than maximize R^2 alone.

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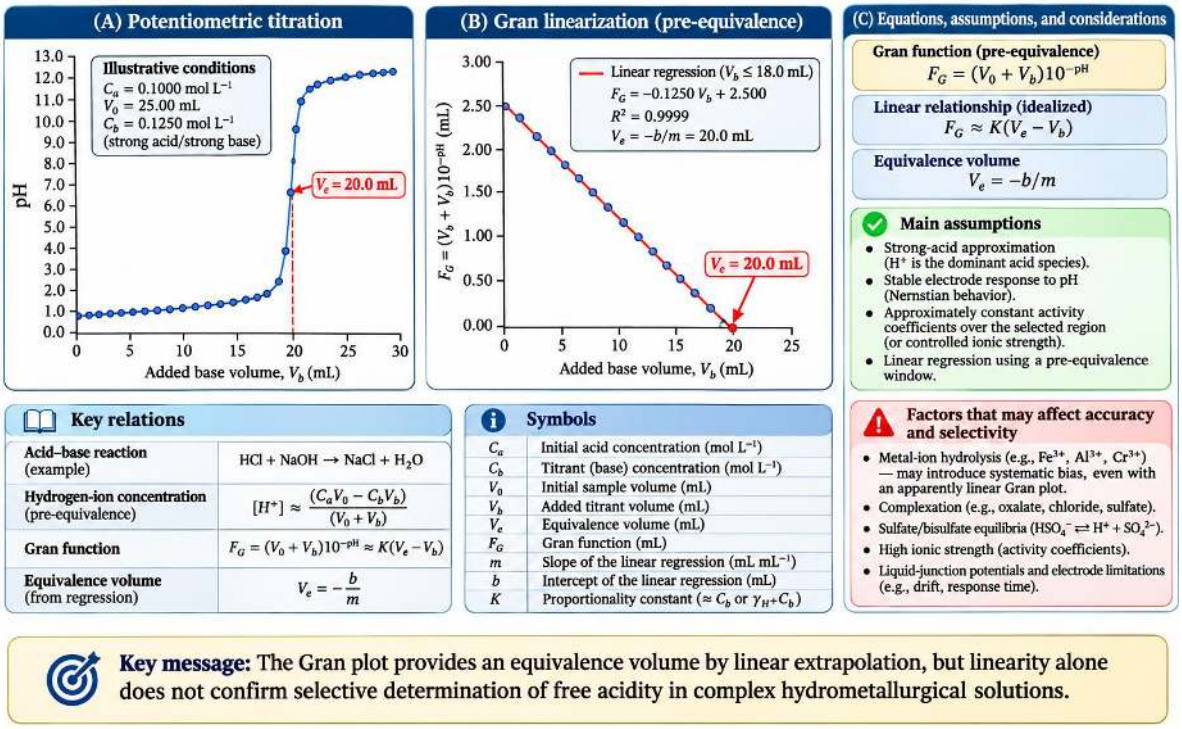


Figure 1. Mathematical principles of pre-equivalence Gran linearization and equivalence-volume determination, including assumptions and potential analytical bias.

Note. Original conceptual schematic developed by the author with AI-assisted graphical generation; numeric values, where shown, are synthetic illustrative examples, not experimental observations or method acceptance criteria.

The useful question is not whether a straight line can be fitted, but whether the extrapolated intercept corresponds to the chemically defined free-acid measurand. Table 2 makes these assumptions explicit.

Table 2. Gran formulation: assumptions and failure modes

Element	Simplifying assumption	Potential deviation
Electrode response	Stable Nernst slope	Drift, junction potential, salt effects
Acid equilibrium	Single strong-acid neutralization	Bisulfate dissociation, weak acids, metal hydrolysis
Activity correction	Constant proportionality factor	Changing activity coefficients on dilution
Regression	Single linear domain	Curvature, heteroscedasticity, endpoint-window sensitivity
Result conversion	Known titrant molarity and aliquot volume	Standardization, volume, and dilution uncertainty

Note. Conceptual derivation based on the Gran limiting model; the selected electrode sign convention must be consistent throughout the calculation.

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5. Experimental Procedures and Analytical Implementation

Obtain a representative specimen from a process location with a defined residence time and mixing state. Sample cooling, oxidation, evaporation, and filtration can change the amounts and oxidation states of dissolved constituents before titration begins. For Fe^{2+}-bearing liquors, air exposure can alter the population of hydrolyzing ions; for concentrated chloride media, loss of volatile species or electrolyte changes can modify the reference-electrode junction environment. These effects should be documented alongside sample preservation time and temperature.

Operational control requires a standardized base titrant, verified volumetric apparatus, temperature equilibration, and electrodes qualified over the specific electrolyte range. The potentiometric method should record potential or pH versus added volume at a sufficiently fine resolution to characterize the pre-equivalence window. Computation should retain raw data, fit-window selections, calculated residuals, and the full dilution factor, rather than archiving only a reported concentration.

For sodium hydroxide, record the standardization procedure and frequency, concentration uncertainty, protection against atmospheric CO2, relevant titrant-temperature corrections, and any blank subtraction. Log filtration status, pore size, delay between sampling and filtration, and temperature; removing a colloid or precipitate can alter the operational acidity if that phase exchanges protons. For Fe-bearing samples, record Fe(II)/Fe(III), storage duration, atmosphere, and preservation temperature, because oxidation changes hydrolysis behavior.

Figure 2 proposes independent checks for matrix evaluation, fitting, and recovery. Before routine use, supplement replicate blanks and laboratory controls with matrix spikes, a compositionally relevant reference material (if available), and a chemically independent measurement. Set acceptance limits according to process decisions and observed analytical performance, not uncritically borrowed from dilute-water titration practice.

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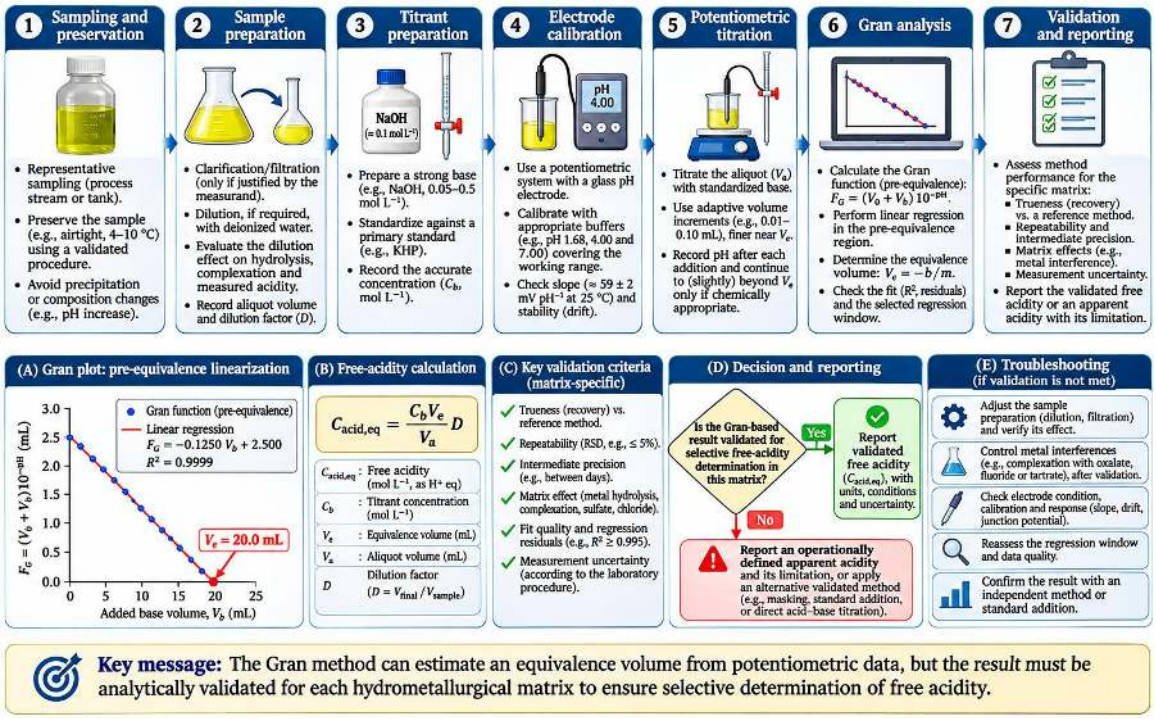


Figure 2. Analytical workflow for sampling, sample preparation, potentiometric titration, Gran-function regression, and matrix-specific validation.

Note. Original conceptual schematic developed by the author with AI-assisted graphical generation; numeric values, where shown, are synthetic illustrative examples, not experimental observations or method acceptance criteria.

6. Interference from Hydrolyzable Metal Ions

Dissolved metal ions affect titration through hydrolysis, proton release, changes in ionic activity, soluble complex formation, and precipitation. A simplified first hydrolysis step, $M^{3+} + H_2O \rightleftharpoons MOH^{2+} + H^+$, shows why adding base may neutralize protons created by the metal ion itself, not just the original strong acid. The extent of this contribution depends on oxidation state, ligand distribution, temperature, concentration, and the time allowed to reach equilibrium during each titrant increment.

Ferric iron is particularly relevant because hydrolysis and subsequent precipitation can occur over an analytically important pH region, and ferric sulfate species can complicate attribution of proton release. Ferrous iron does not behave identically: its role may change after oxidation during storage or titration. Aluminum similarly produces hydroxo species and can develop polymeric or precipitated forms, whereas chromium(III) may react comparatively slowly under some conditions. Nickel, cobalt, copper, zinc, manganese, vanadium, and

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titanium require separate consideration rather than a single universal interference threshold. The published literature on hydrolyzable cations (von Barsewisch & Hasty, 1985; Ganesh et al., 2011a, 2011b) supports investigating metal interference explicitly instead of relying on the visual quality of an endpoint.

Figure 3 shows these pathways without a fixed metal-specific bias direction. Depending on fitting region and speciation, a metal may increase apparent acid demand or distort the curve, underestimating intercepts. Table 3 summarizes mechanisms and qualitative concerns; reference metadata alone cannot support universal numerical thresholds.

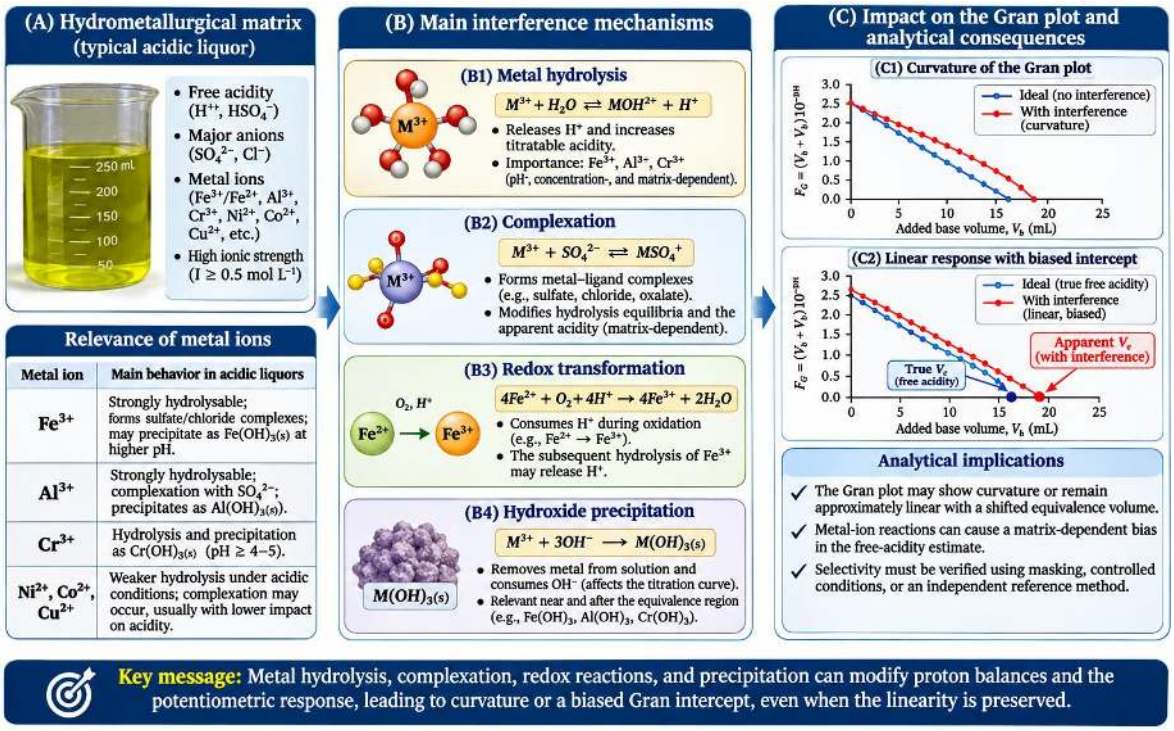


Figure 3. Metal-ion hydrolysis, complexation, redox transformation, and precipitation as sources of matrix-dependent bias in Gran titration.

Note. Original conceptual schematic developed by the author with AI-assisted graphical generation; numeric values, where shown, are synthetic illustrative examples, not experimental observations or method acceptance criteria.

Table 3. Hydrolyzable metal ions: potential sources of interference

Species	Mechanistic concern	Recommended qualification
Fe^{3+}	Hydrolysis, sulfate association, precipitation	Matrix spike; oxidation-state control; compare masked method
Fe^{2+}	Potential oxidation to Fe^{3+}	Preservation and controlled oxidation check
Al^{3+}	Hydroxo species, polymerization, precipitation	Spike recovery with Al concentration series

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Cr^{3+}	Complexes and potentially slow hydrolysis	Equilibration time and ligand control
Ni^{2+}/Co^{2+}	Changes in hydrolysis and complex populations	Matrix-specific high-concentration check
Cu^{2+}/Zn^{2+}/Mn^{2+}	Hydrolysis and ion pairing	Ligand-matched comparison
V/Ti species	Oxidation-state and condensation effects	Speciation-informed test under process conditions

Note. Qualitative risk matrix; no universal concentration threshold is asserted from the supplied metadata.

7. Solution Chemistry and Operating Conditions

A change in solution concentration affects several variables at once: hydrogen-ion activity, sulfate/bisulfate distribution, metal complexation, and electrode liquid-junction behavior. Consequently, the frequent practical remedy of diluting a concentrated sample is not automatically chemically neutral. Dilution may reduce matrix interference but can also transform the identity or balance of titratable species. Where process control requires an equivalent concentration in the original liquor, the dilution correction must be supported by preservation of the chosen operational measurand.

A dilution-recovery challenge should compare independently prepared aliquots at nominal dilution factors of 1, 2, 4 and 8 after converting results to the original liquor basis: $C_0^{(1)}$, $C_0^{(2)}$, $C_0^{(4)}$ and $C_0^{(8)}$. Systematic trends beyond matrix-specific uncertainty suggest that the operational measurand or electrode response is not conserved through dilution; visually improved titration plots alone do not establish accuracy.

Temperature and mixing-time control are equally consequential. Precipitation and complex dissociation are not necessarily instantaneous, while gas exchange and redox reactions can proceed during an automated sequence. Apparent robustness across replicate titrations made under identical conditions does not rule out a common matrix-induced bias. Analysts should examine the result's sensitivity to ionic strength, titration interval, electrode conditioning, and time between additions.

8. Analytical Performance and Sources of Measurement Error

Accuracy requires an external reference concept, whereas replication can estimate precision. The quantities must not be conflated: a tight cluster of fitted equivalence volumes may represent a systematically shifted endpoint. Reproducibility across operators, days, electrode lots, and instruments is especially important before incorporating a procedure into

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operational setpoint decisions. When low acid concentrations are sought against a high metal salt background, establish the effective quantification limit from matrix blanks, dispersion, and acceptable relative uncertainty.

Fit-for-purpose validation follows the 2025 Eurachem guide: the analytical target and decision risk determine required bias, precision, working range, uncertainty, and ongoing quality control (Eurachem, 2025). For independently prepared matrix spikes, Recovery (%) = $100(C_{spiked} - C_{unspiked})/C_{added}$; when a sufficiently independent reference is available, Bias (%) = $100(C_{Gran} - C_{ref})/C_{ref}$. The assays must span the intended acid–metal envelope, not a single spike. An oxalate masking procedure is a qualified comparator, not an automatically unbiased reference; its own ligand and kinetic interferences must be evaluated. Repeatability, between-day/operator variability, and matrix-specific limits of quantification are distinct from trueness.

A simplified concentration equation, C_acid, eq = C_b Ve D / V_a, connects titrant concentration C_b, extrapolated equivalence volume Ve, dilution factor D, and aliquot volume V_a. For approximately independent contributions, the relative uncertainty contains terms associated with each input, but the covariance between slope and intercept and systematic endpoint effects must be treated separately. Because regression estimates derive from a transformed signal, assess propagated uncertainty from the original instrument response when possible.

The primary reported result for mixed or polyprotic electrolytes should, when appropriate, be $C_{acid,\ eq}$ in mol H^+ equivalents L^{-1}. Reporting g L^{-1} as H_2SO_4 requires an explicitly stated equivalent-to-molecule stoichiometric convention and must not imply that all proton equivalents belong to free molecular sulfuric acid. The factor D must be defined consistently with aliquot and titrant volumes and with the chosen original-sample reporting basis.

Table 4 translates these ideas into the minimum performance evidence expected of an industrial procedure. Do not use a journal report lacking raw titration data, spike recoveries, or comparator experiments to establish a universal numerical bias or maximum acceptable metal concentration.

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Table 4. Recommended analytical validation evidence

Property	Minimum evidence	Interpretive safeguard
Selectivity	Acid standard and metal-salt spike series	Separate hydrolysis demand from free-acid response
Repeatability	Independent aliquots across the operating range	Do not equate precision with accuracy
Trueness	Matrix-appropriate comparator or reference sample	State comparator assumptions
Robustness	Dilution, temperature, delay, electrode and fit-window tests	Evaluate chemical as well as numerical stability
Uncertainty	Titrant, volume, calibration, regression and matrix contributions	Report systematic bias separately
Range and LOQ	Matrices spanning acid and metal operating envelopes	Define intended decision threshold

Note. Proposed validation framework, not a set of numerical acceptance limits extracted from primary reports.

9. Comparison with Alternative Free-Acidity Methods

Conventional direct endpoint titration is simple but may be unreliable where the titration curve lacks a distinct chemical endpoint. Derivative approaches can locate inflection regions but do not automatically correct the chemical meaning of those regions. Gran plots may better exploit pre-equivalence data, yet they preserve the same dependence on electrode activity and equilibria. Potassium oxalate and other masking strategies can potentially change metal speciation and thereby improve free-acid discrimination, but their selectivity depends on the matrix and on complexation conditions. The oxalate-based comparison (Pereira et al., 2025) and the broader free-acidity synthesis (Srinivasan & Vasudeva Rao, 2014) indicate why a chemically separate comparator is needed when hydrolysis distorts ordinary neutralization.

Other approaches include selective complexation, barium hydroxide titration, conductometry, optical probes, and thermodynamic titration-curve modeling. A useful comparison must report the definition of the acid measurand, reagent compatibility, analysis time, interference range, reproducibility, and implementation cost. Methods developed for nitric acid or simple pickling solutions should not be transferred to high-sulfate metal-rich liquors without challenge experiments.

Table 5 sets out a conditional method comparison. The entries are hypotheses for method screening, not evidence that one technique is universally superior.

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Table 5. Comparison of candidate free-acidity determination approaches

Approach	Potential strength	Major limitation
Gran extrapolation	Uses points outside a poorly resolved endpoint	Relies on linearity and chemical selectivity assumptions
Derivative potentiometry	Accessible on automated titrators	Endpoint may include hydrolyzing metal demand
Oxalate/masking titration	May suppress selected cation contributions	Ligand-dependent selectivity and possible side reactions
Conductometric/optical	Alternative observable to electrode pH	Calibration and matrix-specific spectral/conductivity effects
Speciation-fitted titration	Explicitly accounts for equilibria	Needs reliable constants and uncertainty propagation

Note. Proposed comparison criteria; suitability must be demonstrated for the actual plant liquor.

10. Industrial Applications in Hydrometallurgical Processing

The operational significance of free acidity differs across atmospheric leaching, high-pressure acid leaching, heap and column leaching, electrowinning, solvent extraction, and effluent neutralization. In laterite processing, acid demand and metal dissolution are tightly coupled; in copper circuits, gangue reactions and Fe chemistry can evolve; and in rare-earth or secondary-resource liquors, impurity-control reactions may create distinct apparent titration responses. An analytical method should be validated within the expected composition envelope instead of treated as a universally portable unit operation.

Industrial studies describing acid dosing, selective precipitation, or dissolved-metal removal help define the relevant process matrices and sampling locations. Their findings, however, are not substitutes for a paired study of Gran results against a reference free-acid determination. The application question is whether a reported value enables a reliable operating decision with known uncertainty, not merely whether acid addition correlates with extraction performance. For example, the distinction between leaching acid dosage and analytical free acidity is particularly relevant in laterite processing (Pereira, 2026b); this process literature does not, by itself, validate Gran titration.

Table 6 links representative matrix families to likely analytical risks and the evidence needed to authorize routine Gran use.

Table 6. Industrial matrix and analytical decision requirements

Matrix family	Dominant consideration	Validation priority
Sulfate leach liquor	Fe/Al hydrolysis and bisulfate speciation	Acid–metal challenge experiments

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Chloride leach or regeneration	Metal-chloride pairing and electrode junction	Matrix-matched electrode and comparative method
Nitrate reprocessing liquor	Hydrolyzable ions and redox-active additives	Selective acidity comparator
Neutralization liquor	Precipitation and transient buffering	Time-resolved titration response
Solvent-extraction raffinate	High ionic strength and organic carryover	Sample preparation and matrix control

Note. Qualitative, matrix-dependent synthesis; specific thresholds require experimental determination.

Table 7 synthesizes what each cited evidence category can and cannot establish for industrial Gran authorization. The entries intentionally distinguish demonstrated analytical relevance from data not established by the present narrative review.

Table 7. Evidence classes and reporting gaps for free-acidity method qualification

Representative source	Nature of evidence	Limits for industrial Gran authorization
Gran (1952); Michałowski et al. (2005)	Gran linearization methodology	Mathematical endpoint estimation does not establish selectivity in metal-rich liquors.
von Barsewisch & Hasty (1985).	Direct free-acidity evaluation with hydrolyzable ions	Transferability depends on matrix, procedure, and endpoint definition.
Ganesh et al. (2011a, 2011b)	Free-acid analytical procedures	Published evidence requires matrix-specific appraisal; complete performance metrics were not re-extracted here.
Pereira & dos Santos (2025).	Fe/Al interference in sulfuric-acid solutions	Experimental conditions do not establish universal Fe/Al thresholds.
Srinivasan & Vasudeva Rao (2014).	Methodological review of free acidity with hydrolyzable ions	Supports method selection but provides no universal accuracy guarantee.
Leaching, AMD and precipitation literature	Contextual process and solution chemistry	Process data alone do not validate Gran-specific bias, selectivity, or uncertainty.

11. Thermodynamic Modeling and Computational Interpretation

A chemically meaningful simulation of Gran titration should represent acid dissociation, metal hydrolysis, ligand complexation, precipitation where relevant, and non-ideal activities. In sufficiently dilute regimes, simplified corrections may suffice; concentrated sulfate and chloride solutions may require stronger interaction models such as SIT or Pitzer, with parameters validated for the measured species and temperature. A numerically converged equilibrium computation is not evidence that its equilibrium constants or activity model are correct for an industrial matrix.

To reproduce the method, not just the equilibrium composition, each simulated base addition should update volume, total analytical concentrations, acid dissociation, metal–ligand

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complexes, hydrolysis, activity coefficients, and any precipitate. The predicted electrode potential should include temperature, slope, offset, and a plausible junction-potential model. The synthetic observations must be processed with the same Gran transformation and window selection as measured points. SIT or Pitzer should be chosen by ionic-strength range and independently available species-interaction/temperature parameters, not by software convenience; parameter uncertainty and model discrepancy should be varied separately from regression error.

An appropriate simulation predicts the titration curve as additions change volume and composition, converts modeled hydrogen-ion activity into the same measurable electrode variable, and subjects the simulated points to the same Gran-fitting workflow used experimentally. This permits separation of error caused by linearization from error introduced by the definition of free acid. Sensitivity analysis should vary critical stability constants, metal concentrations, temperature, and response slope rather than relying on a single best-fit parameter set.

12. Critical Synthesis, Method Selection, and Future Research

The combined evidence supports a hierarchy of claims. The mathematical endpoint estimate is supported when the chosen Gran transformation yields stable, well-behaved fits. The analytical claim of free-acid selectivity requires additional evidence that hydrolysis and complexation do not contribute unacceptable bias. Finally, industrial suitability requires that the result remain fit for a specified process decision across its expected composition and temperature envelope. A favorable first stage cannot substitute for the later stages.

Figure 4 offers a screening sequence: define the chemical measurand, characterize the dominant ions, test a Gran method on standards and challenge matrices, obtain comparison data where interference is expected, and explicitly report limitations. This approach accommodates future development of matrix-specific Gran functions, thermodynamic correction, more stable reference electrodes, automated fit selection, and uncertainty-aware data algorithms. Prospective machine-learning tools should be constrained by chemical interpretability and evaluated on independently prepared liquors rather than trained solely on repeated measurements from one plant stream.

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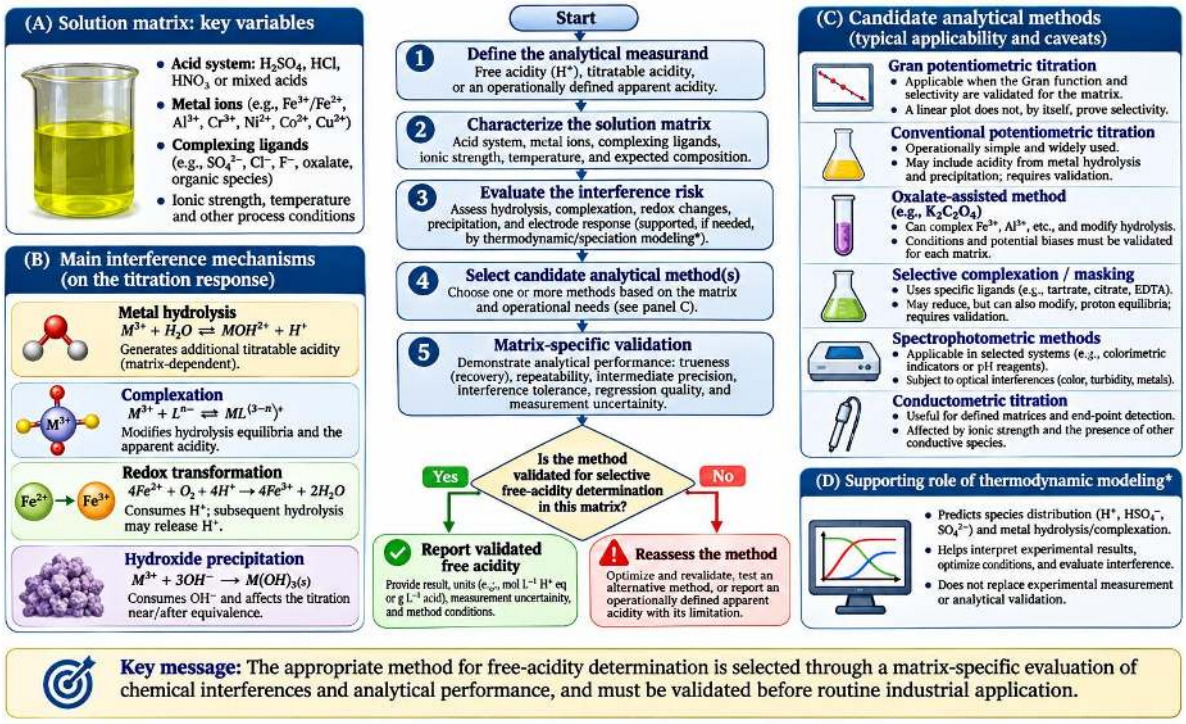


Figure 4. Decision-making framework for selecting and validating free-acidity determination methods in hydrometallurgical solutions.

Note. Original conceptual schematic developed by the author with AI-assisted graphical generation; numeric values, where shown, are synthetic illustrative examples, not experimental observations or method acceptance criteria.

A high-priority experimental program would compare sulfate, chloride, and nitrate matrices over factorial variations in free acid, Fe^{3+}, Al^{3+}, relevant divalent ions, and ionic strength; couple raw potentiometric curves with speciation calculations; and report both statistical endpoint uncertainty and observed chemical bias. Interlaboratory exercises could then determine whether a common operational definition and reporting convention are transferable.

12.1. Distinguishing Direct Analytical Evidence from Supporting Chemistry

A reliable evidence hierarchy begins with titration studies that identify a free-acid measurand and challenge it against hydrolyzable cations. The classic discussion by von Barsewisch and Hasty (1985), the free-acidity review by Srinivasan and Vasudeva Rao (2014), and the two experiments described by Ganesh et al. (2011a, 2011b) provide more direct methodological context than reports that merely use acid as a leaching reagent. Their procedures nevertheless cannot be assumed equivalent: matrix composition, masking

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chemistry, endpoint definition, and uncertainty reporting determine whether findings are transferable.

Gran linearisation itself must be judged separately from chemical selectivity. Gran (1952) formalized the extrapolation principle, while Michałowski et al. (2005), Andrade (2020), and Granholm et al. (2015) offer complementary perspectives on linearisation or potentiometric data processing. A satisfactory mathematical fit establishes an intercept under the fitted model; confirmation that the intercept represents the intended free mineral-acid concentration requires a separate chemical test.

12.2. Matrix Effects and the Limits of Transferability

For metal-rich sulfate solutions, Fe(III) hydrolysis, Al(III) hydrolysis, and sulfate association can change the proton balance during base addition. Geochemical descriptions of Fe/Al precipitation, such as Nordstrom (2020), inform the likely reaction pathways but do not quantify Gran-method bias without paired acid measurements. Analogously, an acid mine drainage neutralization curve does not demonstrate selectivity for uncomplexed mineral acid. The distinction between process-relevant chemistry and validated analytical performance should remain explicit throughout this review.

Chloride and nitrate matrices require their own evidence. Chen and Zhu (2020) describe potentiometric free-HCl determination in pickling liquor; the comparison is relevant to electrode and endpoint practice but cannot establish accuracy in ferric-sulfate laterite liquors. Oxalate-based determination (Pereira et al., 2025) is another potential comparator whose applicability depends on the specific ligand, competing-metal inventory, and definition of acidity. Method-selection claims should therefore be conditional rather than categorical.

12.3. Research Gaps and Validation Priorities

A decisive validation study would employ independently prepared acid standards and synthetic multi-metal matrices at matched ionic strengths; quantify Fe(II)/Fe(III), Al(III), sulfate/bisulfate, chloride, and temperature; and compare Gran-derived concentrations with an independent reference procedure. To distinguish model-fitting error from true chemical bias, include raw potential–volume observations, the chosen fitting window, regression covariance,

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matrix-spike recovery, and between-day variability. An acceptance range should be linked to the plant decision rather than presented as universal.

The evidence base is broader than the subset of papers directly testing Gran-derived free acidity in hydrolyzable-ion matrices. Accordingly, process studies on leaching, neutralization and precipitation are treated as contextual chemistry; quantitative method-performance claims require direct titration data, appropriate comparator experiments or matrix-specific spike tests. Table 7 makes these distinctions explicit without assuming that absence of reported information proves absence of an experiment.

13. Conclusions

The central finding is that a Gran plot provides a model-based equivalence-volume estimate, not intrinsic evidence that neutralization selectively measures free mineral acid. Reporting a qualified result requires three distinct evidential stages: (i) mathematical validity of the selected acidic- or basic-branch transform and fit window, including covariance-aware uncertainty; (ii) analytical validity for an explicitly defined free-acidity measurand, established by electrode qualification and matrix-sensitive recovery/comparator experiments; and (iii) industrial fitness for purpose over the actual process-composition and temperature envelope. Hydrolysis, complexation, redox evolution, precipitation, sample handling, and non-ideal electrode response can make a highly linear fit chemically biased. Neither replicate precision nor routine pH-buffer calibration replaces matrix-dependent validation. The proposed workflow is a falsifiable authorization framework rather than a universal correction factor, and it claims no new measurements.

Declarations

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Conflict of Interest

The author declares no conflict of interest.

Data Availability

No new experimental datasets were generated. All quantitative values discussed in the review are traceable to the cited literature.

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Author Contributions

The author performed conceptualization, critical analysis, literature synthesis, visualization, and manuscript preparation.

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